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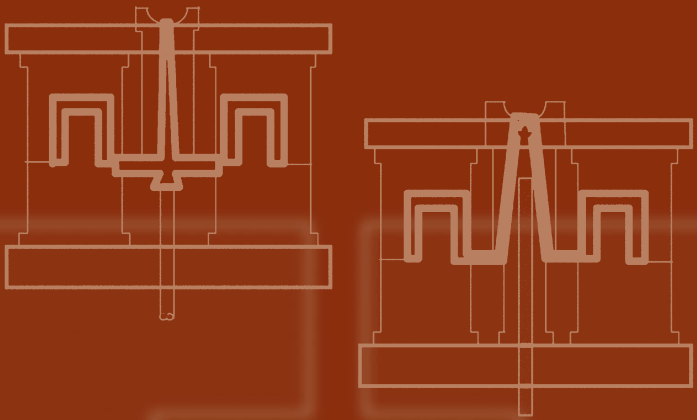

Phenolic Resins: A Century of Progress

Springer

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Louis Pilato
Editor

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Preface

The legacy of Leo Hendrik Baekeland and his development of phenol formaldehyde resins are recognized as the cornerstone of the Plastics Industry in the early twentieth century, and phenolic resins continue to flourish after a century of robust growth. On July 13, 1907, Baekeland filed his "heat and pressure" patent related to the processing of phenol formaldehyde resins and identified their unique utility in a plethora of applications. The year 2010 marks the Centennial Year of the production of phenolic resins by Leo Baekeland. In 1910, Baekeland formed Bakelite GmbH and launched the manufacture of phenolic resins in Erkner in May 1910. In October 1910, General Bakelite began producing resins in Perth Amboy, New Jersey. Lastly, Baekeland collaborated with Dr. Takamine to manufacture phenolic resins in Japan in 1911. These events were instrumental in establishing the Plastics Industry and in tracing the identity to the brilliance of Dr. Leo Baekeland.

Phenolic resins remain as a versatile resin system featuring either a stable, thermoplastic novolak composition that cures with a latent source of formaldehyde (hexa) or a heat reactive and perishable resole composition that cures thermally or under acidic or special basic conditions. Phenolic resins are a very large volume resin system with a worldwide volume in excess of 5 million tons/year, and its growth is related to the gross national product (GNP) growth rate globally. Yet it is a mere 2% of total global production of plastics that amounts to 250 million tons in 2008. Phenolic resins continue to be an important bonding agent for a diversity of uses encompassing the joining of metals, glasses, wood, paper, rubber to other substrates with favorable cost–performance characteristics that surpass most other polymeric resins. As phenolic resins embark into the twenty-first century, the outlook continues to be optimistically favorable.

The global commitment to Nanotechnology has not evaded phenolic resins. Although results are somewhat preliminary, selective phenolic resin mechanical properties are improved and offer promise for continued efforts in this new and exciting technology. Nanotechnology has been applied to phenolic resins, benzoxazines, and cyanate esters using an array of nanomaterials such as nanoclay, carbon nanofiber, carbon nanotubes, POSS® and others. Thus, ablation improvement because of reduced thermal erosion for rocket motors, improved thermooxidative stability of carbon–carbon composites, and better scratch-resistant flooring are current developments that have occurred through Nanotechnology.

The bold commitment of the commercial aircraft manufacturers (Boeing and Airbus) to fabricate the entire fuselage and other critical components involving over 50% of aircraft weight with fiber reinforced composites for reduced weight and greater fuel efficiency has become a "lightning rod" for the re-assessment of product performance with greater emphasis on composites. Although phenolic resin-based composites enjoy an enviable position as the preferred composition for aircraft interiors and cargo liners due to the extraordinary fire, smoke, and toxicity (FST) characteristics, the quest to develop a "load bearing" phenolic resin composite structure with FST behavior that meets or exceeds the mechanical properties of an epoxy resin based composite is desired. Efforts in closely related phenolic systems such as benzoxazine or phenylene bisoxazolines (PBO) may provide encouragement.

New areas in the use of phenolic resins continue to be developed. Carbon foam is prepared by the carbonization of open cell phenolic foam or by the expansion/cure of mesophase pitch at elevated temperature. These newly developed materials are attractive compositions for high temperature composite tooling and floor paneling clad with fiber reinforced prepreg. Significant efforts have resulted in the commercialization of benzoxazines, a closely related phenolic material, into the preparation of fiber reinforced composites, electronics applications, and prepreg intermediate. Phenylene bisoxazolines are being revisited by reacting them with selected novolaks to yield novel polyaryl ether amide resins that possess performance characteristics equal to or better than high T_g multifunctional epoxies but with improved toughness and hot wet strength. Group appendage involving reactions directed to the phenolic hydroxyl such as epoxy, cyanate ester, or allyl groups or ring formation through the use of formaldehyde with a primary amine to yield benzoxazines expands the versatility of phenolic resin chemistry.

Newly developed novolak process by Asahi (known as Phosphoric Acid Phase Separation (PAPS)) involves the use of a high amount of phosphoric acid as catalyst/phase reactant. Asahi proposes "Phase Transfer Catalysis" as the method and results in a rapid process for novolak preparation. The resulting novolaks are predominately high in para content, possess minimal amounts of free phenol or dimer, slower curing with hexa, and exhibit a lower bulk viscosity than conventional novolak prepared by oxalic acid. The PAPS resins are in the early stage of development and require additional time before Asahi commits to full scale commercial production.

Renewable raw materials, particularly those that would reduce the amount of expensive phenol, continue to be examined and can be used in limited amounts. Materials such as cashew shell nut oil, tannins, soy, and furfural are being examined for an economic benefit without a corresponding unfavorable product performance. Other renewable materials such as tung oil and linseed oil continue to be used in limited amounts in the usual applications such as electrical laminates (tung oil) and friction for linseed oil. The emergence of "Biorefineries" in Europe as well as the

US to process lignocellulose waste into fuels and chemical raw materials will result in the availability of pure lignin as a phenolic-like material for utilization in phenolic resin preparation. Lignin economics will be a factor for its potential use in phenolic resins.

The escalating cost of energy and its impact on phenolic resin raw materials, resin production, and processing of phenolic resins by customers is of paramount importance. Low energy systems are stressed by resin customers in spite of cure limitations of phenolic resin chemistry. Efforts directed to the use of resorcinol and tannins as well as newly developed latent cure catalyst of Bac2 in fast cure systems may provide some benefit in energy reduction. Economic value versus energy reduction will need resolution. The current shift to more offshore oil exploration and in greater depths will require the manufacture of more fire resistant composite platforms, deluge pipe, and other items closely related to offshore oil activities. Pultrusion of platforms, phenolic foam paneling for thermal insulation are expected to be in great demand.

Selective non-formaldehyde or non-hexa curing agents are being examined and consist of glyoxal, oxazolidine, solid resole, epoxy, resorcinol, and tannins. In some cases these non-formaldehyde curing agents require less energy for full cure of phenolic resins.

Yet there are some concerns as they relate to large volume applications of phenolic resins. Wood adhesives and mineral fiber binders for thermal insulation are application areas under intense pressure for all formaldehyde containing resins (UF, MF, and PF) due to the environmental movement to reduce or eliminate formaldehyde containing resins in wood and thermal insulation consumer products. Coupled to these considerations is the uncertainty of the status of formaldehyde – whether formaldehyde will be classified as a human carcinogen. These potential shifts in these large consumer markets will surely impact and reduce volume sales of liquid phenolic resins. Thus, gains in increased sales in many of the newly emerging areas mentioned above may be offset by reduced sales in wood adhesives and mineral fiber binder areas.

It is appropriate to acknowledge several individuals who endorsed initially the outline of the book and provided key personnel as authors. These are Harald Steindl, Kazuhisa Hirano, Larry Gollob, James Lamb, William J. McKillip, and Shinichi Ozeki.

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Chapter 1
Introduction

Louis Pilato

The title of this book is selected appropriately to describe a century of progress for phenolic resins. The contributions of Leo Hendrik Baekeland are immense! He was not easily discouraged as he attempted to harness the reaction of phenol and formaldehyde into a manageable, commercial product. In spite of some of the great organic chemists who examined the reaction of phenol and formaldehyde and obtained intractable, useless materials, he prevailed. The legacy of Leo Hendrik Baekeland and his development of phenol formaldehyde resins are recognized as the cornerstone of the Plastics Industry in the early twentieth century whereby phenolic resins and other polymeric systems continue to flourish after a century of robust growth. On July 13, 1907, Baekeland filed his "heat and pressure" patent related to the processing of phenol formaldehyde resins and identified their unique utility in a plethora of applications. Bakelite as coined by Baekeland was considered "the material of a thousand uses!" Phenol formaldehyde resins or Bakelite as they were commonly referred to became the first truly synthetic polymer to be developed. The perseverance and diligence of Baekeland and those who followed him in the ensuing years attest to their significant contributions that are identified with a variety of thermosetting and thermoplastic polymeric materials within the Plastics Industry. Further, it is remarkable that after a century of existence phenolic resins continue their preferred status in a number of applications that were developed during Baekeland's era to this very day.

Previous phenolic resin publications and commemorative conferences were successful largely due to the global interest and successful business activities of phenolic resin technology. The more recent centennial conference, "Baekeland 2007 Symposium: Thermosets, 100 Years after Bakelite," held from September 23–26, 2007 in Ghent, Belgium where Baekeland was born and educated, was a resounding success. It is indeed a hallmark of achievement that, after a century of

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existence, phenolic resins are an important component in those industries where it is best qualified.

Since the publication of the phenolics resins book by Springer in 2000, phenolic resins remain a versatile resin system featuring either a stable, thermoplastic novolak composition that cures with a latent source of formaldehyde (hexa) or a heat reactive and perishable resole composition that cures thermally or under acidic or special basic conditions. It is a very large volume resin system with a worldwide volume in excess of 5 million tons/year, and its growth is related to the gross national product (GNP) growth rate globally.

During the early twenty-first century, there has been a rationalization of phenolic resin businesses whereby venerable Bakelite AG, a company that traced its origin to Baekeland and identified as the first phenolic production location in Germany in May 1910, was acquired by Apollo Management and merged with Borden Chemical to form Hexion Specialty Chemicals, one of the large global phenolic resin manufacturers. Further rationalization occurred within Dynea when the Dynea North American phenolic resin operation was sold to Teachers' Private Capital (Ontario, Canada) and renamed Arclin. Another business unit of Dynea, Vyncolit, the phenolic resin molding powders technology, was sold to Sumitomo Bakelite of Japan. Thus, more rationalization is anticipated as phenolic resin technology expands in China, Russia, and India.

As phenolic resins embark into the twenty-first century, the outlook continues to be extremely favorable. However, there are some vigilant activities that relate directly to phenolic resin consumption. The concern over free formaldehyde emissions and their presence as one of the components in the binder for wood panels have resulted in newly proposed rules by California Air Resources Board (CARB) for lower formaldehyde emissions in wood panels in two distinct phases: Phase I (by January, 2009) a reduction of FF value to 0.08 and 0.18 ppm. in hardwood plywood and particle board respectively, and reduced further to 0.05 and 0.09 ppm for the same panels for Phase II by January 2011. These CARB proposals will involve some production modifications when using phenolic resins but is expected to result in additional phenolic resin opportunities by displacing possibly urea formaldehyde resin in particle board panels. The use of phenolic resins as wood adhesives is undergoing many changes due to new wood composite processes coupled with continuous line equipment that are placing greater performance standards on improved wood adhesives. These increased improvement demands coupled with volatile emissions reductions are providing great challenges to wood adhesive manufacturers, many of which are discussed in the wood chapter. As it will be mentioned in wood adhesive area, hybrid resins such as MUF and PMUF are being developed to reduce the amount of formaldehyde emissions in wood panels ensuring the use of UF resins with reactive co-reactants and thus reducing formaldehyde emission.

By contrast, Johns Manville has commercialized a fiber glass insulation product which is "formaldehyde free" and involves a binder that is based on a cured acrylic resin system. It is uncertain whether these modified acrylic binders will lead to a substantial shift in the use of phenolic resins as binders for fiber glass insulation.

It should be noted that once formaldehyde is incorporated into the phenolic resin structure, it is permanently bonded to phenol and no formaldehyde is emitted during processing of the resin. Yet in those instances when the level of free formaldehyde (unattached formaldehyde) in the resin is reduced by the addition of a formaldehyde scavenger like urea, some formaldehyde can be emitted during processing due to a shift in the equilibrium reaction of formaldehyde and urea. In a perceptive manner, some of the benefits of selective basic catalysts used to prepare mineral wool binders with reduced crystalline dimer are mentioned in the mineral wool insulation binders chapter as well as the multiplicity of roles that ammonium sulfate experiences in the final mineral wool binder mixture.

Renewable raw materials, particularly those that would reduce the amount of expensive phenol, continue to be examined and are discussed in several chapters. Materials such as cashew shell nut oil, tannins, soy, and furfural are being examined for an economic benefit without corresponding unfavorable product performance. Other renewable materials such as tung oil and linseed oil continue to be used in limited amounts in the usual applications such as electrical laminates (tung oil) and friction (linseed oil). The emergence of “Biorefineries” in Europe as well as the US to process lignocellulose waste into fuels and chemical raw materials may result in the availability of pure lignin as a phenolic-like material for utilization in phenolic resin preparation. Lignin economics will be a factor for its potential use in phenolic resins.

The escalating cost of energy and its impact on phenolic resin raw materials, resin production, and processing of phenolic resins by customers is of paramount importance. Low energy systems are stressed by resin customers in spite of cure limitations of phenolic resin chemistry. Efforts directed to the use of resorcinol and tannins in fast cure systems may provide some benefit in energy reduction. Economic value versus energy reduction will need resolution.

The global commitment to Nanotechnology has not evaded phenolic resins. Although results are somewhat preliminary, some attractive phenolic resin mechanical properties are improved and offer promise for continued efforts in this new and exciting technology. Thus, ablation improvement due to reduced thermal erosion for rocket motors, improved thermooxidative stability of carbon carbon composites, and better scratch resistant flooring are current developments that have occurred through Nanotechnology.

The bold commitment of the commercial aircraft manufacturers (Boeing and Airbus) to fabricate the entire fuselage and other critical components involving over 50% of aircraft weight with fiber reinforced composites for reduced weight and greater fuel efficiency has become a “lightning rod” for re-assessment of product performance with greater emphasis on composites. Although phenolic resin based composites enjoy an enviable position as the preferred composition for aircraft interiors and cargo liners, the quest to develop a “load bearing” phenolic resin composite structure that meets or exceeds the mechanical properties of an epoxy resin based composite is desired. Efforts in closely related phenolic systems such as benzoxazine or phenylene bisoxazolines (PBO) may provide encouragement.

The proposal to broaden the recognized FST characteristics of phenolic resins as an additive into thermoplastic resins for UL VO flame retardant behavior is a consideration.

Weight savings for greater fuel efficiency are related to the replacement of metals and ceramics in the auto industry by many of the newly developed phenolic molding compounds involving long glass fiber (for greater toughness/impact) and carbon fiber reinforced phenolic molding compounds. As the auto industry addresses the need for greater fuel efficiency involving corresponding reduction in auto body weight and auto components, the weight of friction parts will also be reduced. Thus, the frictional load applied to the friction element is expected to increase and will necessitate phenolic resins with greater heat resistance.

New areas in the use of phenolic resins continue to be developed. Carbon foam is prepared by the carbonization of open cell phenolic foam or by expansion/cure of mesophase pitch at elevated temperature. These newly developed materials are attractive compositions for composite tooling and for paneling clad with fiber reinforced prepreg. Phenolic foam for thermal insulation is being reassessed in North America by producing fiber reinforced phenolic foam with a pH close to neutral. There is a reported possible opportunity to replace balsa core with pultruded high density phenolic foam in US naval ship structural sandwich panels.

Significant efforts have resulted in the commercialization of benzoxazine resin, a closely related phenolic material, as well as formulation of benzoxazine resin into fiber reinforced composites, electronics applications, and prepreg intermediate. Benzoxazines appear to be versatile in that they can undergo co-reaction with a variety of materials such as epoxy, isocyanates, and BMI.

Phenylene bisoxazolines are being revisited by reacting them with selected novolaks to yield novel polyaryl ether amide resins that possess performance characteristics equal to or better than high T_g multifunctional epoxies but with improved toughness and hot wet strength.

The current shift to more offshore oil exploration and in greater depths will require the manufacture of more fire resistant composite platforms, deluge pipe, and other items closely related to offshore oil activities. Pultrusion of platforms and phenolic foam paneling are expected to be in great demand. Proppants and emulsifiers will grow.

Selective non-formaldehyde or non-hexa curing agents are being examined and consist of glyoxal, oxazolidine, solid resole, epoxy, resorcinol, and tannins. In some cases these non-formaldehyde curing agents require less energy for full cure of phenolic resins.

Co-reaction of phenol formaldehyde with urea, melamine, olefin, and others occurs readily within the PF structure. Group appendage involving reactions directed to the phenolic hydroxyl such as epoxy, cyanate ester, or allyl groups or ring formation through the use of formaldehyde with a primary amine to yield benoxazines expands the versatility of phenolic resin chemistry. Post cure or reaction with B, N, or P type components provides improved thermal stability.

Newly developed novolak process by Asahi (known as Phosphoric Acid Phase Separation [PAPS]) and Sumitomo Bakelite (who later abandoned the method) involves the use of a high amount of phosphoric acid as catalyst/phase reactant. Asahi proposes “Phase transfer catalysis” as the method and results in a rapid process for novolak preparation. The resulting novolaks are predominately high in para content, possess minimal amounts of free phenol or dimer, better thermal stability, slower curing with hexa, and exhibit a lower bulk viscosity than conventional novolak prepared by oxalic acid. This new novolak process is mentioned in the chapter on resin chemistry.

Timely and concurrent information related to the key phenolic resins raw materials, modern analytical techniques used in phenolic resins analyzes/testing, and various application areas are written by experts who are engaged in daily technical problem solving activities. This new phenolic resins book is global in technical content and attempts to provide a worldwide view of phenolic resins technology as it is applied globally in all market sectors.

Part I
Raw Materials

Chapter 2
Phenols

Manfred Weber and Markus Weber

Abstract Up to the end of the nineteenth century, phenol was recovered primarily from coal tar. With the commercialization of the phenolic resins, the demand for phenol grew significantly. Currently, the cumene-to-phenol process is the predominant synthetic route for the production of phenol. It is accompanied by acetone as a co-product. Cumene is oxidized with oxygen to form cumene hydroperoxide. The peroxide is subsequently decomposed to phenol and acetone, using a strong mineral acid as catalyst. The products are purified in a series of distillation columns. The cumene-to-phenol process is described in more detail in this chapter. An overview is given about synthetic routes via direct oxidation of benzene. None of these alternative routes has been commercialized. The chapter also gives an overview of global supply and use of phenol in 2008. Finally, the main natural sources and synthetic routes for cresols, xylenols, resorcinol, and bisphenol-A are described. These components are used as comonomers for special phenolic resins.

Abbreviations

ACP	Acetophenone
AMS	α-Methylstyrene
BP	Boiling point
BPA	Bisphenol-A
BWWT	Biological Waste Water Treatment
CHP	Cumene hydroperoxide
DAA	Diactone alcohol
DCP	Dicumyl peroxide

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DiPB	Diisopropylbenzene
DMBA	Dimethyl benzyl alcohol
H_2	Hydrogen
H_2O	Water
H_2O_2	Hydrogen peroxide
MOX	Mesityloxide
MAK	Maximale Arbeitsplatzkonzentration
MHP	Methyl hydroperoxide
MP	Melting point
MW	Molecular weight
NaOH	Caustic soda
NaPh	Sodium phenate
NH_3	Ammonia
NO_x	Nitrogen oxides
N_2O	Nitrous oxide
PEL	Permissible exposure limit
SADT	Self-Accelerating-Decomposition-Temperature
TriPB	Triisopropylbenzene
TWA	Time weighted averages (over 8 h)

Phenols are aromatic components which contain one or more hydroxyl groups that are attached to an aromatic ring. For the production of phenolic resins, mostly mono-hydroxybenzenes, especially phenol, are of the greatest importance. Besides alkylphenols (cresols and xylenols), resorcinol (di-hydroxybenzene) and bisphenol-A are used sparingly for the production of phenolic resins. In Table 2.1, the main physical properties of these various phenols are summarized. Compared to aliphatic alcohols, phenols are weak acids. Thus, phenols can be easily extracted from organic solutions with aqueous sodium hydroxide. This is the preferred method to recover phenol and cresols from coal tar [1].

Table 2.1 Physical properties of phenols [6, 29, 32, 33]

Name		MW	MP (°C)	BP (°C)	pK_a 25°C
Phenol	Hydroxybenzene	94.1	40.9	181.8	10.00
o-Cresol	2-Methylphenol	108.1	31.0	191.0	10.32
m-Cresol	3-Methylphenol	108.1	12.2	202.2	10.09
p-Cresol	4-Methylphenol	108.1	34.7	201.9	10.27
2,3-Xylenol	2,3-Dimethylphenol	122.2	72.6	216.9	10.54
2,4-Xylenol	2,4-Dimethylphenol	122.2	24.5	210.9	10.60
2,5-Xylenol	2,5-Dimethylphenol	122.2	74.9	211.1	10.41
2,6-Xylenol	2,6-Dimethylphenol	122.2	45.6	201.0	10.63
3,4-Xylenol	3,4-Dimethylphenol	122.2	65.1	227.0	10.36
3,5-Xylenol	3,5-Dimethylphenol	122.2	63.3	221.7	10.19
Resorcinol	3-Hydroxyphenol	110.1	109.8	276.5	–
Bisphenol-A	2,2-Bis(4-hydroxyphenyl)propane	228.3	157.3	–	–

2.1 Phenol

Up to the end of the nineteenth century, phenol was recovered primarily from coal tar. Presently, a small amount of phenol is still obtained from coal tar. Yet in 1898, Felix Hoffmann filed his patent [2] for the synthesis of acetylsalicylic acid (*Aspirin*), which required phenol as starting material.

At the dawn of the twentieth century, the demand for phenol grew significantly with the commercialization of the phenolic resins (*Bakelite*). Leo Baekeland launched his first phenolic resins plant in May 1910 in Germany since phenol was readily available from coal tar. Much later the use for bisphenol-A (polycarbonates and epoxide resins) became an important factor for the substantial market growth of phenol. Synthetic routes were developed at the end of the nineteenth century to meet the increasing demand for phenol.

The first synthetic method for the production of phenol involved sulfonation and later chlorination of benzene. Details are described in [3]. These processes are no longer used for the commercial production of phenol.

After the Second World War, the cumene-to-phenol process (Hock-Process) was developed and commercialized. It is currently the predominate route for the production of phenol. It is accompanied by acetone as a co-product. Details are described in Sect. “Phenol Production from Cumene”.

In the 1960s, the first commercial plant using toluene as the feedstock was launched. The process was developed simultaneously by Dow [4] and the California Research Corp. [5]. The process is described in more detail in [6]. However, all commercial plants were closed in 2006. Currently, there is no commercial production of phenol from toluene.

Several attempts have been explored during the past two decades to synthesize phenol via the direct oxidation of benzene. Unlike the cumene process route, the direct oxidation of benzene does not produce acetone as a co-product and offers the potential for economy of operation without by-product.

One route is the direct oxidation of benzene with nitrous oxide N_2O, which was mainly developed by Solutia in cooperation with the Boreskov Institute of Catalysis in Russia [7, 8]. The oxidation of benzene is made on zeolite catalysts (ZSM-5) in the gas phase at 300°C to 450°C. The greenhouse gas (N_2O) is a main component in the off-gas from the adipic acid production. Its use for the phenol production would therefore be ideally suited to the adipic acid manufacturers. However, the off-gas requires careful purification to remove various nitrogen oxides (NO_x) and oxygen. As an alternative, N_2O could be produced deliberately by catalytic oxidation of ammonia NH_3 with air [8] without relying on it as a by-product from adipic acid plants.

In [9–11], an overview is presented on the use of oxygen or hydrogen peroxide H_2O_2 for the direct oxidation of benzene with various catalysts. When using oxygen, the benzene conversion is limited to only several per cent due to low selectivities. With hydrogen peroxide, higher conversion rates should be possible. For example, Bianchi et al. [12] reported a three-phase process operating at around 100°C using aqueous hydrogen peroxide as a first liquid phase followed by an organic benzene/sulfolane mixture as the second phase, and a titanium silicalite catalyst (TS-1) as the third phase. However, conversion rates of benzene are still low of only around 10% with selectivities to phenol of around 90%.

None of the above described routes via direct oxidation of benzene have been commercialized. The use of either NH_3 or H_2O_2 is questionable since both are valuable chemical intermediates, and their role as oxygen carriers must be considered in any economical assessment of a direct oxidation of benzene to phenol.

2.1.1 Physical Properties of Phenol

Various physical properties of phenol are shown in Table 2.2.

At ambient temperatures, phenol is a solid and appears as a white amorphous material. It possesses a melting point of 40.9°C. In the molten state, pure phenol is a clear, colorless liquid. When exposed to air, phenol rapidly turns to a pink color due to certain trace impurities such as iron and copper that are present in its production process or during storage.

Table 2.2 Physical properties of phenol [6, 34]

CAS registration number	108–95-2
EG registration number	604–001–00–2
MAK limit	2 ppm/7.8 mg/m^3
OSHA PEL (TWA)	5 ppm
MW	94.1
MP	40.9°C
BP	181.8°C
Relative density	1.092 (0°C) 1.071 (20°C) 1.050 (50°C)
Specific heat	1.256 kJ/kg K (0°C) 1.394 kJ/kg K (20°C) 2.244 kJ/kg K (50°C)
Heat of vaporization	511 kJ/kg (181.8°C)
Vapor pressure	0.02 kPa (20°C) 0.25 kPa (48.5°C) 5.0 kPa (98.7°C) 50 kPa (158.0°C) 100 kPa (181.8°C) 500 kPa (247.7°C) 1,000 kPa (283.0°C)
Mutual solubility of phenol and water	72.16 wt% phenol in phenol phase vs. 8.36 wt% phenol in water phase at 20°C, consolute point at 68.4°C
Lower explosion limit	1.3 vol%
Upper explosion limit	9.5 vol%
Flash point ("closed cup")	82°C
Ignition temperature (DIN 51794)	595°C

The melting and solidification temperature is lowered considerably by traces of water - approximately 0.4°C per 0.1 wt% water. Phenol becomes liquid at room temperature when around 6 wt% water is added.

At temperatures below 68.4°C, phenol is only partially miscible with water. Phenol is soluble in aromatic hydrocarbons, alcohols, ketones, ethers, acids, and halogenated hydrocarbons. It is less soluble in aliphatic hydrocarbons. Phenol forms azeotropic mixtures with water, cumene, and α-methylstyrene (AMS) as reported in reference [13].

2.1.2 Chemical Properties of Phenol

The chemical properties of phenol are unique. They are due to the presence of a hydroxyl group and an aromatic ring which are complementary to each other in facilitating both electrophilic and nucleophilic type of reactions. Phenol has an extremely high reactivity of its ring toward electrophilic substitution and assists its acid catalyzed reaction with formaldehyde leading to phenolic resins. Further phenol is a weak acid and readily forms sodium phenate (NaPh). In the presence of NaPh, nucleophilic addition of the phenolic aromatic ring to the carbonyl group of formaldehyde occurs. A base catalyzes the reaction by converting phenol into the more reactive (more nucleophilic) phenate or phenoxide ion for reaction with formaldehyde - see Chap. 4, Resin Chemistry. Thus phenol's unique ability to react with formaldehyde under acidic or basic conditions leading either to novolaks resins (via acid conditions) or resole resins (basic conditions), were the resin reactions that fostered the commercialization of phenolic resins, Bakelite, by Baekeland.

The unshared electron pair located on the hydroxyl group is delocalized over the aromatic ring leading to an electron excess at the ortho and para positions. Classical electrophilic reactions are halogenation, sulfonation, and nitration. The reaction of bromine in aqueous solution results in 2,4,6-tribromophenol in high yields.

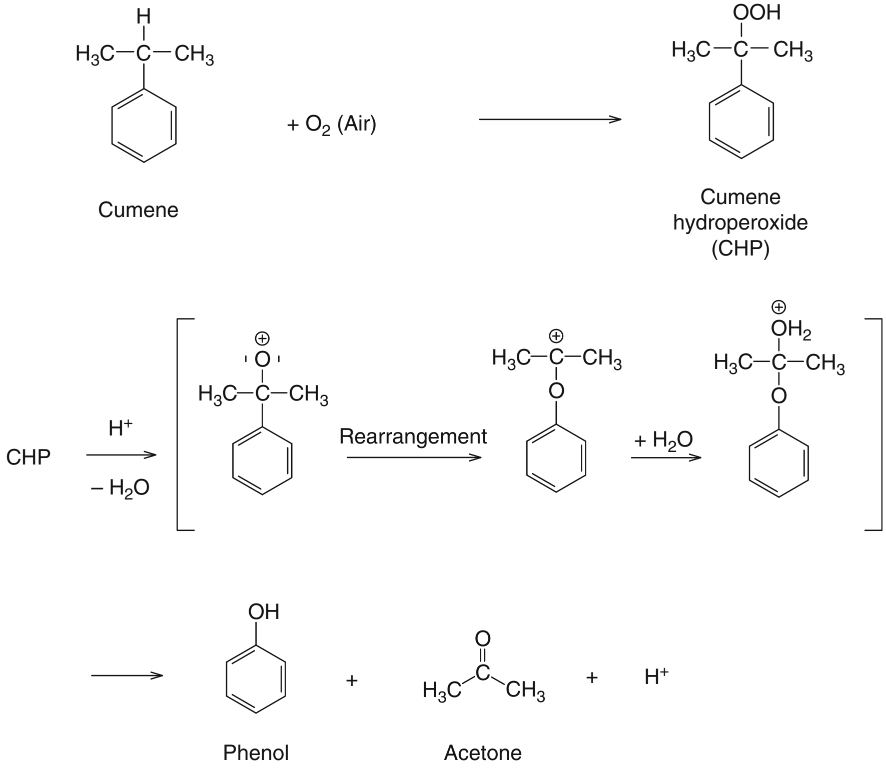
Under special conditions acid catalysts facilitate the conversion of phenol with formaldehyde to bisphenol-F or reaction of acetone to bisphenol-A.

Phenol can be hydrogenated on palladium catalysts to cyclohexanone with high selectivities [14, 15]. Cyclohexanone is the feedstock for the production of caprolactame monomer for Nylon 6.

2.1.3 Phenol Production from Cumene

Presently the cumene-to-phenol process is the predominant route for the production of phenol. In 2008, more than 97% of the phenol worldwide was produced by this process. The process was first reported by Hock and Lang [16], see Sects. "Phenol" and "Alkylphenols" below. Cumene is oxidized with oxygen (from air) to form cumene hydroperoxide (CHP). The peroxide is subsequently decomposed to phenol and acetone, using a strong mineral acid as a catalyst. Figure 2.1 shows the flow sheet of the cumene-to-phenol process.

Cumene as a feedstock for this process is produced from benzene and propylene. Formerly the alkylation reaction was carried out in solution with acidic catalysts like phosphoric acids and aluminium chloride. Currently, most of the cumene is produced commercially with heterogeneous zeolite catalysts. Licensors are UOP, Badger Licensing and CDTech. Details are described in [17].



After World War II, the cumene-to-phenol process was developed on a commercial scale by The Distillers Co. in Great Britain and the Hercules Powder Company in the USA. The first production plant was commenced in 1952 in Shawinigan, Canada. Today, several licensors offer their technology such as KBR or UOP. Although all these processes use the principles of the Hock synthesis, there are differences in the design and operation of the reaction units and the distillation unit.

The world's biggest phenol producer is Ineos Phenol, formerly Phenolchemie, which constructed the first production plant in Gladbeck, Germany, in the early 1950s. The production was initiated in 1954 with a capacity of 8,000 tons phenol per year. Currently the capacity is 650,000 tons/year. In 1993, a new plant was started up in Antwerp, Belgium. After several expansions, the capacity is currently

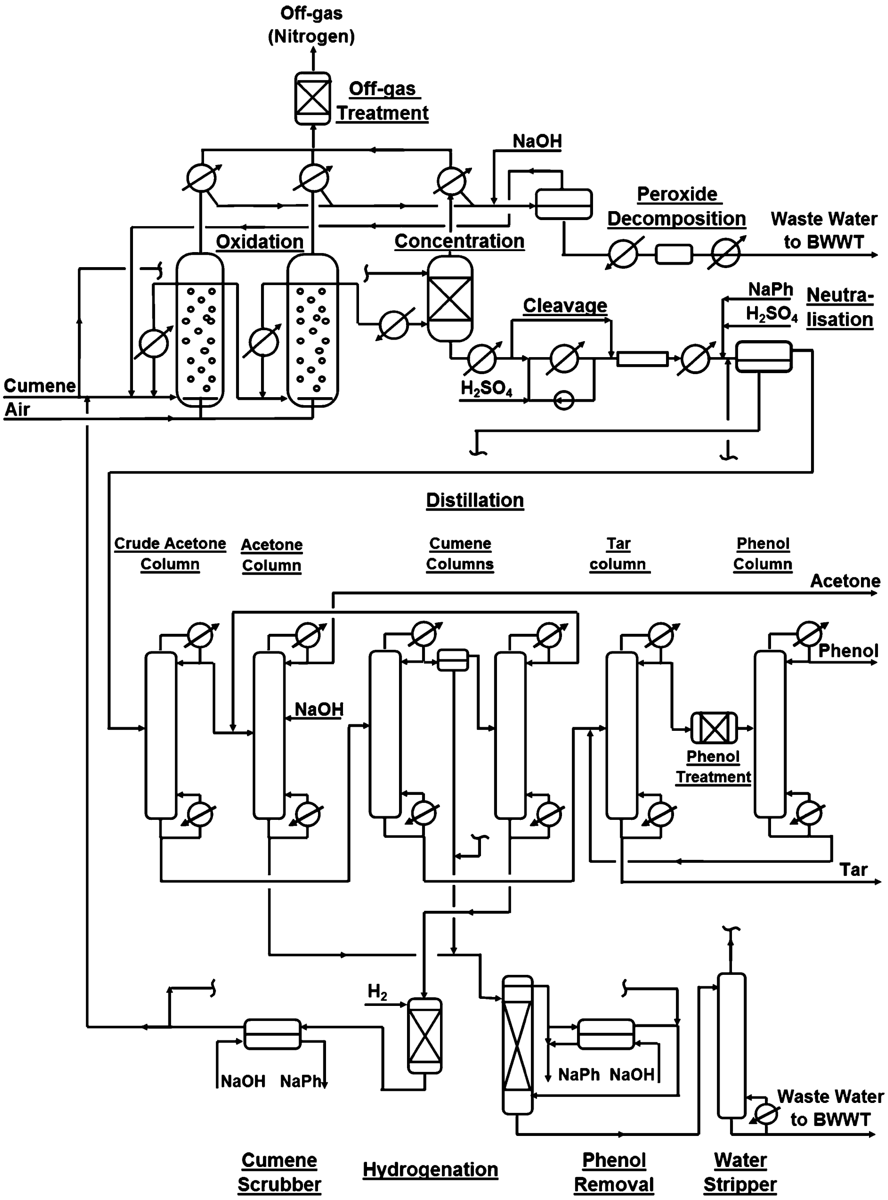


Fig. 2.1 Cumene-to-phenol process flow diagram

680,000 tons/year. In 2000, yet another plant was placed into operation in Mobile, Alabama. The actual capacity there is 540,000 tons/year.

Referring back to Fig. 2.1, cumene is first oxidized with oxygen from air to CHP. Fresh and recycle cumene flow through a cascade of large bubble columns. Air is added at the bottom of each reactor. Oxygen transfers from the air bubbles into the cumene. The reaction in the liquid phase proceeds by a complex radical mechanism [18]. The reaction is auto-catalyzed by CHP. The liquid phase in such large reactors is intensively mixed by the rising gas bubbles. This mixing characteristic plays a critical role in conversion rates and yields [19]. The bubble columns operate at pressures ranging from atmospheric to around 700 kPa. The temperatures are typically in the 80°C–120°C range. The reaction is exothermic with a heat of reaction of -117 kJ/mol. The residence time in the reactors is several hours. The temperature is controlled by internal or external heat exchangers. The final CHP concentration is in the 20–40 wt% range.

Several by-products are formed in the oxidation step. The overall process selectivity is mainly dependent on the formation of dimethylbenzyl alcohol (DMBA) and acetophenone (ACP). DMBA is dehydrated in the cleavage unit to AMS and partially forms high-boiling components. ACP leaves the process with the high boilers from the distillation unit. It can also be recovered as a pure product. Other by-products are formic and acetic acid. Small amounts of methyl hydroperoxide (MHP) are formed and removed with the off-gas. Phenol is a strong inhibitor for the oxidation reaction. Any recycle cumene must be treated to remove even small traces of phenol.

From a safety point of view, great care is required in the design of the air inlet devices (sparger) at the bottom of the reactors. Any backflow of peroxide containing liquid into the air line must be avoided. It is also important to monitor and ensure a low final concentration of oxygen in the off-gas at the top. This is to avoid an explosive mixture in the gas phase and in the subsequent units for the off-gas treatment [20]. Another important aspect is thermal stability of a reactor after a shut-down. It is important to know at what temperature a reactor has to be cooled down to avoid subsequent heating up from the ongoing exothermic decomposition of CHP. This is the so-called *Self-Accelerating-Decomposition-Temperature* (SADT) [19].

The off-gas from the reactors, that is mainly nitrogen and other organics, is cooled to around 0°C to condensate and separate most of the cumene. Residual impurities can be removed from the off-gas with activated carbon adsorbers [21] or with regenerative thermal oxidizers [22]. Off-gas, which is purified under pressure on activated carbon, can be used as *technical grad*e nitrogen for blanketing or venting of process equipment. It can also be used to dry adsorbers after regeneration with steam.

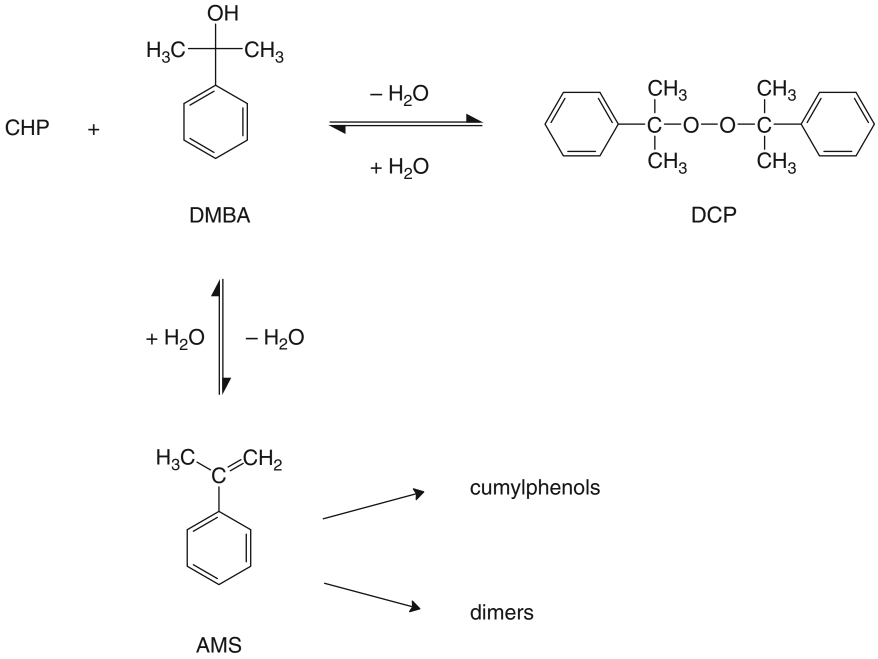
Besides cumene, the water phase is condensed from the off-gas, in which MHP is present. After treatment with diluted caustic soda, the cumene is recycled to the oxidation unit. The water phase is treated at temperatures above 100°C and a high pH to decompose the MHP to methanol. Disposal of MHP in the aqueous stream is not allowed since it is toxic to fish. The water is then sent to a biological waste water treatment (BWWT).

The product from the oxidation unit is concentrated from 65 to 90 wt% CHP. This is accomplished in a one- or multiple-step vacuum distillation, the so-called concentration unit. Cumene is separated at temperatures below 100°C to minimize thermal decomposition of CHP. Highly efficient structured packings are used in these columns. Fresh cumene can be used for reflux. The distilled and recycled cumene is washed with diluted caustic soda to remove organic acids and traces of phenol.

During any shut down, especially in case of a total power failure, the equipment in the concentration unit must be flushed with cumene to avoid runaway reactions of the hot and concentrated CHP. Therefore, a certain amount of pressurized cumene, so-called *flush cumene*, must be available at all times.

The first part of the cleavage unit is a circulation loop. One or several heat exchangers are installed as reactors within the loop. Small amounts of sulphuric acid are used as the catalyst. CHP is added to the loop and is spontaneously diluted with the product from the reaction which is mainly phenol, acetone, and residual cumene. In the event of a shut down, the injection point is flushed with cumene to separate CHP from acidic cleavage product in the loop. CHP decomposes while passing through the heat exchanger. The reaction is exothermic with a heat of reaction of −252 kJ/mol and occurs within 1 min. The temperature is controlled at around 50°C. DMBA is partially dehydrated to AMS, which reacts in consecutive reactions with phenol to high-boiling cumylphenols, see below. AMS also forms high-boiling dimers. DMBA reacts with CHP to dicumyl peroxide (DCP) and water.

Other by-products are hydroxyacetone from the reaction of CHP and acetone, 2-methylbenzofurane (2-MBF) from the reaction of hydroxyacetone with phenol, diacetone alcohol from the self-condensation of acetone, and mesityloxide (MOX) from the dehydration of diacetone alcohol. Some aldehydes are also formed, especially acetaldehyde. All these by-products require special conditions in the distillation unit to separate them from phenol and acetone. An overview of all these reactions is given in [23].



The product from the reaction loop is finally treated in a plug-flow reactor at temperatures above 100°C. The temperature is increased by adding again CHP [24] or by indirect heating with steam. In this reactor, DCP reverts to CHP and DMBA. CHP is cleaved spontaneously to phenol and acetone, while DMBA is completely dehydrated to AMS and water.

The product from the cleavage unit is cooled. All acid-catalyzed reactions from AMS are stopped by adding sodium phenate (NaPh) in the neutralization unit. Additional sulphuric acid may be needed if excess NaPh needs to be decomposed to recover phenol. Salts from organic acids, mainly sodium sulphate from the decomposition of NaPh, are extracted in the aqueous phase. This process water is further treated in the phenol removal unit to recover phenol by liquid-liquid extraction with cumene as the extraction solvent. Phenol is recovered from the cumene as NaPh by washing with caustic soda in a separate scrubber. Parts of the cumene in the phenol removal unit may be refreshed with purified recycle cumene or fresh cumene. NaPh and discharged cumene are routed to the neutralization unit. The process water is finally treated in a water stripper to remove dissolved acetone and cumene.

The product from the neutralisation unit is sent to the distillation unit. In the crude acetone column, acetone and some water are separated as the top product. Pure acetone is recovered in the acetone column as the top product. As an alternative, pure acetone may be separated as an upper side stream to allow removal of light-boilers at the top. Caustic soda is added to this column to convert aldehydes to high-boiling components. The bottom product of this column, which is mainly water, is treated in the phenol removal unit to remove the organic components. It can also be recycled to the neutralization unit.

The bottom product from the crude acetone column is sent to the first cumene column. The cumene with AMS and some phenol as well as water are separated as the top product. The water is separated in a decanter and treated in the phenol removal and in the water stripper to remove phenol, acetone, and cumene. All process water is sent to the final treatment in a BWWT.

The cumene is separated from low boilers, mainly acetone and water, in the second cumene column. The AMS is hydrogenated to cumene in the hydrogenation unit on selective palladium catalysts. These catalysts are highly selective toward the hydrogenation of AMS without any interfering hydrogenation of phenol. Phenol is then separated from the cumene in a cumene scrubber, again using aqueous caustic soda as the extraction solvent. The NaPh is routed to the neutralization unit. The cumene is recycled back to the oxidation unit.

The bottom product from the first cumene column is sent to the tar column. All high-boiling components are separated at the bottom. The tar is typically used as fuel to produce steam. Crude phenol is separated as the top product. As an alternative, crude phenol may be taken as an upper side stream to remove residual amounts of hydrocarbons at the top. Traces of hydroxyacetone, 2-MBF, and MOX in phenol are converted to high-boilers in the phenol treatment unit. Acidic ion exchange resins are used in fixed-bed reactors to accomplish conversion to high boilers [25]. These high-boilers are separated from pure phenol in the phenol column and routed to the tar column. In the phenol column, pure phenol may be separated at an upper side stream to remove light-boilers at the top.

2.1.4 Sources for "Natural" Phenol

The recovery of "natural" phenol from coal tar is still a fully operational method to recover phenol. Coal tar is a complex mixture of condensable organic components, emerging from coal carbonization [1]. During the fractionation of the coal tar, so-called *carbolic oil fraction* is separated and contains 30–35 wt% phenolic components. These phenols are called *tar acids*. The carbolic oil is treated with diluted caustic soda to extract the phenols as sodium phenolate salts. The aqueous phenolate solution is then treated with carbon dioxide to liberate the phenols from the salts.

This crude phenol fraction from carbolic oil consists of phenol, cresols, and xylenols. A typical composition is 30 wt% phenol, 12 wt% *o*-cresol, 18 wt% *m*-cresol, 12 wt% *p*-cresol, 8 wt% xylenols, 15 wt% water, and 5 wt% tar [1].

Phenol and *o*-cresol can be isolated by distillation. The separation of *m*- and *p*-cresol requires more effort due to the similar boiling points, see Table 2.1. Some methods are described in [1]. The xylenol isomers can be separated by combined distillation and extraction steps.

Besides coal tar, other sources of "natural" phenols are the liquid byproducts from gasification processes [26]. Phenol, cresols, and xylenols are recovered from the aqueous phase by solvent extraction, for example with the Lurgi Phenosolvan process. A large source of natural phenols is the liquid by-products from Sasol's gasification process in South Africa [27]. The phenols are produced and marketed by Merisol, a joint venture between Sasol and Merichem (USA), with a total production of phenols (phenol, cresols, xylenols) of about 110,000 metric tons per year in 2003 [28]. Another large source is the recovery of phenols from the gasification process of lignite coal at Dakota Gasification Company (USA). The annual production of phenol there is about 20,000 metric tons.

2.1.5 Global Supply and Use of Phenol

In 2008, the world-wide phenol capacity for phenol production was around 9.9 million tons, with 98.5% based on the cumene-to-phenol process. The total production in 2008 was around 8.7 million tons. Table 2.3 shows the major phenol producers in the world.

In 2008, the largest use with around 44% was for the production of bisphenol-A, followed by phenolic resins (26%), cyclohexanone/caprolactame (12%), and others like alkylphenols (4%).

Table 2.3 Major phenol producers in the world (2008)

Company	Phenol capacity in thousands of tons per year
Ineos Phenol	1,870
Sunoco	800
Mitsui Chemicals	750
Shell	600
CEPSA Quimica	600
Polimeri Europa	480
FCFC	400
MtVernon Phenol (Sabic)	340
Kumho	330
Dow	300
Taiwan Prosperity	200
Mitsubishi Chemicals	250
Chiba Phenol	230
Georgia Gulf	230
LG Chem	200
Chang Chun PC	200
Rhodia	195
NOVAPEX	180

2.2 Alkylphenols

Alkylphenols are phenols with one or more of the aromatic hydrogens being replaced by an alkyl group. Mixtures are called *cresylic acids*. More specifically, if they are recovered from coal tar, they are called *tar acids*. Cresols are monomethyl derivatives of phenol. Xylenols are dimethyl derivatives.

Higher alkylphenols such as 4-*tert*-butylphenol, 4-*iso*-octylphenol, and 4-nonylphenol are used in phenolic resin production.

2.2.1 Cresols

The three isomers of cresols are *o*-, *m*-, and *p*-cresol. Like phenol, *o*- and *p*-cresol are crystalline solids at room temperature while *m*-cresol is viscous oil. Compared to phenol, they are less soluble in water.

Like phenol, cresols can be recovered from coal tar and other natural sources, see Sects. “Sources for ‘Natural’ Phenol”. Currently synthetic processes are an important route for the production of cresols. These routes are either based on toluene or phenol [29]:

- Chlorination of toluene and hydrolysis of chlorotoluene with caustic soda to sodium cresolate
- Sulfonation of toluene and conversion with caustic soda to sodium cresolate
- Alkylation of toluene with propylene to cymene, oxidizing to cymene hydroperoxide and subsequent cleavage to cresols and acetone

- Methylation of phenol, either in gas phase on aluminium oxide catalysts (350°C) or in liquid phase on aluminium methylate or zinc bromide (350°C, 50 bar).

The chlorination and sulfonation processes are similar to the former production routes to synthetic phenol. The synthesis via cymene hydroperoxide is also similar to the cumene-to-phenol process (Hock process). But the process is more complex, due to the formation of all three cymene isomers. In addition some methyl groups are oxidized to primary peroxides and cause more costly distillation procedures. Mainly *m*- and *p*-cresol are finally recovered from this process. Main product from the methylation of phenol is *o*-cresol.

Besides the use for phenolic resins, other applications for cresols are the production of herbicides, fungicides, disinfectants, and plasticisers.

2.2.2 *Xylenols*

Xylenols or dimethylphenols are available as six isomeric forms, see Table 2.1. They are all crystalline materials at room temperature. Compared to cresols, xylenols are less soluble in water, but can still be extracted from organic mixture with aqueous caustic soda. Xylenols can be recovered from the same natural sources as cresols and phenol.

Besides *o*-cresol, 2,6-Xylenol is the preferred product in the phenol methylation gas phase process [29] and the desired monomer for poly 2,6 dimethylphenylene oxide or PPO and used to make Noryl, a high performance thermoplastic resin. In the phenol methylation liquid phase process, mainly 2,4-xylenol besides 2,6-xylenol is formed.

There are similar routes for xylenols via chlorination and sulfonation as for cresols. Instead of toluene, xylenes are the precursors.

Finally, it is possible to produce 3,5-xylenol via alkylation of *m*-xylene, oxidizing to the corresponding peroxide and subsequent cleavage to 3,5-xylenol and acetone [30, 31].

Besides phenolic resins, other applications for xylenols are their use as solvents and disinfectants.

2.3 Resorcinol

Resorcinol or 3-hydroxyphenol is a white crystalline compound. Compared to phenol, it has significantly higher reaction rate toward formaldehyde.

Resins from resorcinol and formaldehyde (RF resins) are mainly used in the rubber industry. RF resins are used as adhesives for joining rubber with reinforcing materials, for example in tires and conveyer belts. Another important use is the high-quality wood adhesives. Special resins from resorcinol, phenol, and formaldehyde increase the curing rate in structural wood adhesives and allow cure at ambient temperatures. Resorcinol is also used as a light stabilizer for plastics and for the production of sunscreen preparations for the skin (ultraviolet absorbers).

Resorcinol is produced via sulfonation of benzene to benzene-1.3-disulfonate (INDSPEC Chemical Corp., USA) or via hydroperoxidation of *m*-diisopropylbenzene (Sumitomo, Japan) [32].

In the sulfonation process, benzene reacts with sulphur trioxide at around 150°C. In excess caustic soda, the benzene-1,3-disulfonate is converted into disodium resorcinate at 350°C. The salt is dissolved in water and neutralized with sulphuric acid. Resorcinol is extracted with an organic solvent such as diisopropyl ether.

In the hydroperoxidation process, benzene and a recycled benzene–cumene mixture is alkylated with propylene to diisopropylbenzene isomers. After addition of recycled *p*-diisopropylbenzene (*p*-DiPB) and triisopropylbenzenes (TriPB), the mixture is processed in an isomerisation/transalkylation unit to convert most of the *p*-DiPB and TriPB to *m*-diisopropylbenzene. (*m*-DiPB). The *m*-DiPB is then oxidized to *m*-diisopropylbenzene hydroperoxide. The peroxide is crystallized and dissolved in acetone. The handling of the solid organic peroxide requires special safety measures. The cleavage is carried out under acidic conditions to convert the peroxide into resorcinol and acetone. Usually, sulphuric acid is used as the catalyst in a boiling acetone mixture.

2.4 Bisphenol-A

Bisphenol-A (BPA) or 2,2-bis (4-hydroxyphenyl) propane is used for the production of special resins for coating applications in the phenolic resin area. Presently the main use for BPA is the production of polycarbonates and epoxide resins.

BPA is produced from phenol and acetone in the presence of an acidic ion exchange resin catalyst. Phenol is used in high molar excess. After the reaction, light boilers like acetone and water are separated by distillation. Acetone is recycled to the reactor. BPA is then crystallized in phenol. After mechanical separation and washing of the crystals with phenol, molten BPA is further purified. Excess phenol from the crystallization and from distillation is recycled back to the reactor.

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Chapter 3
Formaldehyde

Stefan Kowatsch

Abstract Formaldehyde, as an aqueous solution ranging from 37 to 50 wt%, continues to be the preferred aldehyde for reaction with phenol for the preparation of phenolic resins. Over 30 million metric tons of formaldehyde represent the global worldwide consumption of formaldehyde for an array of products, besides phenolic resins. These include urea formaldehyde resins, melamine formaldehyde resins, polyacetal resins, methylenebis (4-phenyl isocyanate) , butanediol, pentaerythritol, and others.

The two basic processes to produce formaldehyde from methanol – the silver catalyst process and the metal oxide process – are described along with the strengths and weaknesses of the respective processes. Furthermore, methanol plant siting location is a factor due to raw material (natural gas) and energy costs.

The controversy regarding the classification of formaldehyde as a human carcinogen remains unsettled. In 2004, the International Agency for Research on Cancer (IARC) of the World Health Organization reclassified formaldehyde from a group 2A substance (probable carcinogen to humans) to a group 1 (carcinogenic to humans) substance. Yet no government regulating agency has classified formaldehyde as a known human carcinogen. The studies that acknowledged formaldehyde to be a human carcinogen are being re-analyzed with additional research by IARC to re-examine its current classification of formaldehyde. By end of October 2009, despite strong disagreement among participants of the voting body, who were evenly split at the vote, IARC concluded that there is sufficient evidence in humans of a causal association of formaldehyde with leukemia. Industry disagrees with this conclusion and believes that the weight of scientific evidence does not support such a determination. A review of all of these data is still in process but impact on possible governmental reclassifications expected to be seen in 2010.

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3.1 Introduction

The public is accustomed to products that contain formaldehyde almost every day without any apparent awareness of the presence of formaldehyde in the product. Various industries such as the residential construction industry, the automotive industry, the aircraft industry, and even the health care industry are just a few examples of its broad utility. Even more surprising and unknown to many persons is the fact that human bodies produce formaldehyde, and it occurs naturally in the air we breathe. The use of formaldehyde for embalming purposes was one of the earliest and most widely known applications but represents far less than 1% of consumption.

Products that contain formaldehyde or materials made from formaldehyde enjoy a vital role in world economies, but their dependence on formaldehyde is largely invisible to the public. Statistics are not always well designed to identify or quantify the value of formaldehyde to consumers or the contribution of the formaldehyde industry to the economy in terms of jobs, wages, and investment [1].

3.2 Chemistry

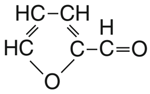
3.2.1 Aldehydes

Formaldehyde is practically the only aldehyde-containing material used in the synthesis of industrial phenolic resins. Special resins are made with other aldehydes, for example, acetaldehyde, butyraldehyde, furfural, glyoxal, or benzaldehyde, but these have not achieved much commercial importance. Ketones are also rarely used. Physical properties of some aldehydes [2–4] are compiled in Table 3.1.

3.2.2 Formaldehyde

Formaldehyde, the first of the series of aliphatic aldehydes, was discovered in 1859 by Butlerov and has been manufactured on a commercial scale since the beginning

Table 3.1 Physical properties of some aldehydes

Type	Formula	MP (°C)	BP (°C)
Formaldehyde	$CH_2{=}O$	−92	−21
Acetaldehyde	CH_3CHO	−123	20.8
Propionaldehyde	CH_3–CH_2–CH	−81	48.8
n-Butyraldehyde	$CH_3(CH2)_2$–CH	−97	74.7
Isobutyraldehyde	$(CH_3)_2CH$–CHO	−65	61
Glyoxal	O=CH–CH=O	15	50.4
Furfural		−31	162

of the twentieth century. Because of its variety of chemical reactions [5, 6] and relatively low cost (basically reflecting the cost of methanol), it has become one of the most important industrial chemicals.

Formaldehyde is a hazardous chemical [7–11]. It causes eye, upper respiratory tract, and skin irritation. Significant eye, nose, and throat irritation does not generally occur until concentration levels of 1 ppm. The Environmental Protection Agency (EPA) has classified formaldehyde as a "probable human carcinogen" (group B) under its "Guidelines for Carcinogen Risk Assessment" [12]. However, no evidence exists for identifying formaldehyde as a "probable human carcinogen" (group B). Facilities that manufacture or consume formaldehyde must strictly control workers' exposure following workplace exposure limits. Further information on toxicology and risk assessment of formaldehyde is mentioned in Sect. 3.6 of this chapter.

3.2.3 Chemical Properties of Formaldehyde

At ordinary temperatures, formaldehyde is a colorless gas with a pungent odor. Physical properties are shown in Table 3.2. It is highly reactive and commonly handled in aqueous solutions containing variable amounts of methanol where it forms predominantly adducts with the solvent [5, 6], that is, equilibrium mixtures of methylene glycol (3.1), polyoxymethylene glycols (3.2), and hemiformals of these glycols with methanol (3.3). Even in concentrated solutions, the content of nonhydrated HCHO is very small ($<0.04\%$). MWD of the oligomers was investigated by NMR [13] and GPC techniques. The chemical equilibria of polyoxymethylene glycol formation in formaldehyde solutions in water (and D_20) and of polyoxymethylene hemiformal formation in methanolic formaldehyde solution were examined by ^{1}H and ^{13}C NMR spectroscopy [13]. For similar formaldehyde concentration, the chain length of formaldehyde oligomeric products in aqueous solution is larger than in methanol solution. This fact explains why precipitation of solids (long-chain oligomer) occurs at a lower overall formaldehyde concentration in aqueous solutions than in methanol solution and why solid precipitation from aqueous formaldehyde solution can be avoided by adding methanol. Furthermore, with increasing temperature, the average chain length decreases in solution, whereas in methanolic formaldehyde solution temperature has a negligible effect on chain length. More recent NMR studies of formaldehyde in solution are discussed in Chap. 5, Analyses/Testing.

Table 3.2 Physical properties of formaldehyde [2, 3, 8]

GAS registration number	50–00–0
EG registration number	605–002–01–2
MAK limit	0.5 ppm
OSHA STEL	2 ppm
MW	30.03
MP/BP	−19.2°C/118°C
Dissociation constant, H_20 at 0/50°C	$1.4 \times 10^{-14}/3.3 \times 10^{-13}$
Flash point, 40% solution	60°C
Explosion limits LEL/UEL	7%/173%

In acidic solutions, hemiacetals are transformed into acetals by elimination of water.

$$\mathrm{HO - CH_2 -\ OH} \tag{3.1}$$

$$\mathrm{HO - (CH_2 - O)}_n \mathrm{- CH_2 - OH} \tag{3.2}$$

$$\mathrm{CH_3 - OH + HO - CH_2 - OH \longleftrightarrow CH_3 - O - CH_2 - OH + H_20} \tag{3.3}$$

With the action of basic catalysts, formaldehyde easily undergoes a disproportionation reaction to methanol and formic acid, known as the Cannizzaro reaction (3.4).

A surprising development related to the Cannizzaro reaction was reported by Ashby and coworkers [14]. The Ashby group showed that formaldehyde reacts with NaOH (Cannizzaro conditions) to yield formic acid and hydrogen quantitatively. Typically, conditions exist in which both hydrogen formation and classical Cannizzaro reaction proceed simultaneously. This is far different from the report of Loew in 1887 suggesting a very small quantity of hydrogen as being formed in the Cannizzaro reaction. Ashby showed that the reaction of 4 mol 1^{-1} NaOH with 15 mmol 1^{-1} formaldehyde resulted in the formation of hydrogen from 31% of formaldehyde, the remainder going to normal Cannizzaro products. Chrisope and Rogers [15] point out that with only 0.5 mol 1^{-1} NaOH, 20 mmol l^{-1} formaldehyde solution can be converted into 1–2% hydrogen and the remainder into Cannizzaro products. Depending on ratio of NaOH to formaldehyde, it is possible to generate some hydrogen resulting in potentially hazardous conditions.

Depending on manufacture and storage, formaldehyde solutions always contain trace amounts of formic acid (around 0.05%).

$$\mathrm{2\ H_2C = O + NaOH \longleftrightarrow CH_3OH + H_3C - COONa} \tag{3.4}$$

With concentrations ranging from 37 to 56 wt%, aqueous formaldehyde solutions used normally in resin production are unstable. Both formic acid and paraformaldehyde formation depend on temperature, time, and metallic ions (iron) concentration. Low temperature storage lowers the formic acid formation rate, but increases the tendency towards paraformaldehyde precipitation. Commercial formaldehyde grades are, therefore, stabilized with various amounts of methanol up to 15%. Other stabilizers consist of different guanamines, polyvinylalcohol, or isophthalobis-guanamine at concentrations from 10 to 1,000 ppm. Storage containers should be made of stainless steel; iron containers are not suitable. Containers with plastic linings or made from reinforced plastics may also be used. Solutions of formaldehyde higher than 50% are obtained by the addition of paraformaldehyde.

3.3 Manufacturing Processes

There are two basic processes to produce aqueous formaldehyde [16] from methanol by using either a silver or an iron oxide-molybdenum oxide catalyst. Each process possesses many variations, most of which are available to licensees.

3.3.1 Silver Catalyst Process

The silver catalyzed reaction occurs at essentially atmospheric pressure and 600°C–650°C with two parallel reactions:

$$CH_3OH + 1/2\ O_2 \rightarrow HCHO + H_2O \tag{3.5}$$

$$CH_3OH \rightarrow HCHO + H_2 \tag{3.6}$$

In a typical silver catalyst process, the feed mixture is prepared below the flammability limit by spraying air into heated methanol and combining the vapor with steam. The mixture is sent through a super heater to the reactor equipped with a bed of silver crystals or layers of silver gauze. The product is rapidly cooled and fed to an absorption tower. The bulk of the methanol, formaldehyde, and water is condensed in the lower water cooled section of the absorber; the nearly complete removal of the remaining methanol and formaldehyde occurs on the top of the tower by a countercurrent contact with clean process water. Absorber bottoms go to distillation where methanol is recovered and recycled to the reactor. The base stream from distillation, an aqueous solution of formaldehyde, is usually sent to an anion exchange unit where the formic acid is reduced to specification. The product contains up to 55% of formaldehyde and less than 1.5% of methanol. Vented gas can be recovered and used as boiler fuel or recycled.

Formaldehyde yields from the silver catalyst process are lower than from the metal oxide process, but this disadvantage is offset by a lower initial capital investment. The reactors can be very large, allowing producers to achieve economies of scale. Yields range from 80% to 92% of theoretical, with a typical yield of 87–88% of methanol for most well-maintained silver processes, requiring 6.8 Gal of methanol to produce 100 pounds of 37% formaldehyde solution (0.45 metric ton of methanol per metric ton of 37% solution). A slightly lower (82–83%) methanol yield is achieved with more poorly maintained silver processes (Fig. 3.1).

The catalyst for silver-based formaldehyde processes with the conversion of methanol to formaldehyde is electrolytic-generated pure silver crystals (content min. 99.99% Ag) with a typical temperature range of 500°C–700°C for operation. The total of other metal impurities should not exceed a maximum of 100 ppm. The most modern silver catalyst processes use a thin bed of silver crystals (Fig. 3.2).

The licensees of silver catalyst processes include Derivados Forestales, Dynea, ICI, Josef Meissner,

Mitsubishi Gas, ORKEM and Polimex–Cekop.

3.3.2 Metal Oxide Processes

The metal oxide process involves the catalytic oxidation of methanol by a mixed oxide catalyst containing iron and molybdenum. Other metals, such as chromium,

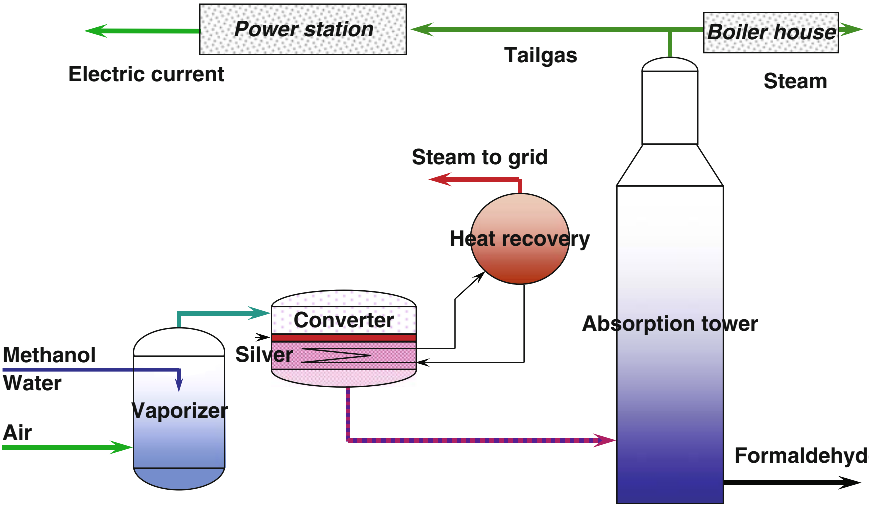


Fig. 3.1 Formaldehyde – Production using silver catalyst (Dynea)

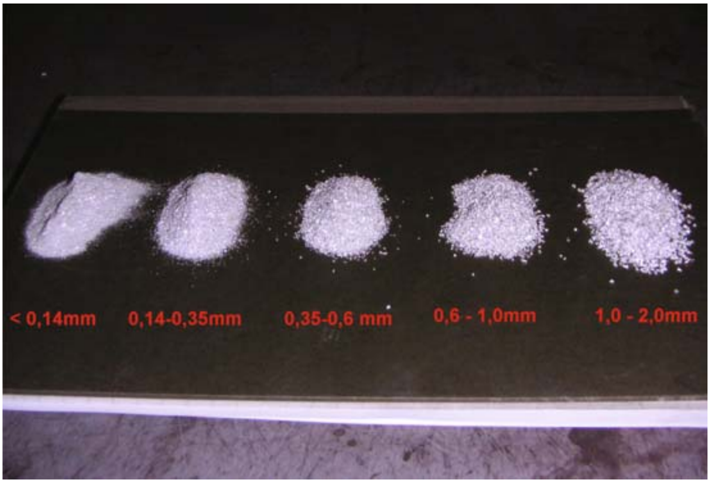


Fig. 3.2 Standard fractions of silver (Dynea)

are often used as catalyst promoters. The reaction is performed at essentially atmospheric pressure (0–6 psig) and approximately 300°C in a recirculation loop. Vaporized methanol is mixed with air and recycle gas to be on the methanol lean side of a flammable mixture, It is preheated to about 250°C and sent to the reactor. Methanol and oxygen react to formaldehyde in the tubes filled with an iron oxide-molybdenum oxide catalyst. The ferric-molybdate catalyst, in the form of spheres, granules, or cylinders, is placed in multiple fixed bed reactors; the shape of the catalyst affects energy costs. Small sized catalyst particles provide higher surface and such a better utilization; however, small-sized particles also increase the flow resistance in the reactor. Thus, the choice of the particle size very much depends on process efficiency as well as reactor geometry. Vaporized methanol and filtered air are fed to the reactors. The tubes of the reactors are surrounded by a boiling heat transfer fluid, usually diphenyl oxide, to which the heat of reaction is transferred and recovered as steam. The reacted gas which exits the reactor at about 290°C is cooled to 130°C before entering the absorber. In the absorber, the formaldehyde is absorbed in water or urea solution. The methanol conversion can be greater than 99%, yielding a product with up to 55% formaldehyde and less than 1% methanol. Formic acid is removed by ion exchange. The tail gas, essentially nitrogen and oxygen, with small amounts of methanol, formaldehyde, dimethyl ether, and carbon monoxide, is incinerated. The absence of a methanol recovery tower is an obvious advantage over the silver process. However, large capacity equipment is used to handle a greater flow of gas (three times greater). The metal oxide catalyst is more tolerant to trace contamination and requires less frequent changes compared to silver. Many metal oxide facilities produce urea-formaldehyde condensates by using urea in place of water at the quenching stage.

The two leading metal oxide processes are Perstorp and D.B. Western. The process was developed by Reichhold Chemicals, Inc. and subsequently sold to Perstorp AB. The Formox® process produces close to 90% yields, requiring 0.43 metric ton of methanol per metric ton of 37% formaldehyde. The D.B. Western process has been in use since 1981 and is employed in over 20 plants worldwide. The conversion of methanol is above 99%, with selectivity to formaldehyde of 91–92%. The D.B. Western process requires 0.42 metric ton of methanol per metric ton of 37% formaldehyde. The other licensees of metal oxide processes include Haldor Topsoe, Josef Meissner, and Nippon Kasei.

There has been significant research activity to develop alternative routes to formaldehyde, but without commercial success. The direct oxidation of methane with air at 450°C and 10–20 bar pressure on an aluminum phosphate catalyst should be mentioned among these processes. However, the process is not commercial.

3.4 Stabilizer

Although methanol is one of the more reasonably priced stabilizers, it is used only for special applications, for example, pharmaceutical industry. For acceptable results, methanol is added to 10%, and in some cases, up to 15%. By contrast, melamine is widely used to stabilize aqueous formaldehyde solution in the range of 40% (weight) and concentrations of melamine used are typically 0.25%–1.0%.

Guanamine such as benzo-guanamine and aceto guanamine is widely used to stabilize formaldehyde solutions with up to 45% w formaldehyde. The required amount depends strongly on the formaldehyde storage temperature and storage duration. Typically, 0.02–0.25% of guanamine is used.

Caprinoguanamine is one of the most effective stabilizing agents for formaldehyde. It is mainly used to stabilize highly concentrated formaldehyde solutions at even low storage temperature. It is effective up to formaldehyde concentrations of 55% w. The required amount depends on concentration, storage temperature, and storage duration. It can be in the range of 0.02–0.25% w. Caprinoguanamine tends to build up a stable foam which can lead to difficulties in resin manufacturing processes, especially when the hardener is added from the top of the reactor.

Finally, industry may use several stabilizers containing polyvinyl acetate and/or polyvinyl alcohol together with various other substances as the active component. Effective concentrations vary between 10 and 500 ppm depending on the stabilizing requirement but typically for lower concentration formaldehyde solutions.

3.5 World Market

Worldwide, most phenol resin producers without a captive phenol source are very often engaged in formaldehyde production for their consumption. Formaldehyde producers represent a rather unique oligopoly industry and a highly competitive one. The availability and access of low-cost methanol feedstock is a very important competitive factor for these resin manufacturers who are backward integrated into formaldehyde production.

3.5.1 Methanol

About 90% of the methanol produced is based on natural gas as feedstock. Others include naphtha, heavier oil fractions, and coal. The cost of natural gas is the most significant factor besides plant size (capital charges) in siting a plant at a specific location [17, 18]. For example, comparing a 200,000 tons per year methanol plant in the Middle East or in Germany, gas and energy costs in the Middle East account for about 10% of the total methanol production cost, whereas in Germany, it is about 40%. Competitive sizes of newer plants are in the range of 700,000 tons per year, leading to a cost decrease of about 20% compared to a 200,000 tons per year plant (German cost situation 1995).

Methanol process [19] consists of three main sections: synthesis gas preparation, methanol synthesis, and methanol purification. Because of extensive heat recovery and recycle streams, there is a considerable interaction between the three. The principal, highly exothermic synthesis reactions are as follows:

$$CO + 2H_2 \rightarrow CH_3OH \tag{3.7}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{3.8}$$

All methanol synthesis processes employ a synthesis loop to overcome equilibrium conversion limitations during typical catalyst operating conditions. The high-pressure process was rendered obsolete when ICI in the United Kingdom and Lurgi in Germany developed a highly active and selective copper-zinc-alumina catalyst. The resulting low-pressure process [20] dominates the methanol production. Four basic reactor types are in use, quench converter, multiple adiabatic, tube-cooled, and steam-raising converter. Crude methanol is purified by conventional distillation with one to three towers depending on the purity required.

Formaldehyde production in the U.S. is reasonably stable, but the production in Southeast Asia is growing and offsets decreases in other parts of the world. The global formaldehyde production is expected to increase at a rate of $>2\%$ per year.

Commercially formaldehyde is the most important aldehyde. Urea-, phenol-, and melamine-formaldehyde resins (Urea formaldehyde (UF), Phenol formaldehyde (PF), and Melamine formaldehyde (MF)) accounted for nearly 60% of world demand in the year 2006.

Other large applications include polyacetal resins, pentaerythritol, methylenebis (4-phenyl isocyanate) (MDI), 1,4 butanediol, and hexamethylenetetramine (HMTA). Formaldehyde producers are primarily concerned with satisfying their own captive requirement for forward integrated products rather than supplying local merchant markets.

World trade in formaldehyde is minimal and accounted for less than 5% of the total production in 2006.

The United States, Europe, and China are the largest markets and drove world consumption of formaldehyde (37%) close to 30 million metric tons in 2006. The global capacity utilization was estimated to be 70–80% in 2006. The growth on world consumption is estimated to be 5–6%.

3.5.2 Market Performers

The economic performance of individual countries or regions is still the best indicator of future developments for formaldehyde. However, there are some further aspects to consider, which strongly influence future demand and its impact on success in the market.

The availability and access to low-cost methanol feedstock is one of those aspects, followed by downstream integration into derivatives, and lastly, a continuous striving for sustainable developments in the wood panel industries. Any setbacks in economic developments that influence the growth in construction may result in further consolidations in the formaldehyde industry.

Besides raw material and energy costs, environmental regulations (Kyoto protocol) affect wood logging and the availability of raw wood resources. In some applications, formaldehyde-based wood adhesives are currently being substituted but this substitution is quite price-sensitive. Furthermore, discussions related to health problems caused by formaldehyde [20] (even though scientific opinions are not consistent) [21] are resulting in confusion amongst consumers, followed by erratic buying behavior. Nevertheless, these developments have led to further restrictions on formaldehyde emission levels, which are "in place" already. CARB (California, US) restrictions have become effective January 1, 2009. (See Chap. 8, Wood Composites Adhesives).

3.6 Formaldehyde Uses

The consumption of formaldehyde depends mainly on the construction, automotive, and furniture markets. In the developed world, growth in demand will typically track the gross domestic product, although it will be strongly correlated to the construction industry. In that sense, formaldehyde is an essential component used in the manufacture of numerous daily products such as automobile parts, computer chips, plywood, decorative surfaces, furniture, radio and TV sets, various sports equipment, and much more (Fig. 3.3).

As it was mentioned earlier, it is also used in the health care industry in prenatal diagnostics and in the preservation of vaccines.

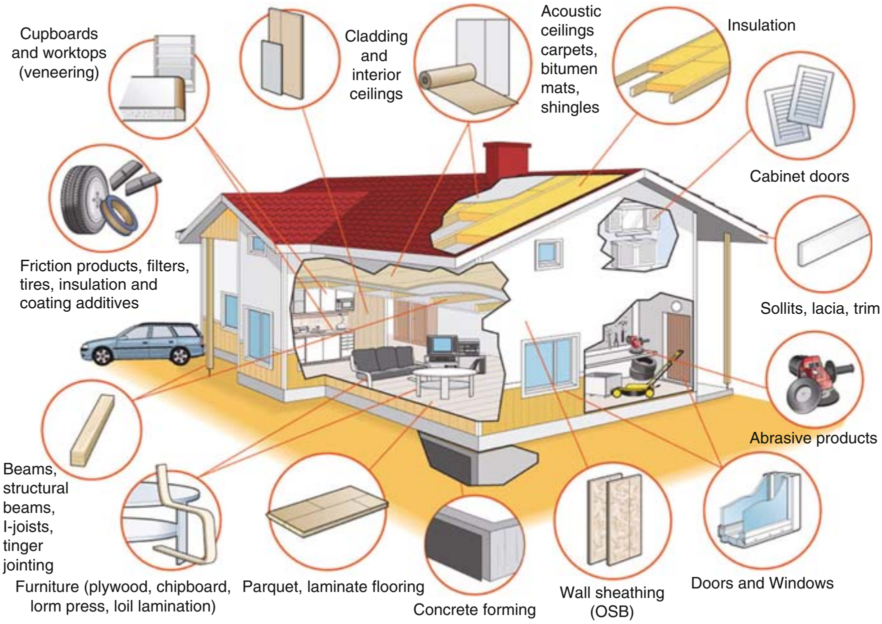
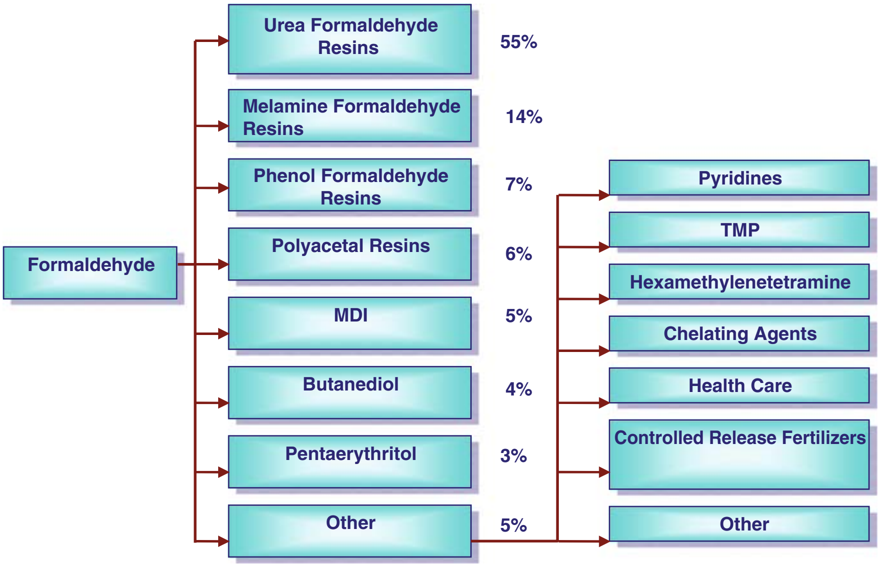


Fig. 3.3 Formaldehyde uses (Dynea)
Source: http://www.formaldehyde-europe.org/common_uses.uses.0.html

Table 3.3 Product tree for formaldehyde, 2004



Source: FormaCare

Formaldehyde is supplied as a 37–50% aqueous solution, with 37% being the most widely used composition which may also contain 0–15% methanol and a polymerization inhibitor (stabilizer, see Sect. 3.3).

Table 3.3 illustrates the array of products or product tree for formaldehyde.

UF resin is one of the mainstays in the building and construction industry. About 95% of UF resins are used as a binder or adhesive in particleboard and medium density fiberboard for composite panels. In these applications, it has a predominant market share. There are substitutes for each application but no substitute material has the broad range of properties of UF resins which consist of low cost, dimensional stability, hardness, clear glue line, and a fast curing process.

MF resin is used widely in the building and construction industries in the form of laminates and surface coatings, which account for more than 95% of its consumption. Its combination of properties allows it to maintain a dominant market position in certain applications, such as high pressure laminates for exterior decorative surfaces, in spite of its higher cost. Other resins, or different materials, may be substituted for MF resin-based products, but are more costly and less appealing to the consumer.

PF resin is another important product for the building and construction industry. Approximately, 60% of PF resins are used in this sector for applications such as insulation binder, wood products, and laminates. Other important end uses include automobile applications (e.g. friction materials) and foundry binders. Like UF resins, it has a predominant market share in its major applications. There are substitutes for each application but no substitute material has the broad range of properties of PF resins where high strength, dimensional stability, the ability to resist water, and thermal stability are required. In addition, current production methods are designed and integrated for the continuing use of PF resins. Other potential competitive substitutes to PF resins would require some/many changes in the existing processes and may lead to different processing/product properties.

Some formaldehyde is used in the preparation of MDI. The majority of MDI is used in the manufacture of rigid polyurethane foams. These products are commonly used in construction applications for their superior insulating and mechanical properties. In addition, MDI rigid foam applications include appliances (e.g., refrigerators, freezers, and air conditioners), packaging for high-end electronics, and transportation. In the absence of MDI, consumers would be required to use less effective materials and would experience significant losses in performance (e.g. inferior insulation properties, increased breakage, or spoilage).

Other materials such as alternate resins can be substituted for formaldehyde-based materials in many uses; but these resins which are frequently more costly, result in reduced consumer benefits because the resulting products with these alternate costly resins are generally inferior to that of formaldehyde-based resins in many instances.

3.7 Health and Safety

Formaldehyde is classified as a chemical irritant. At concentrations above 1 ppm, formaldehyde vapor causes irritation on contact with the eyes, nose, throat, and lungs. Contact with liquid formaldehyde causes eye burns, may cause allergic skin reaction, and is likely to irritate the skin. Moreover, formaldehyde has mutagenic activity in bacterial or mammalian cell culture test systems, but is generally negative in whole animal systems. Concerns over possible human carcinogenicity from exposure to formaldehyde continue to be a controversial issue. Many studies assessing the human risk of flow-level exposure to formaldehyde have been conducted; the interpretation of scientific studies has been variable. The lack of conclusive evidence has led to widespread disagreement among industry, government agencies, and unions regarding the appropriate risk assessment of formaldehyde.

In 1987, the U.S. EPA classified formaldehyde as a probable human carcinogen (group B-l) on the basis of sufficient evidence of animal carcinogenicity and limited evidence of human carcinogenicity. In June 2004, the World Health Organization's International Agency for Research on Cancer (IARC; an advisory board to the World Health Organization) reclassified formaldehyde from a group 2A substance (probably carcinogenic to humans) to group 1 (carcinogenic to humans). This reclassification was primarily based on the results of a National Cancer Institute (NCI) study of workers with occupational exposure to formaldehyde indicating that formaldehyde causes nasopharyngeal cancer (NPC) and is associated with leukemia. Although an outright ban on formaldehyde use in wood-based products is currently not likely, because industry is depending on current efficient technologies. Nevertheless further restrictions on formaldehyde emissions can be expected. No governmental regulatory agency has, as of yet, classified formaldehyde as a known human carcinogen. Subsequent to the NCI study linking formaldehyde to NPC, a re-analysis of the original study and additional research has led the IARC to re-examine its reclassification. The NCI is updating and re-examining its original studies in an effort to improve the accuracy of its findings as well as conducting new studies. The IARC has reviewed all studies and updates in preparation for a review of its formaldehyde carcinogen classification. End of October 2009, despite strong disagreement among participants of the voting body, who were evenly split at the vote, IARC concluded that there is sufficient evidence in humans of a causal association of formaldehyde with leukemia. FormaCare disagrees with this conclusion and believes that the weight of scientific evidence does not support such a determination. The U.S. EPA has maintained its classification of formaldehyde as a probable human carcinogen and is waiting to examine the results of the NCI update before initiating a review of formaldehyde's cancer classification. Within the European Union, formaldehyde is classified as a substance that has limited evidence of carcinogenic effect, and as such, represents category 3 in the list of carcinogenic substances.

In Western Europe, the exposure levels in the workplace vary from country to country. The United Kingdom sets a limit of 2 ppm, while Germany, Switzerland, and some Scandinavian countries operate within a limit of 0.2–0.8 ppm (SCOEL).

3.8 Other Formaldehyde Materials

3.8.1 Paraformaldehyde

Paraformaldehyde is a white, solid low molecular weight polycondensation product of methylene glycol with the characteristic odor of formaldehyde. The degree of polymerization ranges between 10 and 100. It is obtained by the distillation of formaldehyde solutions under different conditions depending on the temperature, time, and pressure during distillation. Commercial grades contain up to 6% water (Table 3.4).

Paraformaldehyde is seldom used in resin production because of the high costs compared to aqueous formaldehyde solutions, solids handling, and severe problems with the high heat evolution during the start-up phase. Some possible reasons for its use in special instances are resins with high solids content or to avoid distillation of waste water. Paraformaldehyde and/or aqueous formaldehyde is used in the new "PAPS" novolak resin technology (Resin Chemistry, Chap. 3). Paraformaldehyde can be used with acidic catalysts to cure novolak resins or to cure resorcinol

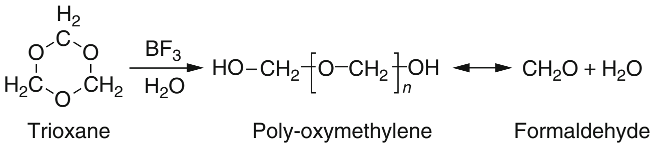
Table 3.4 Properties of paraformaldehyde [22]

Content of formaldehyde	90–97%
Content of free water	0.2–4%
Specific weight	1.2–1.3 g/cm3
Flash point	71°C
Melting range	120°C–170°C

prepolymers in cold setting structural wood adhesives. At low cure temperatures, the separation of formaldehyde is tolerable, and the reaction rate depends on the degree of polymerization.

3.8.2 Trioxane and Cyclic Formals

Trioxane, a cyclic trimer of formaldehyde or methylene glycol, is a colorless solid (MP 62°C–64°C, BP 115°C) and can be prepared by heating paraformaldehyde or a 60–65% formaldehyde solution in the presence of 2% sulfuric acid.



(3.9)

Trioxane can be used as a source of formaldehyde in prepolymer formation or as a resin curing agent. Cyclic formals, 1,3-dioxolane, 4-phenyl-1,3-dioxolane, and 4-methyl-1,3-dioxolane, have been recommended [23] as curing agents for novolak resins and high-solids, low-pressure laminating systems, taking into account their action as solvent.

3.8.3 HMTA

HMTA is by far the most important compound to cure novolak resins. It is prepared from formaldehyde and ammonia according to (3.10).

$$6\ CH_2O + 4\ NH_3 \longleftrightarrow (CH_2)_6N_4 + 6\ H_2O \qquad (3.10)$$

In reverse, HMTA decomposes at elevated temperatures. In aqueous solution, HMTA is easily hydrolyzed to aminomethylated compounds and is often used as a catalyst in the resole synthesis instead of ammonia. HMTA is quite soluble in water (Table 3.5), but less soluble in methanol or ethanol. The aqueous solution exhibits a weak alkaline action with a pH in the range of 7–10. In powder form, HMTA is prone to dust explosions; it is rated as a severe explosion hazard.

Table 3.5 Physical properties of HMTA [24]

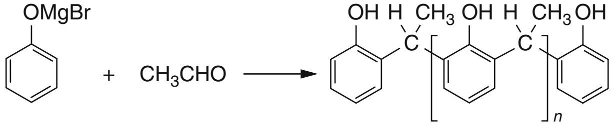
MW	140.2
Relative density	1.39 g/cm3
Behavior at heating	Sublimation at 270°C–280°C
Solubility in 100 g H20, 20°C/60°C	87.4/84.4 g

3.9 Other Aldehydes

Like formaldehyde, acetaldehyde is a gas at ambient temperature (BP 20.8°C). Acetaldehyde is miscible with water in all proportions and most common organic solvents. The liquid phase oxidation of ethylene is the process of choice for the manufacture of acetaldehyde (Wacker - Hoechst Process) using palladium and cupric chloride catalyst at 130°C. It reacts with phenol at considerably lower reaction rates as compared to formaldehyde. C_3 through C_{11} aldehydes [2, 4] are highly flammable and explosive, colorless liquids with pungent odor. They are miscible with most organic solvents, for example, acetone, ethanol, or toluene, but are only slightly soluble in water. Butyraldehyde is produced by the oxo reaction of propylene in the presence of cobalt or rhodium catalysts (3.11).

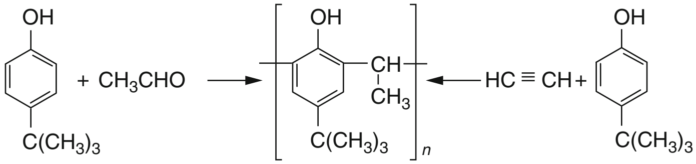
$$H_3CHC = CH_2 + CO \longleftrightarrow CH_3CH_2CH_2CHO + (CH_3)_2CHCHO \qquad (3.11)$$

Higher aldehydes react with phenol at significantly slower rates compared to formaldehyde. The base-catalyzed resole formation is not practical, as higher aldehydes easily undergo aldol and Tischenko condensation and self-resinification reactions. Acidic catalysts are preferred. In particular, non-transition metal phenates (Mg, Zn, or A1) are recommended [25] for the preparation of acetaldehyde phenol novolak resins in an aprotic solvent medium (12 h/120°C). Yields in excess of 90% with an exclusive ortho substitution (3.12) are reported.



(3.12)

The phenol reaction with higher aldehydes is, in general, performed under strong acidic conditions, preferably in a water-free system, by continuous aldehyde addition to the phenol melt. However, only acetaldehyde and butyraldehyde have had limited commercial success, for example, in resins for rubber modification, wood fiber binders, and antioxidants. The structure of novolak resins from acetaldehyde (3.13) corresponds to those obtained by the reaction of acetylene with phenol and cyclohexylamine as a catalyst:



(3.13)

The reaction of unsaturated aldehydes, acrolein, and crotonaldehyde with phenol in acidic medium was studied [26] by ^{13}C NMR and GPC. The alkylation reaction via the double bond seems to be the dominant pathway.

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Chapter 4
Resin Chemistry

Louis Pilato

Abstract During the ensuing years since the last phenolic resins book was published, many new and remarkable developments have occurred in the realm of phenolic chemistry and are given in this chapter.

A critical examination of the first step or addition step (methylolation) in the preparation of resoles is described and how it can be controlled and compared with the typical resole resin preparations. It provides a vision into the preparation of mineral wool/glass insulation resins and ways to minimize the undesirable dimer/oligomer formation.

Different reactivities of the common methylolated phenols and phenol are ranked, and their resulting reactivities differ depending on whether formaldehyde is present or absent in the methylolated phenols.

Use of organic bases such as triethyl amine indicates that a much faster reaction of F with P occurs as compared to the use of NaOH under similar conditions, and primarily ortho directed intermediate 2-methylol phenol is obtained. Further more methylene ether linkages result in the final TEA resole.

Bisphenol F, the simplest oligomer of phenolic novolak, continues to elicit considerable activity related to improved and economical synthetic preparative methods.

A unique, novel novolak process involving heterogeneous/two phase method known as the PAPS process is discussed along with several features and favorable comparisons with existing novolaks. Features such as narrow MWD, high yield, low free phenol, and rapid reaction favor this new process. Current markets that are responding to PAPS novolaks are photoresists and novolak curing agents for epoxy resins.

Nanotechnology is being applied to resoles and novolaks as well as the closely related phenolic materials such as cyanate esters and benzoxazines. With very small

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amounts of nanoparticles ($\leq$5%), these phenolic materials are significantly "upgraded" with resulting nanomodified phenolics exhibiting higher heat strength, higher modulus, T_g, etc., with many of these resin characteristics carrying over into fiber reinforced composites.

A new phosphorous flame retardant additive known as DOPO is reported and is instrumental in providing UL 94 VO behavior to cured novolak epoxy electrical laminates.

Benzoxazines are emerging as a more desirable phenolic resin system available from resin manufacturers as well as formulators such as Gurit (prepreg) and Henkel (FRP matrix). Benzoxazines undergo ring opening without emitting any volatiles during cure and result in a cured product with excellent dimensional stability, low water absorption, and stable, low dielectric properties (many of which are unavailable from typical phenolic resins). These attractive features have been responsible for its large volume use in electronics and FRP.

An overview of all types of natural products used either as partial phenol replacement, solvent or co-reactant, or as a resin modifier are tabulated along with origin/source, role in resin preparation, and different application areas.

An unusual technical development that attracted the interest of the symposium attendees was delivered by Sumitomo Bakelite researchers at the Commemorate Centennial Baekeland 2007 Symposium held in Ghent, Belgium during September 25, 2007. It was proposed that the 3D polymer network of hexa cured phenolic novolak resin can undergo further improvement based on reported curelastomer, T_g values, and DSC data. It is the view of the researchers based on phenolic resin conformations reached by using the Mark-Houwink-Sakarada equation as well as molecular simulations that higher T_g, exceptional strength, and performance driven characteristics of the resulting cured phenolic systems can be attained if an extended, linear novolak with low amounts of branching is cured with hexa. Conventional novolaks possess a "coiled" structure with branching, and during hexa cure, some novolak sites are sheltered or unavailable for cure and result in a 3D polymer network that is not fully cured in spite of the availability of excess hexa.

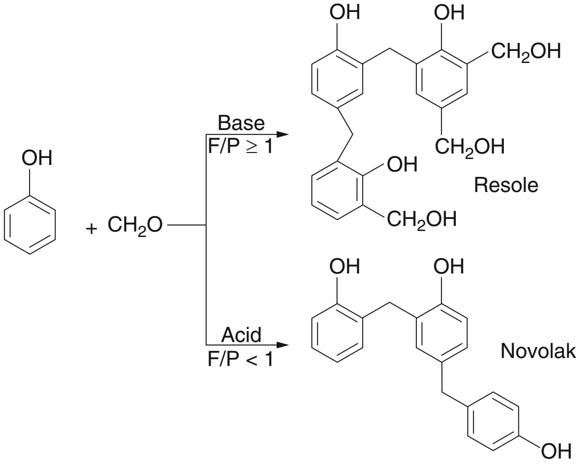
A reaction that is being revisited consists of phenylene bisoxazoline (PBO) reacting with novolak, and this promises to lead to the commercialization of a polyaryl ether amide type polymer possessing high T_g, high strength, and toughness exceeding multifunctional epoxy systems.

The capture and release of formaldehyde by aminoalcohols through the formation of an oxazolidine intermediate to facilitate the cure of phenolic resins has been commercialized as is shown in 2 different application areas. A pultrusion system based on novolak and oxazolidine is claimed to operate at line rates comparable to fast polyester pultrusion speeds. The other application involves the use of oxazolidine with PRF resin in the preparation of fiber reinforced FST duct systems.

The appendage of either an allyl or an ethynyl group to a novolak or resole followed by thermal cure leads to unusually high T_g phenolic materials, close to 400°C and is of interest for ultra high performance organic matrix composites.

4.1 Introduction

A formal understanding of how phenol reacts with formaldehyde under either acidic or basic conditions is necessary to appreciate the variety and versatility of the array of phenolic resins that are available [1]. Further the molar ratio of formaldehyde to phenol with acid or base is a contributing factor. Heat reactive phenolic resins known as resoles are obtained using a base catalyst, and the molar ratio of formaldehyde can vary from below equimolar amount to as high as 3–4 moles of formaldehyde to phenol. However, when less than an equimolar amount of formaldehyde to phenol is maintained under acidic conditions, a novolak resin is obtained.



(4.1)

Besides the use of acidic or basic conditions, the use of a transition metal salt catalyst under mildly acidic conditions yields a uniformly, structured phenolic resin known as high ortho phenolic resin. The salient features for the preparation of these various phenolic resins are best illustrated in Table 4.1.

The table provides a comparison of different catalysts that are utilized in phenolic resin production, resin types, molar ratios of F/P, physical state(s) of the resulting resins, polymer functional groups, resin stability, and method of cure. For the sake of completeness, the rarely used enzymatic coupling of phenol is also listed. Classically individual functionalities of phenol and formaldehyde are recognized as 3 and 2 respectively but deviate as one reacts phenol and formaldehyde under basic or acidic conditions. When a resole is prepared (equimolar or greater amount of formaldehyde to phenol with base catalysis) or when a novolak is desired (less than equimolar amount of formaldehyde to phenol with an acid catalyst), the functionality of formaldehyde is <2 and ≤ 3 for phenol for resoles while values of 2 for formaldehyde and 1.5–1.7 for phenol are reported for novolaks. The apparent difunctionality of formaldehyde applies only in novolak preparation and is less than 2 in resole preparation. The complexity of resole chemistry during resole preparation reduces functionality values of both formaldehyde and phenol. The phenol

Table 4.1 Different catalysts for various phenolic resins

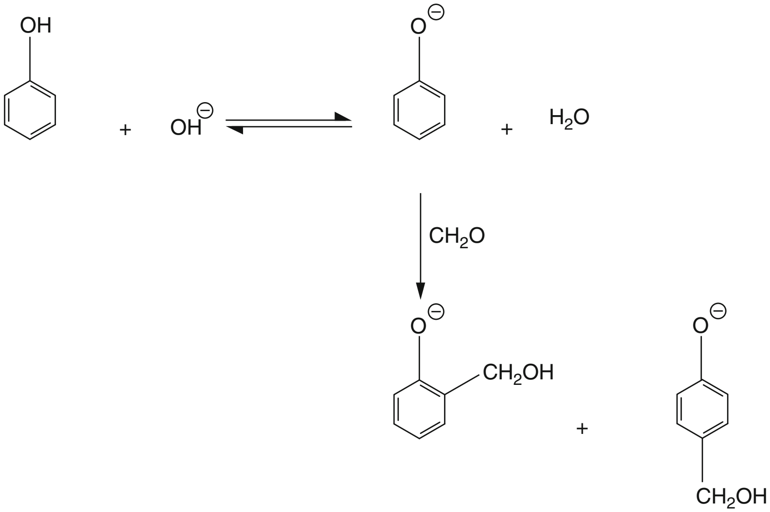
			Functionality f_{actual}					
Catalyst	Resin type	F/P	F	P	Physical state	Product stability (RT)	Functional groups	Mode of cure
Base	Resole	≥ 1	<2	≤ 3	Liquid, solid, solution	Limited	Methylol, phenolic	Acid, base, thermal
Acid	Novolak	<1	2	1.49–1.72	Solid	Stable	Phenolic	Hexa (CH_2O)
Metal salt	Resole or novolak	≥ 1	High	Ortho	Liquid, solid	Liquid-limited solid-stable	Methylol, phenolic	Same as resole or novolak
Enzyme	Pseudo novolak	No (CH_2O)	–	–	Solid	Stable	Phenolic	Resin transformation

functionality value of 1.5–1.7 in novolak preparation is considerably lower than the recognized value of 3 for phenol. The use of a deficient amount of formaldehyde in novolak preparation results in a linear or branched material and not a gelled or potentially cross linked novolak, hence the lower functionality for phenol.

4.2 Resole

4.2.1 Methylol Phenol(s)

Either ortho or para methylol phenol is obtained as phenol and formaldehyde are reacted under basic conditions. They are the simplest phenolic components that can be cured into a phenolic resin. The reaction leading to the *o*- or *p*-methylol phenol involves the addition of F to the phenolate ion as shown in (4.2):



(4.2)

Besides the monomethylol phenols, some dimethylol phenols and trimethylol phenol are obtained when the reaction of phenol is carried with more than an equimolar amount of formaldehyde (Fig. 4.1)

These intermediate methylol phenols are similar to compounds that result from the Lederer–Manasse reaction and one of the forerunner reactions that Baekeland was aware of during his initial experiments. These mono-, di-, and tri-methylolated phenols act as transient intermediates and undergo oligomerization into dimeric, trimeric, and higher oligomers depending on F content, reaction basicity, and temperature during reaction.

Mono, di- and tri-hydroxymethyl phenol (HMP) type intermediates have been examined by Higuchi in a series of papers [2–7] whereby the kinetic fate of 2-HMP, 4-HMP, 2,4-dihdroxymethyl phenol (DHMP) and 2,4,6-trihydroxymethyl phenol

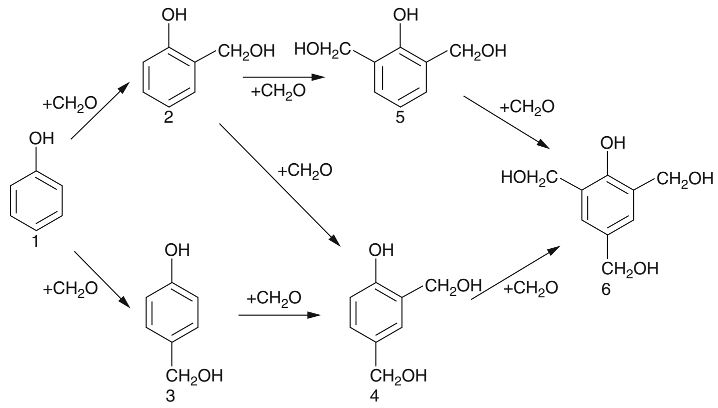


Fig. 4.1 Methylolated phenols

(THMP) was examined: 2-HMP undergoes a first order base catalyzed self condensation involving a quinone methide intermediate; base self condensation of 4-HMP involves simultaneous unimolecular and bimolecular reactions as rate determining steps; and finally both 2,4-DHMP and 2,4,6-THMP undergo simultaneous unimolecular and bimolecular reactions with reaction mechanism changing with the reaction species and, in some cases, with reaction conditions. These model studies were beneficial in understanding the use of propylene carbonate (PC) as an accelerator in the cure of base catalyzed resoles. The authors claim that PC increases the reactivity of 2-HMP through a transesterification of 2-HMP followed by enhanced rate of cure.

Christjanson et al. [8] carried out the melt condensation of 2-HMP and 4-HMP at 120°C with and without NaOH catalyst to determine the fate of these intermediate HMP materials at elevated temperature since they are present within a resole resin. In the absence of NaOH, either of the HMPs is transformed into the corresponding *o*,*o*′ or *p*,*p*′ methylene ether compounds. With a catalytic amount of NaOH and a 50/50 mixture of 2- and 4-HMP, only *o*,*p*′ and *p*,*p*′-dihydroxy diphenyl methylene (DPM) compounds are obtained. These observations allowed the authors to propose that under resole curing conditions (resole as a wood adhesive), some formaldehyde is expected to be emitted when the bimolecular reaction of either 2- or 4-HMP occurs leading to the DPM materials.

4.2.2 Addition – Methylolation

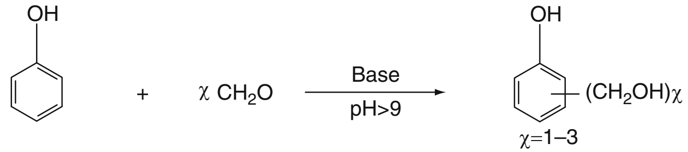
Resoles are a mixture of methylol phenols, oligomers of varying – mer units, and residual amounts of free phenol and formaldehyde. Depending on reaction conditions (molar ratio of F/P, catalyst concentration/type and temperatures) at low temperatures (60°C) only addition of formaldehyde to phenol occurs. In a

Table 4.2 Addition and condensation steps for resole resin

	Addition	Condensation
Temperature	<60°C	>60°C
ΔH_f	−20kJ/mol	−99 kJ/mol
pH	8–9	9–11
Time, hours	2–4	2–4 4–8 (pH 8–9)
Water dilutability	∞	Low
Solids	50	80
Viscosity (mPa s)	50–100	~5,000

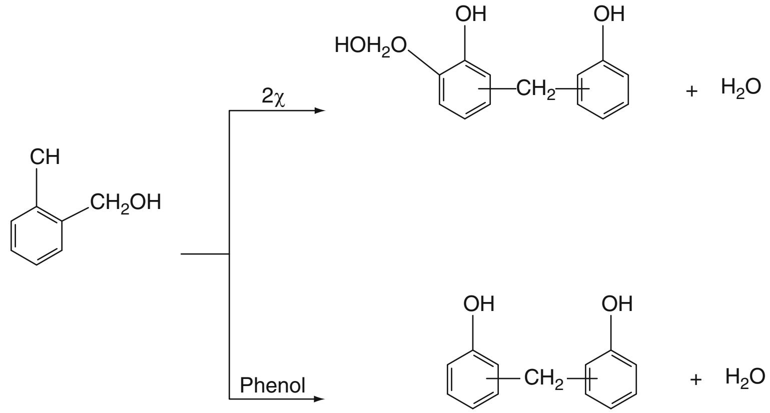
temperature range above 60°C, condensation reactions of methylol phenols with phenol and/or methylol phenols occur and lead to prepolymer or the desired resole resin. Table 4.2 distinguishes conditions for the respective steps of addition and condensation in resole preparation.

Addition (<60°C)



(4.3)

Condensation (60–100°C)



(4.4)

The addition of formaldehyde to phenol results in the formation of several methylol phenol monomers. Earlier studies conducted in the 1950s and 1960s [1] provided kinetic rate data for the formation of various methylolated monomers. Kinetic data was reported with either equimolar ratio of NaOH to P or NaOH/P ratio less than unity. Although these conditions established kinetic rate data for the appearance of the various methylolated phenols, some authors neglected to consider the role of deficient NaOH in their kinetic analyzes since there are differences in acidity among the phenolic compounds emerging during reaction. This, in fact, is why there are differences in the relative values. This was remedied by developing a rate equation involving the concentration of hydroxide ion which changes with the change in reaction composition. Computer simulation showed that F and P reactants and products (five methylolated structures 2–6, Fig. 4.1) can be described as a function of time. With molar ratios of F/P of 2, NaOH/P molar ratio of 0.05, with an initial P concentration of 3 mol/l, and conducted at 70°C, 95% of F is consumed, but greater than 0.2 molar fraction of P remains with trimethylol phenol being the major product (0.5 molar fraction) after almost 7 h time. With similar reactants but higher NaOH/P molar ratio of 0.4, lower temperature of 60°C, and time of 2.5 h, about 98% of F is consumed, free phenol is lower (0.175 molar fraction) and 6 is also lower (0.426 molar fraction). Higuchi's initial study only considered methylolated products for comparison with his earlier work. But temperatures above 60°C facilitate dimer and trimer formation as these studies are being expanded to include these oligomeric materials.

Monni [9] has examined the preparation of resole in more detail by separating the "2 step" reaction and focusing on the first step. In the first stage the starting materials, P and F, were preprocessed in a continuous-flow stirred-tank reactor (CSTR) with a 5 min residence time to combine F and P and to control the reactivity of the solution. The use of CSTR in the preprocessing step was its ability to yield products with a uniform quality in steady state conditions. The experimental arrangement of the preprocessing step consisted of two streams, one containing P, water, and NaOH, while the other contained 40% formalin, mixed and fed into a preprocessing reactor. Products were discharged continuously through a bottom valve of the reactor, maintaining 5 min residence time – alkalinities of 2.4–3.0 wt%, molar ratio of F/P of 2.0–2.3, and a total flow rate of 6.0 ml/min (about 2.9 ml/min of P/additional water/NaOH mixture and 3.1 ml of 40% formalin) and at 56°C to 70°C.

The liquid resole characteristics of those conducted at 60°C after 60 min consisted of viscosities of 6.2–7.5 mPa s with high viscosity due to higher alkalinity and/or temperature.

Samples P2 and P3 (NMR analyzes shown in Table 4.3) are reasonably comparable except for a slightly higher viscosity for P3 or 7.2 vs 6.6 mPa s. These changes in viscosity are attributable to the higher alkalinity of sample P3 (3 wt% for P3 vs 2.5 wt% for P2). Structural NMR analyzes of the solution components of P2 and P3 are tabulated in Table 4.3.

Higher amount of methylol is observed in P3 than in P2, again due to higher alkalinity of P3; fewer free para sites than ortho sites are also noted because para is more reactive to F. Yet greater amount of ortho methylol is observed because there are 2 ortho positions available for reaction with F. Only p,p' ($-CH_2-$) bridges are formed. High amounts of hemiformal are present and anticipated due to high molar ratio of F/P. As will be noted later, the hemiformal is a source of F for the later second step – condensation.

Table 4.3 ^{13}C-NMR Integration results for preprocessed solutions of experiments P2 and P3 (Experiment)

Group	P2	P3
Aromatic Carbons		
• Phenoxy	1.000	1.000
• Free para	0.233	0.230
• Free ortho	0.857	0.851
• Other	3.970	3.933
Formalin hemiacetals	0.071	0.065
Oxymethylenes of formaldehyde oligomers	0.049	0.047
Phenolic hemiformals	0.467	0.426
Methylol groups		
• Para	0.477	0.504
• Ortho	0.840	0.900
Methylene bridges		
• p–p′	0.064	0.033
• o–p′	–	–
• o–o′	–	–
Methanol	0.101	0.106
Total formaldehyde	1.97	1.97

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Table 4.4 DSC analysis of the preprocessed solutions from experiments P2 and P3 and the nonprocessed (Solution from experiment P5)

Experiment	ΔH (J/g)	T_0 (°C)	T_1 (°C)	T_2 (°C)	Onset (°C)	End (°C)
P2	−385	–	145	156	101	163
P3	−371	–	~145	151	106	162
P5	−578	94	~147	151	60[a]	167

[a] Determined for signal T_0

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The reactivities of these preprocessed solutions (P2 and P3) with the reactivity of a starting material solution (sample P5) that did not have a preprocessing stage (sample P5: F/P = 2.1, 3.0 alkalinity, and mixed at room temperature) are shown in Table 4.4 with DSC results.

The released reaction heat (ΔH) of sample P5 agrees with reported literature value of 584 J/g [10] while heat release values of P2 and P3 are reasonably similar with a net effect of lowering heat content by about 200 J/g. Figure 4.2 shows DSC curves of P2, P3, and P5.

The P2 and P3 curves overlap reasonably well, comparing T_1 and T_2 values. The difference of 5°C of onset temperature is due to higher alkalinity of P3. The first signal of P5 DSC curve at 94°C is identified as T_0 in Table 4.4. A low onset temperature value of 60°C as shown in Table 4.4 was determined for signal T_0.

Samples P2 and P3 were then subjected to condensation conditions (B2 and B3) by heating to 90°C for 35 min. Results for B2 and B3 are contained in Table 4.5.

Increased viscosity of 24–34 mPa s increased conversions of P (96%) and F (95%) with a corresponding decrease in free F (~1%) and free P (1.2%). NMR analyzes (Table 4.6) showed decreased amounts of both ortho and para free sites, as well as reduced amount of the para methylol group but increased amount of ortho

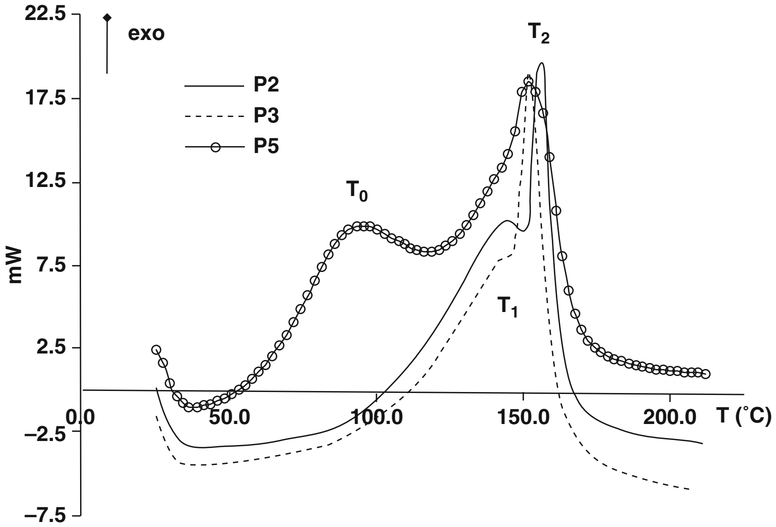

Fig. 4.2 DSC curves of solutions from experiments P2, P3 (with preprocessing), and P5 (without preprocessing)

Table 4.5 End viscosities and results of GC and titrimetric analyzes of solutions from batch reactor experiments B2 and B3

Experiment	End viscosity (mPa s)	Free phenol (wt%)	Conversion of phenol	Free formaldehyde (wt%)	Conversion of formaldehyde
B2	24	1.3	0.960	1.1	0.945
B3	34	1.0	0.967	0.9	0.957

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methylol was observed. A higher reactivity of para methylol is seen with corresponding increased amounts of *p*,*p*′ and *o*,*p*′ methylenes. No *o*,*o*′ methylene is noted. Phenol hemiformal decreased as anticipated. The DSC analyzes of ΔH ~250 J/g, a decrease of ~100 J/g with a corresponding shift to a higher temperature for the onset temperature or ~115°C and the end temperature of 160°C, was the same. Further the authors developed a relationship between conversion of structural groups and decreasing reaction heat during the resole study by comparing NMR and DSC results. A linear correlation was found between the released reaction heat (enthalpy) and the total amount of free ortho and free para carbons.

The earlier comprehensive studies of Grenier-Loustalot who examined resole resin preparation under controlled conditions such as temperature, stoichiometry, catalyst, and pH using a range of techniques such as HPLC, ^{13}C-NMR, FTIR, UV, and chemical assay provide the salient features of various methylolated phenols and oligomers within the resole composition [1]. This is best illustrated by examining Fig. 4.3 and the subsequent appearance of various intermediate products. Even under relatively mild conditions (F/P = 1.5, pH of 8 at 60°C) and low molar ratio of F/P,

Table 4.6 ^{13}C-NMR integration results of batch reactor experiments B2 and B3 (Experiment)

Group	B2	B3
Aromatic carbons		
• Phenoxy	1.000	1.000
• Free para	0.059	0.055
• Free ortho	0.417	0.379
• Other	4.597	4.790
Formalin hemiacetals	0.013	–
Oxymethylenes of formaldehyde oligomers	0.012	0.005
Phenolic hemiformals	0.086	0.044
Methylol groups		
• Para	0.303	0.258
• Ortho	1.245	1.294
Methylene bridges		
• p–p′	0.258	0.258
• o–p′	0.133	0.169
• o–o′	–	–
Methanol	0.105	0.098
Total formaldehyde	2.05	2.04

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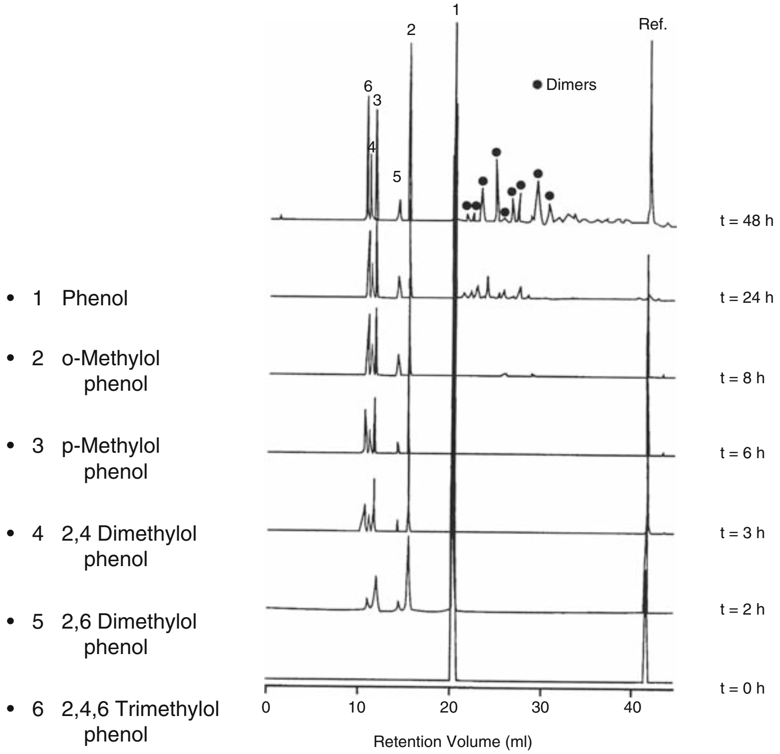


Fig. 4.3 Effect of temperature and time on methylolated phenols and dimers

some THMP is observed. After 8 h and increased pH to 9.25, dimers begin to emerge and continue to increase in content as the amount of phenol decreases. All known methylolated phenols (Fig. 4.3 structures 2–6) as well as many dimers and trimers were formed and were fully characterized unambiguously using HPLC and ^{13}CNMR. Using a low temperature of 60°C, addition products are obtained; even at low molar ratio of F/P some trimethylol phenol (Structure 6) is obtained. Increasing the pH of the reaction medium at 60°C with F/P at 1.5, the amount of dimers increased significantly (HPLC) from pH 8 to 9.25 after 8 h; also residual phenol decreased from 42% (pH 8) to 16% (pH 9.25). As the resulting dimers are formed, only o,p' and p,p' linkages are observed with no o,o' bridged material. The methylene region is conveniently monitored by ^{13}C-NMR and distinguishes all three isomeric linkages.

Thus the studies by Monni clearly distinguish how one can obtain solely addition or methylolated phenols under controlled conditions, especially at temperatures of 60°C or below and at relatively short residence time. These observations may provide some insight into the preparation of mineral wool/glass insulation resins that are mainly methylolated phenols with little or no dimer/oligomer present (see Chap. 10, Mineral Wool Insulation Binders).

Alkali and alkaline metal hydroxides have been evaluated and include Group IA hydroxides: Li OH, NaOH, and KOH as well as Group IIA hydroxides: $Mg(OH)_2$, $Ca\ (OH)_2$, and $Ba\ (OH)_2$ under similar reaction conditions ($F/P = 1.5$, pH 8, 60°C). The rate of F disappearance was related to ionic radius within family groups: $Li > Na > K$ and $Mg > Ca > Ba$. Comparing all the catalysts vs disappearance of F resulted in the following ranking: $Mg > Ca > Ba > Li > Na > K$. Authors propose that the ionic radius and hydrated cation account for the observed trend.

Competitive reactions of each individual mono methylol, dimethylol, and trimethylol compounds with F was carried and the following ranking was attained:

$$k_{\text{phenol}} < k_4 < k_2 < k_3 < k_5 < k_6$$

Compound 5 disappears rapidly in the reaction medium whereas phenol and compound 4 accumulate. The para position is more reactive than the ortho position with regard to F or methylol and leads to o,p' and p,p' methylene linkages; $\underline{\text{no}}$ o,o' is detected. Phenol must be consumed in the early stages of the reaction or it will remain unreacted because functional materials (2–5) are more reactive (more acidic) than phenol in reacting with F or methylol.

In the absence of F, the reactivity [11] of these methylol phenols is as follows:

$$k_{\text{phenol}} < k_2 < k_3 < k_5 < k_4 < k_6$$

Compound 4 is considerably more reactive than 5 and also more reactive than 2 HMP and 4 HMP. It is quite different from the reactivity reported by the Grenier-Loustalot studies.

HPLC studies of the kinetics of resole resin catalyzed by triethylamine (TEA) have been expanded by Mondragon and coworkers [12]. Using a molar ratio of 1.8 for F:P, a temperature of 80°C, and a pH of 8, the rate of disappearance of both F and P was faster for the triethylamine catalyzed system as compared to a similar system with NaOH as catalyst. These TEA studies included F/P molar ratios from

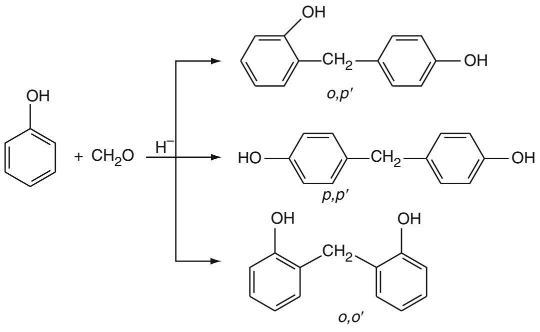
1.0 to 2.2. The amine catalyzed reaction favored the formation of 2 HMP (2) and is "ortho directing". A higher amount of 4 HMP (3) is obtained with NaOH. The introduction of F into 2 HMP goes preferentially to 2,6 DMP. Dimethylene ether bridges are the principal linkage between aromatic structures during polymerization with TEA catalysis and are considered fast reactions with methylene ether quantities increasing with increased molar ratio of F/P. FTIR spectral data of both TEA and NaOH catalyzed resins indicate that prepolymer formed by NaOH presents higher concentration of non-bonded, free hydroxyl groups while TEA prepolymer had a higher amount of hydrogen bonding, aided by the presence of methylene ether bridges. The authors claim that TEA favors addition in the free ortho reactive sites followed by methylene ether formation. An intramolecular loss of water via the quinone methide intermediate is followed by reaction with 2 leads to methylene ether bridge formation. In the case of NaOH, the quinone methide intermediate is expected to be unstable due to the high concentration of OH^- ions, favoring a phenoxide ion pathway leading to methylene linkage between aromatic structures. Mondragon minimizes the concern over high amounts of methylene ether linkages in TEA type resins, as it is a source of latent free F during cure, by stating these ether bridges can be responsible for the presence of oxidized groups in resoles cured at high temperatures. FTIR spectral data suggested the presence of benzophenone-type bridges occurring from the oxidation of methylene ether groups and quinone, aldehyde, and/or carbonyl groups formed as a result of main chain cleavage.

Similar oxidized groups have been reported in the structure of cured resoles by solid state NMR by Kim [13].

4.3 Novolak

4.3.1 Bisphenol F

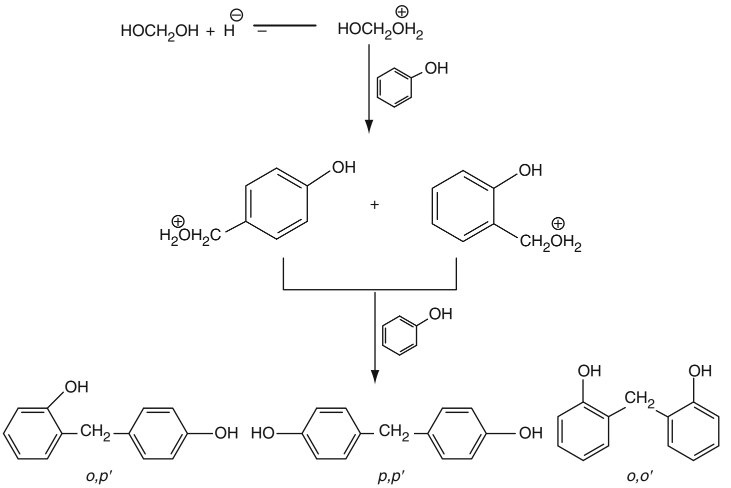
Bisphenol F, the simplest novolak, is prepared by conducting the reaction of P and F with a large excess of phenol under acidic conditions. A mixture of isomers is obtained: *o*,*p*′ isomer predominates, followed by *p*,*p*′ and *o*,*o*′, the lowest (4.5).



(4.5)

It is the simplest but most difficult Bisphenol to obtain (compared with Bisphenol A and other Bisphenols) because of its propensity to undergo oligomerization to higher MW materials (novolaks).

The mechanism of formation involves initial protonation of methylene glycol (hydrated F) which reacts with phenol at the ortho and para positions (4.6).



(4.6)

The intermediate benzyl alcohols (carbonium ions) are transient intermediates (detectable by NMR) as they are transformed into Bisphenol F. Newer processes for the preparation of bisphenol F suggest a two-phase, heterogeneous reaction of the condensation of P with F with large amounts of phosphorous containing acids [14, 15]. These conditions are quite similar to a new novolak preparation process which is discussed later.

The use of H-β zeolite as catalyst is claimed as a selective method for preparing Bis F. Mediocre yields of about 20% are reported using an autoclave at 80°C for 3 h. Isomer distribution is reasonably close to what is expected for Bis F such as 45%–50% for 2,4′, 25%–35% for the 4,4′ and 15%–25% for the 2,2′ isomer [16].

Further efforts by Jana and coworkers [17] using zeolites with a high ratio of Si/Al mol mol^{-1} (increased acidity of zeolite) of 75 exhibited highest yields and selectivity at 90°C. Yields of ~65% with 92% Bis F selectivity with this zeolite in the presence of 15 mol mol^{-1} P/F at 90°C were obtained. Isomer distribution was considerably different from the isomer distribution reported by the previous zeolite study. Much higher ratio of 4,4′ isomer or 57% was obtained as well as 35% 2,4′ and 11% 2,2′ isomer.

A more fundamental approach related to mass and heat transfer rates combined with residence time was undertaken by Daito and coworkers [18]. Using micromixers based on collision/impingement of the fluid segments within the apparati of these micromixers, the authors examined the selective condensation of hydroxybenzyl alcohol with phenol for the preparation of Bisphenol F. The development of two micromixers involving segmentation of either the reactants through fluid dynamics and/or shear allowed high mixing performance for improvement of product selectivity and productivity. A beneficial feature of these micromixer studies is that lower ratios of hydroxybenzyl alcohol to phenol of 15 versus 30 or half the amount required for the batch operation can be used which reduces the lengthy recovery of residual phenol. However costly hydroxybenzyl alcohol or methylol phenol is used as starting material.

Bisphenol F is a desirable material with many attractive applications paralleling Bisphenol A in use but considerably lower in volume. Bisphenol F epoxy resin possesses low viscosity (2,000–3,000 m Pa) and is used in solvent free or high solids coatings, floorings, linings, impregnation, molding, laminates, as well as in some high performance fiber reinforced composite systems. Polycarbonates based on Bisphenol F/Bisphenol A exhibit high T_g's, high impact strengths, low brittle–ductile transition temperatures and flame retarding properties. The latter property is attributable to the Bisphenol F segment. Bisphenol F is combined in a novolak/hexa inorganic filled molding material composition for low pressure injection molded parts with very low flash. Bisphenol F epoxy with high ortho, ortho isomer ($\geq$46%) exhibits lower viscosity (melt and solution viscosity) than typical Bisphenol F epoxy resin containing 10–15% *o,o′* isomer. Methods for preparing *o,o′* Bisphenol F are known and require special conditions such as phenol and paraformaldehyde in xylene in a pressurized reactor.

More recently silica filled Bisphenol F epoxy is used separately or combined with Bisphenol A epoxy as an underfill to surround a solder ball grid array to alleviate thermomechanical stresses in semiconductor devices [19].

4.3.2 Random

Using lower amounts of phenol but maintaining less than equimolar amount of phenol relative to F to avoid gelation, novolaks with varying MW's can be prepared. Depending on the molar ratio of F to P and residual free phenol of less than 1%, low melting solids to materials with softening points above 100°C can be obtained. The overall reaction scheme showing isomeric changes that occur during oligomerization is shown in Fig. 4.4. Beyond Bisphenol F, isomeric changes and number of structural oligomers increases significantly.

The presence of the transient intermediate, methylol phenol has been established by NMR when novolak synthesis was examined by conducting the oxalic acid catalyzed reaction in an NMR tube. Evidence of o-methylolphenol was noted but not the identity of p-methylolphenol (64 ppm.). Yet indirect evidence for the existence of p-methylolphenol is present since *p,p′* and *o,p′* methylene linkages are observed in the latter stages of reaction. It was proposed that the absence of NMR peak being observed for *p*-CH_2OH is probably due to its high instability. o-Methylol formation is more stable than para due to intramolecular H bonding

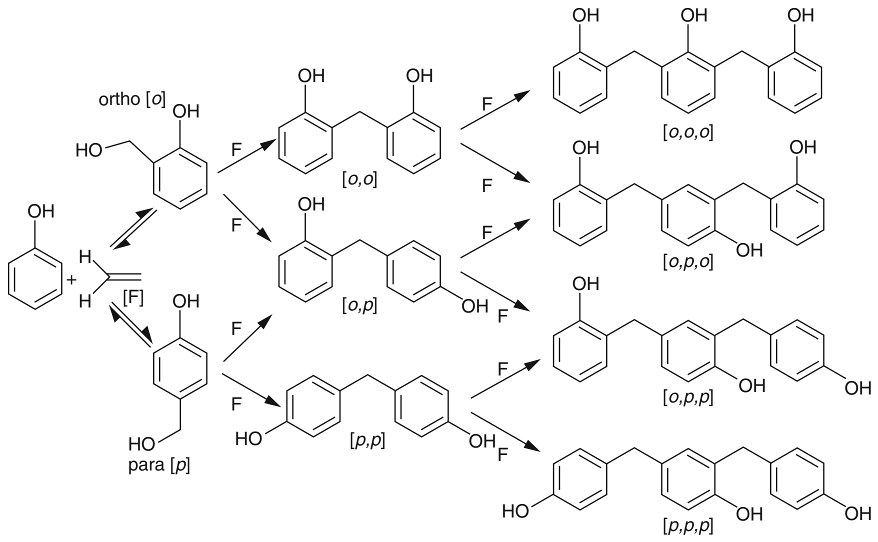


Fig. 4.4 Novolak isomeric transformations

between methylol group and adjacent phenolic group. The first bridging methylene carbons which are characteristic of the resin microstructure are those of *p,p′* linkage, followed by *o,p′*, with *o,o′* being the last to appear. It should be noted that although the *o,p′* methylene group follows the initially formed *p,p′* linkage, the *o,p′* linkage increases and exceeds either *p,p′* and *o,o′* methylene bridges.

The preparation of low ratio F/P novolaks is tedious and results in mediocre yield. A new two-step process proposed by Ube [20] whereby the first step is carried out with a molar ratio of F/P of 0.43 at 100°C with oxalic acid for 5 h and then heated to 160°C to remove water (2 h). The second stage is continued with the addition of an additional mole of formaldehyde, oxalic acid, for 3 h at 100°C. After dewatering and steam distilling, the recovered novolak had a M_w of 455 with no free phenol and 0.7% dimer.

In the preparation of novolaks, branching, free phenol content, substitution patterns, and methylene bridging structures can be ascertained by ^{13}C-NMR. Depending on the type of catalyst, such as a strong acid, a weak acidic metal salt medium, or the "heterogeneous/two phase system," different isomer distribution patterns result. A statistical distribution of *p,p′*: *o,p′*: *o,o′* 1:2:1 is obtained for the acid catalyzed method; the weak acidic conditions (4–6 pH) combined with divalent metal salt leads to high ortho resin exhibiting large amounts of *o,o′* and *o,p′* and low amounts of *p,p′*, (see High Ortho), and the heterogeneous/two phase method yields a high *p,p′* and *o,p′* resin (see Heterogeneous/two phase method). Table 4.7 describes different catalyzed novolaks and varying distributions of methylene bridges.

Table 4.7 Percent methylene bridges in various Novolaks (% methylene bridges)

Novolak	p–p′	o–p′	o–o′
High ortho	2.3	40.2	57.5
Random	25.8	49.1	25.1
Oxalic acid	27.6	49.1	23.3
Sulfuric acid	25.6	48.5	25.9
PAPS	40.1	45.3	14.6

4.3.3 High Ortho

High *o,o′* resins are obtained under weak acidic conditions (pH 4–6) with an excess of P to F and divalent metal salts such as Zn, Mg, Cd, Pb, Cu, Co, and Ni, preferably acetates. The initial reaction is proposed to occur through chelation of phenol and F through metal carboxylate.

The chelated intermediate is then transformed into o-methylol phenol. Firm evidence for o-methylol phenol and its accompanying hemiformal has been reported. Concentration of both materials increases as pH is increased from 4.1 to 6.5. Oligomerization occurs to high *o,o′* resin whose amount of methylene bridging for *o,o′* and *o,p′* is reasonably similar for both linkages (47%–49%) with less than 5% for *p,p′*. Some methylene ether is also noted. A recent publication by Huang [21] described many (19) different catalysts for high ortho resins and confirmed the use of divalent salts (above) as preferred catalysts. Optimum resin reaction conditions required a molar ratio of 1.25 for P/F, 4% Zinc acetate, 5 pH, xylene solvent and 5 h at 125°C. Ortho content was greater than 90%.

4.3.4 Heterogeneous/Two-Phase Process

An unusual heterogeneous, two-phase process for the production of novolaks has emerged through the efforts of some Japanese companies. Sumitomo Bakelite (SB) technical personnel reported [22] the use of large quantities of an organophosphonic acid (usually 20–100 wt% based on phenol),with molar ratios of P/F of 0.5–1.0, and reaction temperature at 110°C–200°C as conditions for preparing novolaks. Water (aqueous F) content is maintained below 30% for favorable high phenol conversion and resin yield. The resulting novolak resin is obtained in high yield with less free phenol and a narrow MWD than a comparable novolak prepared under oxalic acid conditions. They proposed that the organophosphonic acid is very much water soluble whereas phenol has lower water solubility followed by an even lower water solubility of novolak. These differing water solubility characteristics result in a heterogeneous two-phase reaction whereby P and F and low molecular weight materials are within the aqueous organophosphonic phase and react rapidly and emerge out of the aqueous phase as the novolak molecular weight increases. Phase separation is reported to occur. Due to these factors, a novolak type resin with less unreacted phenol and a narrow MWD is obtained in high yield. A preferred acid is 1-hydroxyethylidene-1,1′-diphosphonic acid, also known as Ferriox 115. Aqueous extraction is necessary to remove acid from the novolak. Free phenol contents of about 1%, MWD values of 1.3 to <3, and virtually 100% yield of novolak occurs. After an introductory period of time, this new process novolak was withdrawn from the market by SB.

A somewhat similar heterogeneous two-phase novolak process was reported by the Asahi technical personnel [23] and is in the early stages of commercialization [24, 25]. It is known as the "Phosphorous Acid Phase Separation" (PAPS) process. The heterogeneous process consists of reacting P with 0.4–0.93 moles of F in the presence of at least 25 parts by- mass of phosphoric acid per 100 parts by- mass of P. These ranges of P:F can be subdivided further by considering molar ratios between 0.8 and 0.93 for high MW novolak and lower MW materials with molar ratios of 0.4 to <0.8 of P:F. The first division or high MW novolak has an extremely low amount of free P, low amount of dimer (bisphenol F) ~5%, and an MWD between 1.5 and 2.0. The second or lower ratio of P:F has <3% free P, a much higher amount of dimer varying from 20%–60%, and an MWD between 1.1 and 1.8. The amount of water during the initial reaction should be <40% with the concentration of phosphoric acid ranging between 75% and 89%. It is observed that the heterogeneous phase exhibits a "whitish" appearance with phenol as the main component in the organic phase while the aqueous phase has phosphoric acid and F.

Although it is not mentioned, the low ratio of P:F yields high amounts of low MW product, primarily dimer which is slightly water soluble and remains in the aqueous acid phase as the amount of P is consumed. Narrow MWD is achieved (1.1–1.8). This may be a convenient process to manufacture Bisphenol F. Presently Asahi has commercialized the PAPS process to manufacture novolaks for selected electronic applications such as photoresists and epoxy resins.

The high molar ratio of P:F or 0.8–0.93 novolak involves a phase transfer of the slightly soluble dimeric material into the phenol organic phase resulting in a high MW novolak and low amount of dimer, ~5%, with little free P and narrow MWD of 1.5–2.0.

A later report [25] mentions the use of an unreactive oxygen-containing organic solvent as a reaction co-solvent within the heterogeneous reaction. Diols, ketones, and dioxane are listed along with methanol. Both forms of formaldehyde are used such as 37% aqueous and 92% solid paraform. Besides, phenol, substituted phenols, and Bisphenol A type novolaks can be prepared. Table 4.8 shows a comparison of PAPS resin with an existing resin (oxalic acid catalyzed). High yields of PAPS resins are obtained as compared to existing resins with correspondingly very low MWD of 1.17, lower amount of dimer, and lower bulk viscosity at 150°C.

Figure 4.5 shows the GPC of both resins with a significantly narrow MWD for the PAPS resin while the existing resin is quite broad in MWD. GPC peak for dimer is also reduced substantially for the PAPS resin when compared to the existing resin.

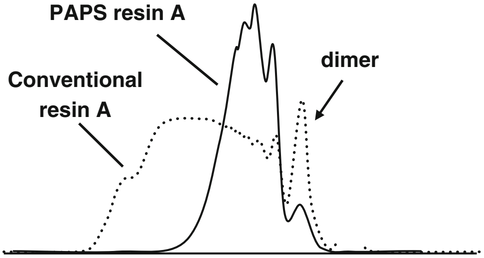
Figure 4.6 provides an overview of the types of PAPS resin that can be obtained by the judicious choice of F/P ratios and phosphoric acid.

Table 4.8 Comparison between PAPS resin and current resin

Novolak	Yield (%)	M_n	M_w	M_w/M_n	Dimer (Area %)	SP (°C)	Viscosity at 150°C
PAPS	100	615	720	1.17	6	83	0.2 Pa s
Current	96	631	2028	3.22	12	85	1.0 Pa s

SP softening point

Fig. 4.5 GPC chart of PAPS resin A and existing resin A



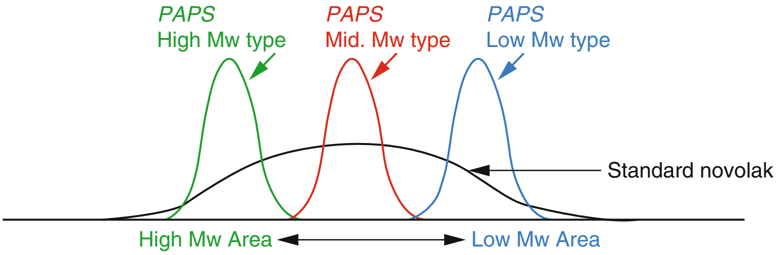


Fig. 4.6 GPC of types of PAPS resins and compared with standard novolak

Table 4.9 Comparison of PAPS resins with current resins

Novolaks		M_n[a]	M_w[a]	M_w/ M_n	Dimer (GPC)	Softening point (°C)	Melt viscosity at 150°C (Pa s)
PAPS resins	Low (1)	340	412	1.21	45	49	0.04
	Middle (2)	615	720	1.17	6	83	0.21
	High (3)	688	1,035	1.50	1	111	3.03
	Ultra high (4)	1,535	7,696	5.01	1	150	–
Current resins	Middle (5)	631	2,028	3.22	12	85	0.97
	High (6)	864	2,623	3.04	11	105	1.38
	Ultra high (7)	950	7,926	8.34	8	120	–

[a] Reduced value (polystyrene)

Table 4.9 contrasts the differences between PAPS resins according to MW, MWD, % dimer, softening point, and melt viscosity at 150°C. Several unique features are apparent such as narrow MWD, low dimer content unless deliberately desired in the low MW material, and unusually low melt viscosity at 150°C.

GPC of low MW and high MW resins (Table 4.9) prepared by the heterogeneous process and comparison with GPC's of oxalic acid catalyzed resins are shown in Fig. 4.7. PAPS resins are narrower in MWD except for the ultra-high MW resins

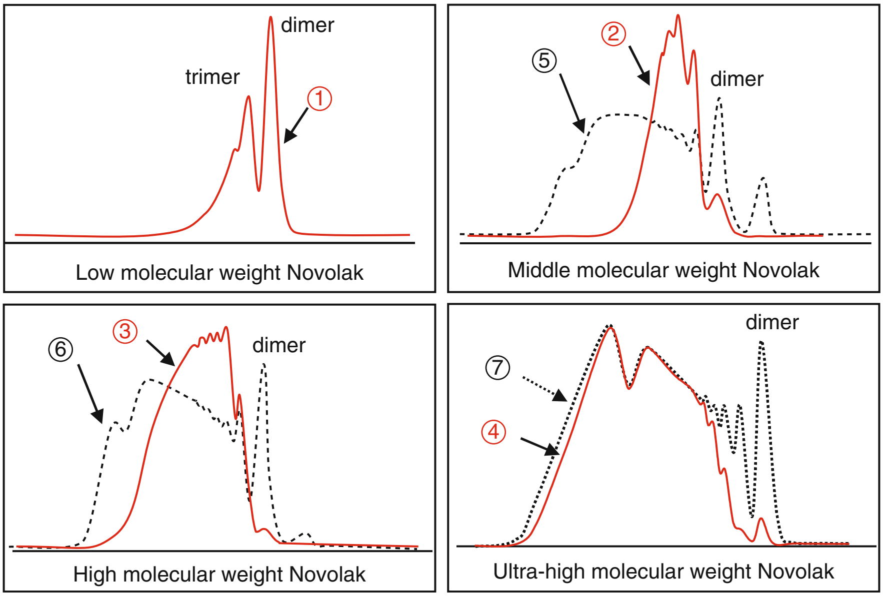


Fig. 4.7 Types of resins and GPC's of PAPS Novolaks With current resins

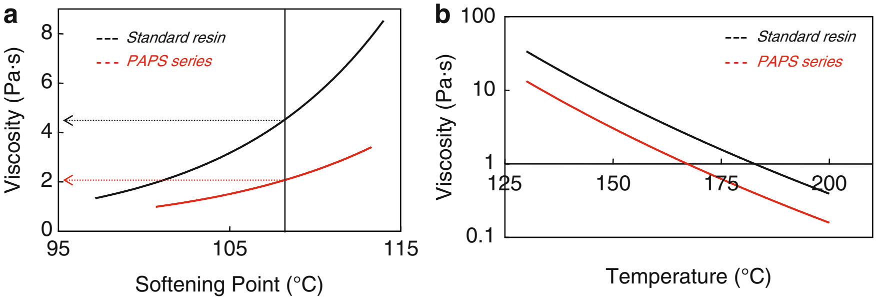


Fig. 4.8a, b Bulk viscosity vs softening point or temperature

which appear to be similar except for the absence of dimer and trimer from the PAPS resin. The low MW PAPS resin provides a convenient preparation of either bisphenol F or the corresponding trimer.

A plot of bulk viscosity versus softening point (Fig. 4.8a) or bulk viscosity versus temperature (Fig. 4.8b) compared with standard or existing novolak indicates that lower bulk viscosity with similar softening point as well as higher softening point for similar bulk viscosity are obtained when a PAPS resin is compared with standard resin.

The *o*/*p* ratio of existing resins and those prepared by the PAPS method are compared in Fig. 4.9. A substantial decrease in the o/p ratio for PAPS resins is indicative of increased *p*,*p*′ functionality in the PAPS microstructure and affects the

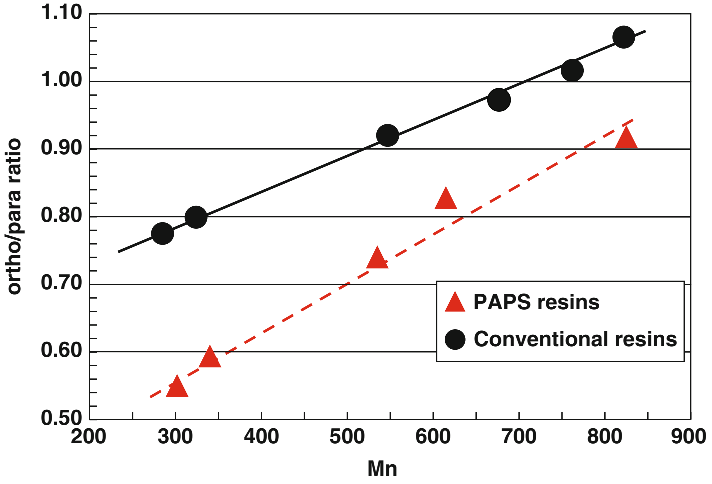
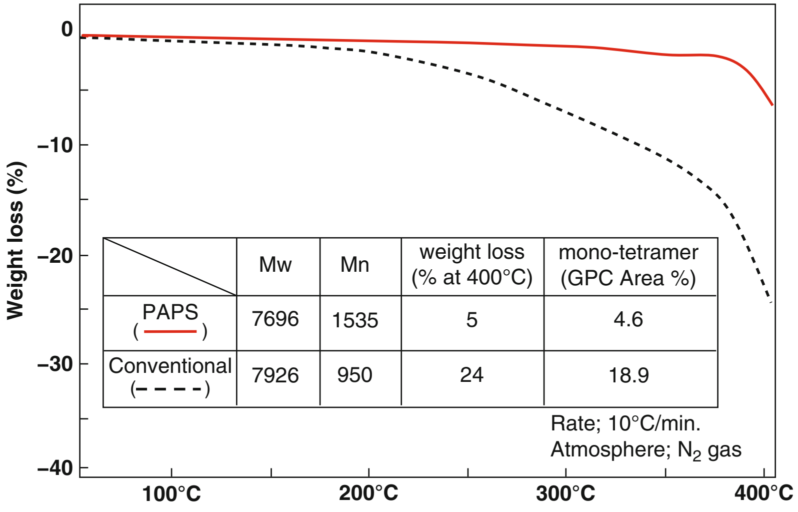


Fig. 4.9 Ortho/para ratio of PAPS resins and existing resins



	Mw	Mn	weight loss (% at 400°C)	mono-tetramer (GPC Area %)
PAPS (——)	7696	1535	5	4.6
Conventional (– – – –)	7926	950	24	18.9

Rate; 10°C/min.
Atmosphere; N_2 gas

Fig. 4.10 Thermal Stability of PAPS resin compared with conventional resin

reactivity of PAPS resins with hexa. PAPS resins are slower in cure with hexa than standard resins cured with hexa.

The PAPS resins exhibit improved thermal stability (Fig. 4.10). A weight loss of 5% for PAPS versus 24% weight loss for existing resin is shown by TGA scan. Both resins had similar M_W values of about 7,600–7,900. GPC comparison data indicated that a larger percentage of mono-tetramer (19%) was present in existing resin while a lower amount (<5%) in PAPS. It is uncertain whether the presence of high amount of mono-tetramer contributes to higher weight loss at 400°C for conventional resin.

4.4 Nanotechnology

An area that has gained prominence within the last two decades has been the use of Nanotechnology to modify various polymeric systems. It is a new, formidable tool that provides multifunctionality to the nanomodified polymer system. The introduction of a nanophase within a polymeric system has been shown to substantially improve the overall physical and mechanical characteristics of the resulting nanomodified polymer [26]. Multifunctional features attributable to the formation of polymer nanocomposite consist of improved thermal resistance and/or flame resistance, moisture resistance, decreased permeability, charge dissipation, chemical resistance, and toughness. The value of nanotechnology as it is applied to polymers is that it provides value-added properties not present in the neat resin without sacrificing the inherent processability and mechanical properties of the neat resin.

The technical approach involves the incorporation of nanoparticles into different phenolic type resin matrix systems (phenolic {resole or novolak}, BZ, or CE) whereby nanoparticles may require surface treatment or functionalization (see later) for suitable hydrophobic interaction with the hydrophobic phenolic, BZ, or CE matrix system. Further these enhanced properties that are developed through nanomodification of the resin matrix are expected to result in enhanced performance of the corresponding fiber reinforced composite.

Various nanoparticles, methods of nanomodification, and performance of nanomodified neat phenolics are described in Table 4.10. Nanomodification of CE and BZ are discussed in CE and BZ sections. Different methods of introducing nanoparticles such as “in situ” polymerization, solution or melt blending processing, and sol-gel hybrid technique are used.

Many different analytical techniques such as wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), and Raman Spectroscopy (for carbon nanotubes) are used to characterize the resulting nanocomposites. The use of TEM is especially important since it provides a means of observing the uniformity of dispersing nanoparticles into the resin matrix as well as an economical and efficient method of observing dispersion uniformity before scaling up and consuming large amounts of expensive nanomaterials.

Entry 7 in Table 4.10 involved the “in situ” preparation of a resole resin in the presence of nanoclay. Figure 4.11 shows the TEM micrograph of 5% HMMT nanoclay in resole resin from this study.

The authors maintain that the HMMT5 resole composition was an exfoliated nanocomposite. The same study provided DMA (Fig. 4.12) data to show how the T_g increased to 315°C with increased amount of clay, up to 5%. When 10% clay was introduced, the T_g was slightly lower or 310°C and possibly attributed to some intercalated clay as well as exfoliated clay, while the 5% clay was wholly exfoliated. The “in situ” method of resole nanomodification provides a high amount of exfoliated phenolic nanocomposite. Yet when attempting to disperse nanoclay into

Table 4.10 Nanomodification of phenolic and related resins

Phenolics				
Resin	Method	Nanoparticle	Result	References
N	In situ	Clay	Improved thermal stability, strength, stiffness	[27]
N/R	In situ	Clay	High bending strength and modulus	[28]
N/R	In situ	Clay	Novolak exhibits favorable behavior in nanomodification	[29]
N	sol-gel	Silica	Increased flex strength, higher LOI, high char yield	[30]
N	In situ	Clay	Increased modulus and flexural strength	[31]
N	Solution	CNF	Increased friction behavior	[32]
R	In situ	Clay	Higher T_g (315°C), higher impact strength	[33]
R	In situ	Copper	Increased stability, proposed friction use	[34]
R	Melt	Clay	Superior heat resistance	[35]
R	In situ	Clay	Increased stability	[36]
R	Solution	Clay	Improved flex strength, impact/fracture toughness	[37]
R	Solution	Cellulose nanocrystals	Increased modulus but decreased strength/elongation of OSB	[38]
R	Solution	Carbon nanotube	Increased modulus and tensile strength	[39]
R	Solution	CNF	Increased T_g's, increased bending storage modulus above T_g	[40]
PRF	Solution	POSS	High temperature stability, char retention, enhanced insulation	[41]
R- Boron modified	In situ	Clay	Increased thermal stability, increased char yields	[42]

N Novolak, *R* Resole, *PRF* Phenol resorcinol formaldehyde, *POSS*® Polyhedral oligomeric silsesquioxane

resole resin via solution conditions, intercalation occurs predominately rather than exfoliation. This may be due to the strong hydrogen bonding that exists between methylol functionality and phenol hydroxyl groups, and it is difficult to disperse and insert these "H bonded" oligomers into clay galleries. The ease of exfoliation of nanoclay in either BZ or cyanate esters (discussed later) is facilitated due to the absence of both of these functionalities (methylol and hydroxyl phenolic group).

Mechanical characterization methods include dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and thermal mechanical analysis (TMA). Fire resistance and/or flame retardancy of nanomodified resin systems is conveniently determined by cone calorimetry. Since phenolic resins are known to exhibit low fire, smoke, and toxicity characteristics (FST), nanomodification provides further enhanced fire resistance [26].

The observation of increased tensile properties and fracture energy of "in situ" novolak as it relates to mass % of nanoclay is demonstrated (entry 1, Table 4.10) in Table 4.11. All novolaks were cured with hexamethylene tetramine. As the amount of nanoclay increased from 2.7 to 8.1 mass (wt)%, tensile properties and fracture

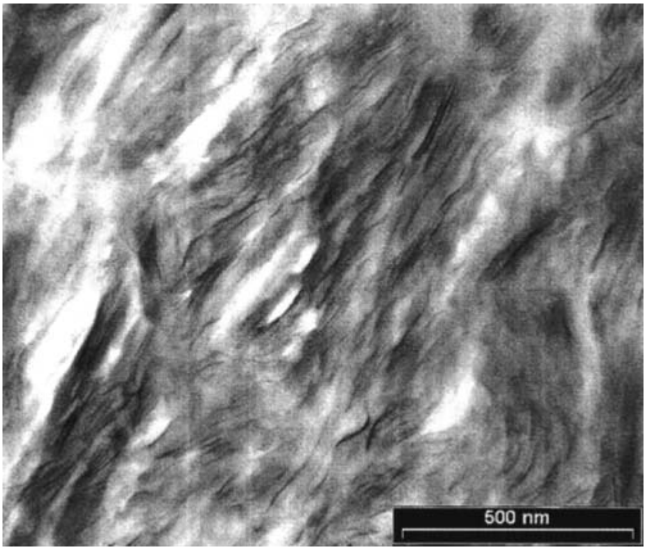


Fig. 4.11 TEM micrograph of HMMT5

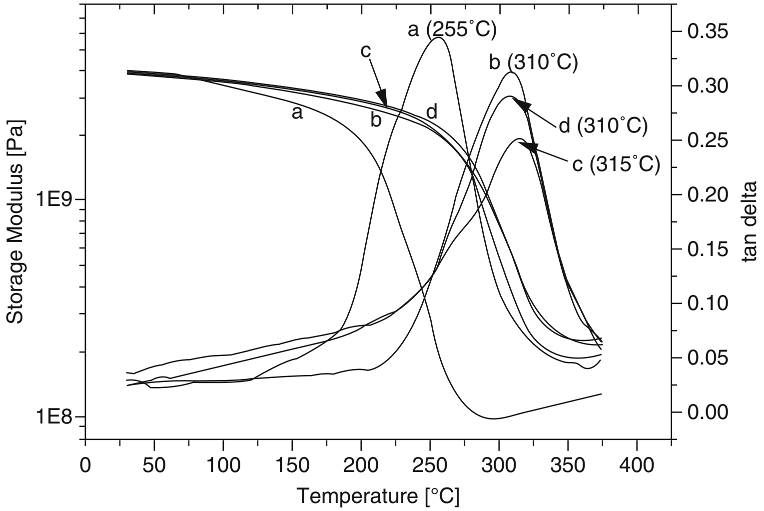


Fig. 4.12 DMA for (**a**) the neat resole, (**b**) HMMT3, (**c**) HMMT5, and (**d**) HMMT10

energy were the highest with 2.7 wt% nanoclay. Macro-sized fillers such as MgO and glass were compared with the nanomodified cured novolaks as well as the neat cured resin. Higher amounts of nanoclay to 8.1 wt% were not as effective as 2.7 wt%.

The least expensive nanoparticle, nanoclay, exhibit favorable performance in the nanomodification of phenolic and related resins resulting in high heat resistance,

Table 4.11 Mechanical properties of Novolak resin modified with nanoclay

Composite (% mass)	Loading	Prestirring (h)	Strain to failure (% elong.)	Tensile strength (MPa)	Tensile modulus (GPa)	Fracture energy (mJ)	Density (g/cm^3)
Pure	0.00	0	3.1	13.3	1.20	252	1.29
Clay	2.70	24	3.6	24.9	1.53	503	1.31
Clay	5.40	2	3.5	14.3	1.11	332	1.31
		24	3.4	18.4	1.69	281	1.30
		48	4.1	18.9	1.65	330	1.30
Clay	8.10	24	3.4	11.5	1.07	242	1.33
		48	4.5	15.9	1.03	408	1.32
MgO	5.4	0	3.5	12.7	1.16	262	1.31
Glass	5.4	0	3.5	7.2	0.66	193	1.32

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increased strength and modulus, high char, and in some cases, improved toughness or impact.

4.5 Modified Novolaks

Various modified novolaks are prepared under acid catalyzed conditions involving selective reactants such as olefins, alkyl halides, phenols, rosin, dialcohols, diethers, and others. Besides these basic reactants, other phenols and aldehydes have been used, particularly, in the preparation of novolaks for photoresist area (see Photoresist) as well as epoxy hardeners for electronic potting products. In some cases the modified novolak is obtained without formaldehyde or any aldehyde.

4.6 Enzyme

The enzymatic oxidative polymerization is a mild reaction and occurs in the absence of formaldehyde. Different enzyme systems such as soybean peroxidase (SBP) or horse radish peroxidase (HRP) in conjunction with hydrogen peroxide oxidize substituted phenols.

The reaction can be carried out in a mixed aqueous solvent system (acetone, ethanol, or isopropanol) at 50°C–60°C with insoluble product removed by filtration and solvents recycled. Although mild reaction conditions (<60°C) and formaldehyde free system are beneficial factors, the overall biocatalytic system is more expensive than conventional novolak catalysts. In addition these substituted novolaks have limited applications. A recent patent [43] describes the reaction of phenol with HRP and hydrogen peroxide in a 1:1 water–ethyl acetate mixture at room temperature for 3 h to yield 22.4% dimer at 49% conversion.

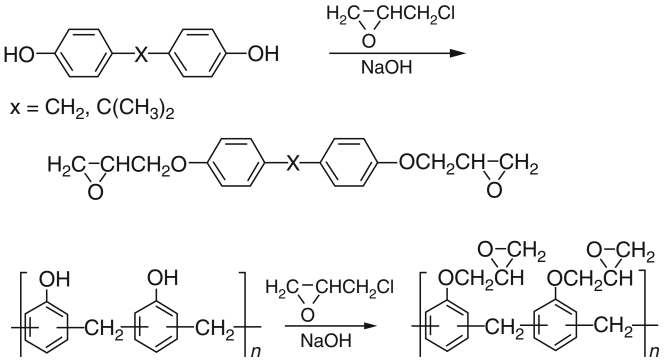
The enzymatic manufacture [44] of PPO (polyphenylene oxide) occurs by the laccase enzymatic oxidation of 4,4′-methylenebis(2,6-dimethylphenol).

4.7 Reactions

Selective reactions can be directed to the hydroxyl functionality of the phenolic group whereby the transformed product has new utility in applications that are nonattainable by the phenolic resin. Moreover in many instances these appendages eliminate water by-product evolution and minimize void content. These transformations are preferably conducted on the stable novolak system. There are some occasions when resole resins are functionalized but only under special conditions due to the reactivity of the methylol group (see a later section, addition cure phenolics). These new functional groups or appendages vary from epoxy, cyanate groups to the formation of an oxazine ring structure, such as benzoxazine. Similar reactions can be conducted with natural products containing phenolic functionality such as lignin, tannin, and cashew.

4.7.1 Functional Group Appendage to Phenolics: Epoxy

The most important transformation of phenolics is the introduction of an epoxy group onto the hydroxyl group leading to a variety of epoxy compounds which can be difunctional (bisphenol) or multifunctional (novolak) (4.7):

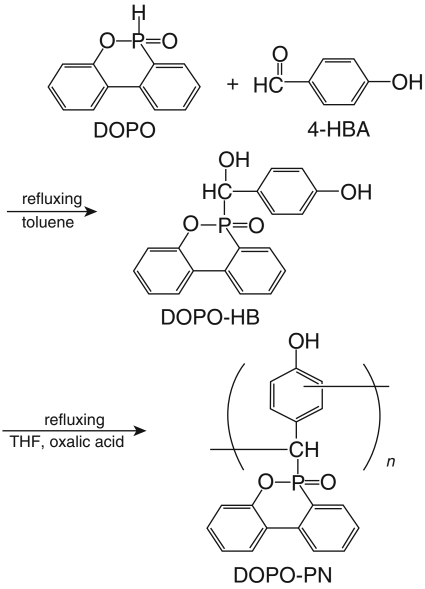


(4.7)

The simplest novolak, Bisphenol F (X = CH_2), is transformed into the corresponding epoxy resin whose value as a low viscosity epoxy resin system was mentioned earlier. Bisphenol A [X = $C(CH_3)_2$] epoxy resin is a large volume commodity epoxy resin used in electrical laminates, coatings, adhesives, composites, and high performance polycarbonate known as Lexan.

The use of high purity epoxy o-cresol novolak (ECN) combined with phenolic novolak hardener represents the general purpose epoxy potting system for encapsulation via transfer molding of solid-state devices such as diodes, transistors, and integrated circuits for electronic applications. These silica filled compositions are characterized by high modulus, high T_g, and low thermal expansion coefficient (TEC). These three characteristics determine to some extent the internal stress in the epoxy molding material and are important considerations in the design of new epoxy/hardener systems. With large chip size and increasing DRAM density, new characteristics such as reducing thermal stress and improving solder crack resistance have become important due to high packaging density and surface mount configuration. The latter requires infrared lamp and vapor phase solder baths (215°C–260°C).

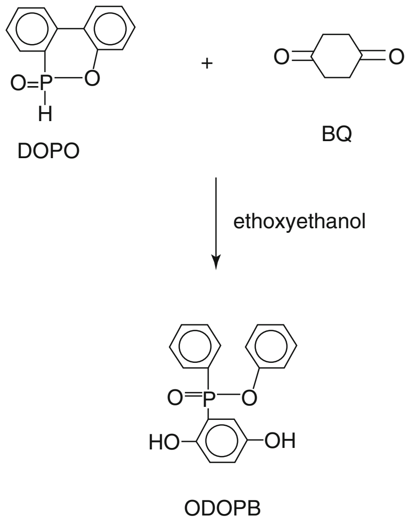
A new phosphorous containing material known as DOPO, 9,10-dihydro-9-oxa-10-phosphaphenanthrene, has been developed as an halogen free flame retardant for epoxy circuit boards [45]. DOPO reacts with 4-hydoxybenzaldehyde via a simple addition reaction to form DOPO-HB.



(4.8)

DOPO-HB is then polymerized under acidic conditions to the corresponding novolak, DOPO-PN (4.8). DOPO-PN is used as a curing agent with *o*-cresol novolak type epoxy resins resulting in high T_g (>160°C), high char yields with high LOI values demonstrating good flame retardancy. Depending upon the amount of DOPO-HB which is usually less than 30%, cured epoxy resins exhibit UL 94 VO behavior.

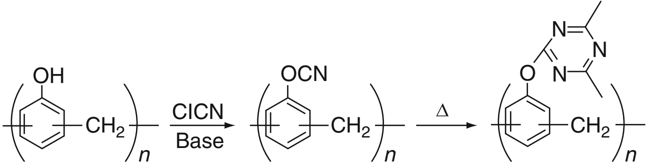
The reaction of DOPO with benzoquinone leads to a phosphorous containing hydroquinone compound known as ODOPB (4.9). When ODOPB is used as a hardener for the cure of o-cresol formaldehyde novolak epoxy (CNE), UL 94 VO behavior is achieved with Phosphorous content as low as 1.1% with a corresponding high T_g of 183°C–187°C [46].



(4.9)

4.7.2 Cyanate Ester

The development of cyanate esters has occurred in a manner analogous to epoxy resins. Both difunctional and multifunctional cyanate esters were commercialized based on bisphenols and phenolic novolaks. Cyanate esters (CE) have been used as matrix resins for fiber reinforced composite systems for nearly 30 years [47]. CE consist of a variety of bisphenols as well as phenolic novolak resins with the cyanate group appended to the phenolic hydroxyl. Cyanate esters as either monomers or oligomers are readily prepared by reacting the phenolic containing material with cyanogen halide to form the resulting cyanate ester (4.10). At elevated temperatures cyanate esters undergo trimerization/crosslinking into a high temperature thermosetting resin system. For example high yields of bisphenol A dicyanate ester are obtained by using cyanogen halide and base. The cyanate ester trimerizes into a cyanurate ring structure at elevated temperatures catalyzed by metal salts yielding a highly crosslinked resin with T_g >250°C.



(4.10)

They are high T_g materials within a range of 250°C–300°C with excellent mechanical properties, heat resistance, low volume shrinkage, and low water absorption. They are particularly useful in both aerospace and electronics industries. Novolak cyanate esters known as PT resins are commercially available from

Lonza AG. The PT family of resins [47] consists of a viscous liquid, semi-solid, and powdered type material. These liquid and solid forms provide broad processing capabilities of PT resin by hot melt (prepreg/adhesives), filament winding, RTM, or powder coating/compression molding. PT resin requires lengthy cure and post cure at elevated temperatures for maximum T_g (350°C–400°C). It exhibits good thermal stability with little change in mechanical properties after ageing for 1,000 h at 288°C or 200 h at 315°C. Char and OSU values are quite attractive and responsible for use in aircraft interior applications.

A well known electrical laminate resin system, Mitsubishi BT resin, consists of Bis A dicyanate and bismaleimide of 4,4′ methylene dianiline and is used in high T_g electrical laminates.

Dicyanate esters are particularly attractive resin systems for electronic applications due to the unusual combination of properties such as low values of dielectric constant (D_k) and dissipation factor (D_f) with an accompanying high T_g [47]. Only Teflon and polyethylene possess lower D_k and D_f values than cyanate esters but Teflon and polyethylene are low modulus materials. Low values of D_k and D_f are highly desirable and allow increased signal speed and circuit density while lowering power requirements and amount of heat generated relative to epoxy or BMI resins. These benefits are extremely important for circuits operating at microwave frequency. Further low $\mathrm{D_k}$ and $\mathrm{D_f}$ values allow increased transmission of microwaves through radome walls, antenna housings, and stealth aircraft composites. Dicyanate esters are established thermosetting resins for insulating high speed, high density electronic circuitry, matrix resins for aircraft composites, geostationary broadcast satellites, radomes and antennas, versatile adhesives, as well as passive waveguides or active electro-optic components for processing light signals in fiber optic communications.

High performance thermoplastic resins such as PES, PSF, PPO, PEI, and PI with T_g's $\geq$ 170°C are soluble in dicyanate esters but phases separate into co-continuous morphologies during cure when concentrations are above15%. The resulting toughened materials exhibit effective impact damage resistance without sacrificing high T_g or elevated temperature modulus.

Nanotechnology has also been applied to cyanate esters. Some selective studies are presented in the following examples (Table 4.12).

The uniform dispersion of nanoclay into a novolak cyanate ester known as PT-15 is shown in Fig. 4.13 [48].

Dispersing SiC nanoparticles into novolak cyanate ester (entry 5, Table 4.12) resulted in improved thermal stability as shown in TGA data (Fig. 4.14). The best

Table 4.12 Nanomodification of cyanate esters

Bis E	Solution	Clay	Improved flex strength, crack resistance	[49]
N	Melt	Clay	High thermal stability, enhanced toughness	[50]
Bis A	Melt/solution	Clay	High T_g, high modulus, toughness, reduced CTE	[51]
N	Melt	f-MWNT	Improved mechanical and thermal properties	[52]
N	Solution	n-SiC	Improve thermal stability	[53]

Bis A Bisphenol A, *Bis E* Bisphenol acetaldehyde, *f-MWNT* functionalized multi-wall carbon nanotubes, *n-SiC* nano-silicon carbide

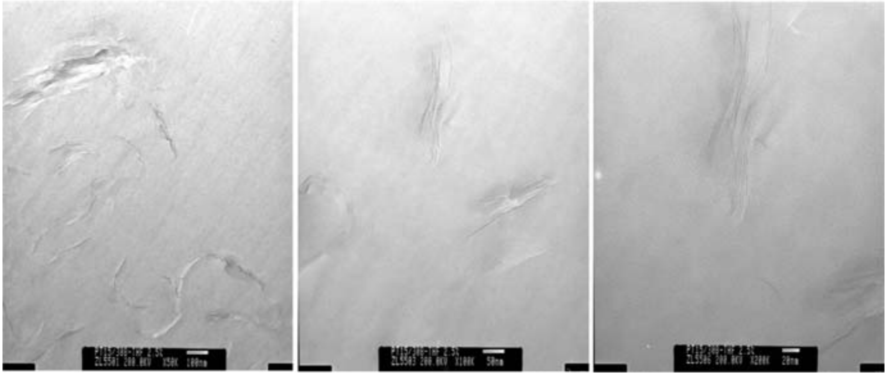


Fig. 4.13 TEM of novolak cyanate ester PT-15/Closite 30B (97.5/2.5%) [26, 48] (Reprinted with permission of Society for the Advancement of Material and Process Engineering)

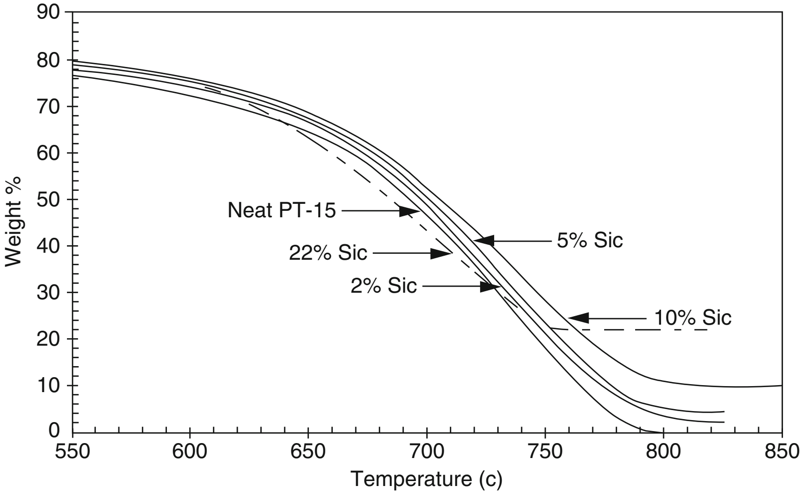


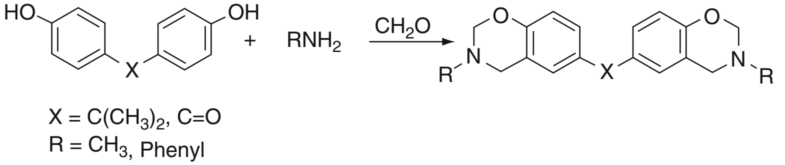
Fig. 4.14 Thermogravimetric analysis of PT15-SiC particles nanocomposites at scan rate of 20°C/min (Reprinted with permission of Society for the Advancement of Material and Process Engineering)

thermal stability was observed with 10 wt% nano-SiC. Samples with amounts above 10 wt% or as much as 22 wt% were actually less thermally stable than the control.

The least expensive nanoparticle, nanoclay, exhibits favorable performance in the nanomodification of cyanate esters as it did in the nanomodifcation of phenolic resins. More recent efforts to improve the interlaminar adhesion between nanoparticle and the phenolic matrix type resins have involved functionalization of the nanoparticle. Multiwall carbon nanotubes are functionalized (entry 4, Table 4.12) with either isocyanate or amine functional groups to achieve bonding between the MWNT and CE resin system.

4.7.3 Benzoxazine

Benzoxazines (BZ) have been developed as a novel type of phenolic resins and differ from traditional phenolics in that the phenolic moieties are connected through the formation of a cyclic structure from the phenolic hydroxyl to the ortho position [–O–CH_2–N(R)–CH_2–] rather than a methylene [–CH_2–] bridge that is associated with traditional phenolics [54–57]. Benzoxazines are easily prepared from phenol type materials (bisphenols or novolak), primary amines, and formaldehyde. Like epoxies and cyanate esters, both monomers and oligomeric BZ materials are available by reaction of bisphenols or novolak with primary amines and formaldehyde (4.11).



(4.11)

Recent reviews by Takeichi [55] and Yagci [57] provide various synthetic strategies for BZ type materials, polymerization reaction mechanisms, and structure–property relationships of cured materials. Polymerization of BZ proceeds through the ring opening of the cyclic component by heat treatment with or without catalyst and, more importantly, without by-product/volatile generation**.** These latter considerations enhance the excellent dimensional stability of the final product. Besides high heat resistance and flame retardant properties, BZ exhibit characteristics that are not observed in traditional phenolic resins such as low water absorption and stable, low dielectric properties. These attributes have contributed to its evaluation by several benzoxazine producers as a matrix resin system in electronic materials, fiber reinforced composites, and adhesives.

Altstaedt and co-workers [58] have examined a variety of tougheners for BZ type resins. Toughness improvement was achieved with increased K_{IC} and G_{IC} values with T_g, flexural strength, and modulus being effected minimally.

Processing performance of BZ can also be improved by a judicious selection of other co-reactive thermosetting oligomers such as epoxy and/or phenolic resins. Ternary systems of BZ, epoxy, and phenolic are reported and exhibit low viscosity on mixing with T_g's as high as 170°C [59]. Further co-reaction can also occur with reactive liquid rubbers, polyurethanes, and polyimides [59]. Electronic uses consist of poly-BZ based films as an underfill material that is used between chip and package components [60–62]. Further two recent reports [63, 64] suggest that BZ provides increased adhesion to the wafer within microelectronic package due to low shrinkage and low CTE. Similar characteristics are reported when BZ is used as resin matrix for printed circuit boards [65].

Favorable RTM components based on BZ have been reported recently [66, 67]. Huntsman researchers [67] conducted an experimental design strategy of Huntsman BZ resin, cycloaliphatic epoxy, a toughening agent, and phenolic resin as catalyst for an optimized BZ formulation. The study involved the role of each component in the selection of a composition for the final RTM material. As a consequence of the study, a new RTM system based on BZ/epoxy composition is processable at 177°C using traditional RTM conditions. The BZ/epoxy RTM product exhibited a T_g in excess of 200°C, and excellent mechanical properties with excellent modulus retention under hot/wet conditions. Further it possessed superior thermo-oxidative stability.

Studies with solely BZ type resins carried out by Xiang and coworkers [66] involved the use of mono and difunctional BZ's. Mono and difunctional aromatic amines were reacted with phenol and formaldehyde. Gel times, pot life, catalyzed and uncatalyzed reactions with mono, difunctional, and mixtures thereof led to RTM conditions suitable for fabrication of a glass reinforced RTM composition with a high T_g (>200°C) and attractive mechanical properties: flexural strength and modulus values of 662 MPa and 30 GPa for warp direction and 546 MPa and 23 GPa for the weft direction. The authors claim that the resulting RTM component is suitable as a high performance structural material.

Recently Gurit has commercialized a BZ prepreg known as P-1000 [68]. Henkel has introduced a new BZ resin system known as Epsilon [69].

Nanomodification of BZ (Table 4.13) is carried out in a manner similar to other phenolic type resins namely resoles, novolaks, and CE.

The use of functionalized multi-walled carbon nanotubes (f-MWNT with isocyanate functional group) to nanomodify BZ (entry 5, Table 4.13) led to increased storage modulus (Fig. 4.15) and increased T_g with f-MWNT varying between 1 and 1.5 wt% (Fig. 4.16). Amounts above 1.5 wt% exhibited lower storage modulus and lower T_g.

4.7.4 Nanomodified Fiber Reinforced Phenolic Type Polymer Matrix Composites

The significance of using nanomodified phenolic resins as well as CE and BZ matrix resins into fiber reinforced composite systems is in the early stages of

Table 4.13 Nanomodification of benzoxazines

Benzoxazines				
Monomer	Melt/ solution	Clay	Lower cure exotherm of BZ, higher T_g (hot, wet strength)	[55]
Novolak	Unknown	Clay	Molding material with high hardness	[70]
Monomer	Melt	Silica	Increased modulus, toughness, high T_g	[71]
Monomer	Melt/in situ	Clay	Precursor to char forming products	[72]
Monomer	Solution	f-MWNT	Increased modulus, increased T_g	[73]
Monomer	In situ and/or solution	Clay	Improved friction material with excellent high temp performance and low wear loss	[74]

f-MWNT functionalized multi-wall carbon nanotubes

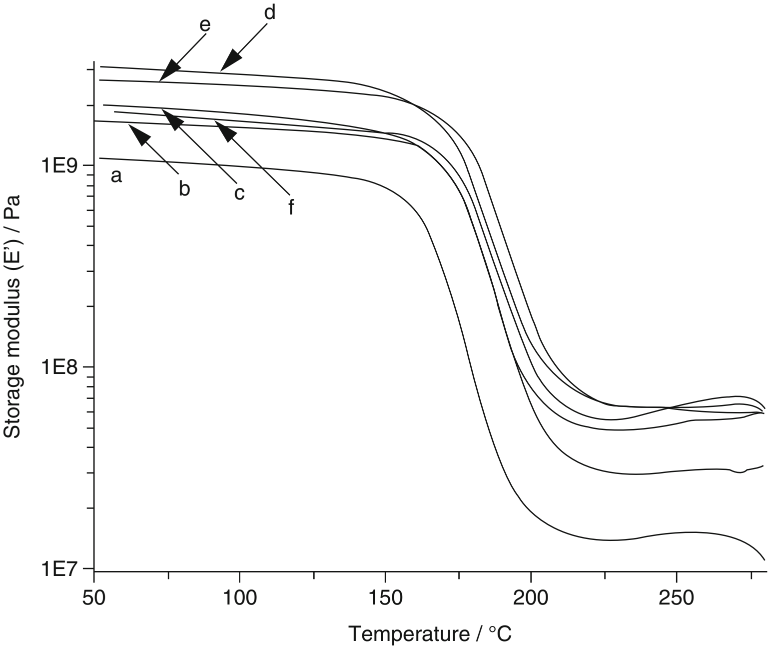


Fig. 4.15 MWNT concentration effect on the storage modulus (E′) of nanocomposites: (**a**) 0, (**b**) 0.2 wt%, (**c**) 0.5 wt%, (**d**) 1 wt%, (**e**) 1.5 wt%, and (**f**) 2 wt% (Reprinted with permission from Elsevier)

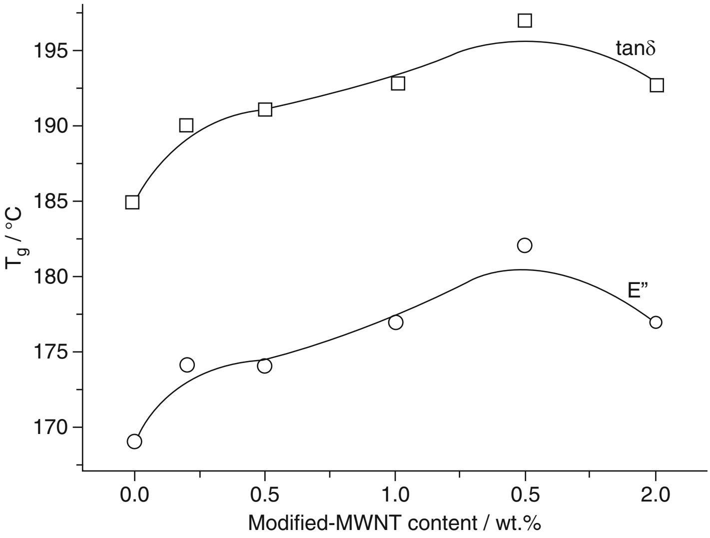


Fig. 4.16 MNWT concentration effect on the T_g of nanocomposites (Reprinted with permission by Elsevier)

Table 4.14 Nanomodified fiber reinforced polymer matrix composites

Resin	Nanoparticle	Fiber	Result	References
Phenolic resole	Clay, POSS, CNF	Carbon	Lower ablation rates, lower backside temperature rise for improved rocket ablative materials	[26, 75]
PRF	POSS	Glass	Low backside surface temperature, reduced mass loss, modulus retention to 400°C	[76]
BZ, monomer	Silica	Carbon	Decreased impact damage, increased toughness	[71]
Cyanate Ester N	Clay, POSS, CNF	Carbon	Transformation of nano-cyanate ester into carbon/carbon composite with improved thermo-oxidative resistance	[26]

development. Some examples of the transformation of these nanomodified phenolic and related systems into nanomodified fiber reinforced polymer matrix composites are listed in Table 4.14 and show improved composite performance due to nanomodification.

Expected and yet unexpected "multifunctional" features in the mechanical performance of these unique nanomodified fiber reinforced polymer matrix composites are obtained. Both nanomodification of phenolic resins and the subsequent incorporation of these nanomaterials into fiber reinforced composites are fruitful areas of research with anticipated benefits to the resulting phenolic resin and/or fiber reinforced composite composition. Efforts by many academic and industrial groups continue in this area.

4.7.5 Compatibilization and/or Toughening Agents

A large variety of compatibilizing agents and to a lesser extent toughening agents are known and used to modify the inherent brittleness of cured phenolic resins. Materials such as alcohols, glycols, sugars, polyvinyl alcohol, epoxies, acetals (polyvinyl butyral or polyvinyl formal), rubbers (chloroprene, nitrile rubber), amides (nylons), sulfonamides, and natural oils such as tung, linseed, and cashew have been used or are still in use in selected applications requiring a modest amount of flexibility in the cured composition. Two phenolic toughening agents available from Nanoresins, Geesthacht, Germany are Albiflex H 1083 S1 and Hypro™ RLP. The former is a phenolic resin/silicone copolymer and provides some toughness and flexibility for phenolic resins. It contains ~40 wt% silicone. Hypro™ RLP is an amine terminated butadiene nitrile liquid oligomer for similar behavior – toughness and flexibility. Thus mechanical properties of the resulting cured phenolic resin system are compromised by the addition of these above mentioned co-reactants.

More recently Sprenger of Nanoresins [77] developed a phenolic resin toughening agent based on Hypro CTBN 1300X8, carboxy acid terminated butadiene acrylonitrile rubber that was reacted with a stoichiometric amount of bis A epoxy resin to yield CTBN with pendant epoxy groups. The latter material was further reacted with phenol, formaldehyde, and sodium hydroxide to yield phenolic resin resole appended to the CTBN via epoxy group. Nanoresins recommend the use of about 5% of the phenolic CTBN for toughening phenolic resins.

Previously a study related to the use of toughening agents for a closely related, brittle phenolic, benzoxazine, by Altstaedt [58] provided an in depth understanding of the effectiveness of different toughness modifiers and apparent difficulties in resolving impact modification of a brittle resin by increasing K_{Ic} and G_{Ic} values while still maintaining glass transition temperature, flexural strength, and modulus values. These modifiers consisted of elastomers (reactive liquid rubbers), thermoplastics, and core-shell polymers. SEM images of fractured surfaces of the amino terminated liquid nitrile rubber that performed best showed an average particle size of 1–1.5 μm and appeared homogeneously dispersed in the thermosetting resin forming circular inclusions. Although the authors are unclear regarding the mechanism of toughness provided by the amine terminated rubber, they postulated that chemical co-reactivity of the rubber may have occurred during benzoxazine cure and resulted in toughness while maintaining mechanical properties characteristics.

4.8 Natural Products

A variety of natural products are used as raw materials either as partial replacement of phenol (cashew, tannin, starch, lignin), as solvent or co-reactant (furfural, furfuryl alcohol, soy), or as modifier (tung oil and linseed oil). In Table 4.15 these materials are listed by identifying their origin/source, their role in resin preparation, and some of the application areas where they are utilized.

Table 4.15 Natural products used in phenolic resins

Raw material	Source	Replace or use	Novolak	Resole
Cashew	Brazil, India, China	Phenol	Friction	Adhesive
Tannin	Argentina, Chile, South Africa, Australia	Phenol	Co-react	Adhesive
Starch	Cellulose	Phenol	Co-react	Co-react
Lignin	Bagasse, wood	Phenol	Co-react	Adhesive, coatings
Furfural, furfuryl alcohol	Oats, corn cobs	Solvent, reactant	Abrasives	Foundry
Tung oil, linseed oil	Plants	Modifier	Friction	Electrial laminates
Soy	Soybean	Modifier/co-reactant	–	Adhesive

Natural products containing phenolic groups within the structure (lignin, tannin, and cashew) undergo similar reactions as novolaks. Epoxy group can be introduced into lignin, hydroxymethylation occurs with lignin and tannin; alkylation or co-reaction of novolak with lignin is reported. There is a concerted effort to utilize many of these renewable materials in many phenolic reactions to lessen the dependence of phenolic resins manufacturers on petrochemical raw materials.

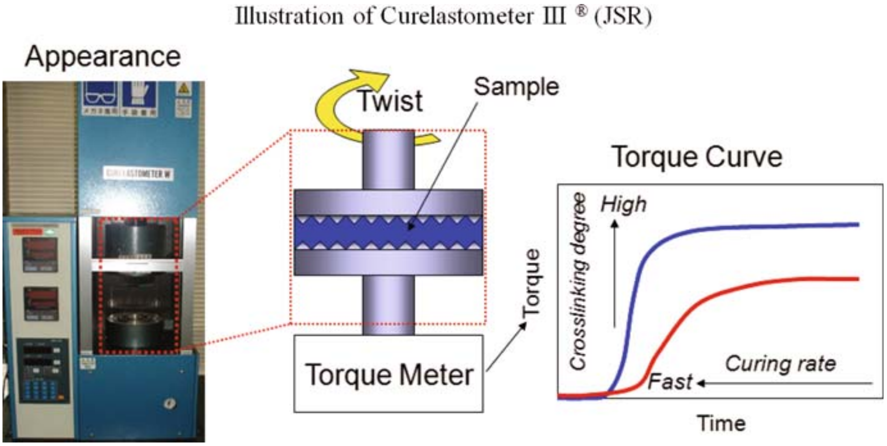
4.9 Mechanism of Cure

4.9.1 Novolak

The mechanism of cure for novolak involves benzoxazine intermediates that are transformed into benzyl amines and other materials such as amides/imides, imines, methyl phenol, benzaldehyde, and other trace materials [1]. Cure of novolak with hexa is generally recognized as a reaction which results in a fully 3D polymer network, especially when sufficient hexa is available for full cure and reaction of all available novolak sites.

An interesting study that relates to network structure of cured novolak and its corresponding cross linked density and conducted by Sumitomo Bakelite personnel was presented by Hirano [78] during the Baekeland Centennial Conference held in Ghent, Belgium from September 24–26, 2007 and raises some uncertainty regarding a fully cured 3D phenolic polymer network.

The influence of molecular weight distribution on cross linking density was examined using the Curelastomer to monitor the degree of cross linking (torque) versus time. The Curelastomer is a special rheometer developed by JSR and used in Asia to evaluate the curing behavior of phenolic resins. The Curelastomer measures viscoelastic behavior of novolak with hexa, glass fiber, and stearic acid at a specified temperature versus time.



It measures cure speed and depending on the torque value can distinguish different levels of cross link density. SB researchers fractionated low (RN-L) and high (RN-H) narrow MWD resins from a random novolak (RN) resin and examined each along with a low MW xylylene modified (XN-L) novolak resin (These resins are recognized as Xylok resins that are prepared by reaction of phenol with xylylene glycol). The narrow (high and low) MWD resins exhibited less torque/viscosity and also low cross link density than the starting material, random novolak. Torque values (Fig. 4.17) showed the following relationship: random> narrow high MWD> low narrow MWD> low MW Xylok. When the random novolak was mixed in equal parts with low MW Xylok, the highest torque value was obtained and indicated that the low MW Xylok resin when combined with random novolak can increase in cross link density. This equimixture exhibited the highest torque value.

This unexpected observation prompted SB researchers to consider novolak chain conformation through the use of the Mark–Houwink–Sakarada equation (MHS) which provides a relationship between intrinsic viscosity and molecular weight such as the resin intrinsic viscosity is proportional to the product of the Huggins constant (*K*) times molecular weight raised to the "α" power. Numerical values of either or both "*K*" and "α" describe whether the polymer is linear, branched, or coiled by "α" values and whether it is a linear or associated resin by "*K*" values.

Literature values for "α" that are greater than 0.5 indicate a linear polymer while values less than 0.5 show that the polymer is branched and coiled. Similarly, *K* values of ~0.3–0.4 are for a linear resin while *K* values greater than 0.5 represent a molecularly associated polymer.

High ortho (HN) and Xylok (XN) resins exhibited "α" values above 0.5 (Xylok was 0.6 and High ortho was 0.70) and was indicative of an extended, linear structure while the random (RN) novolak "α" was 0.3 and identified as a coiled, branched structure (Fig. 4.18). These data suggest that a more linear novolak structure leads to high cross link density, potentially high strength, and improved mechanical properties and lends some support to the SB torque study.

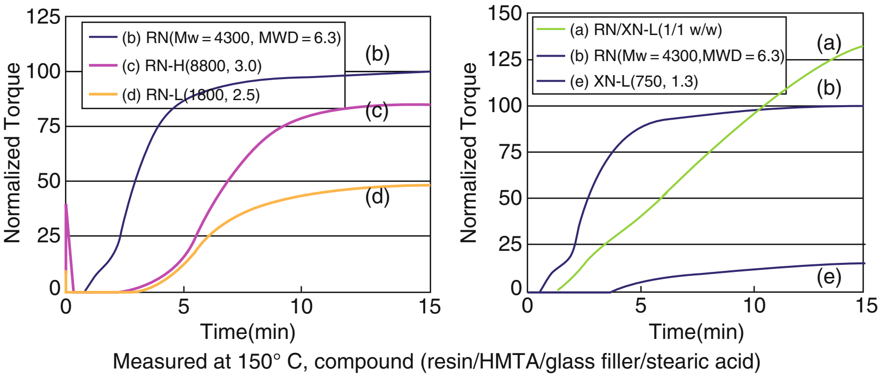
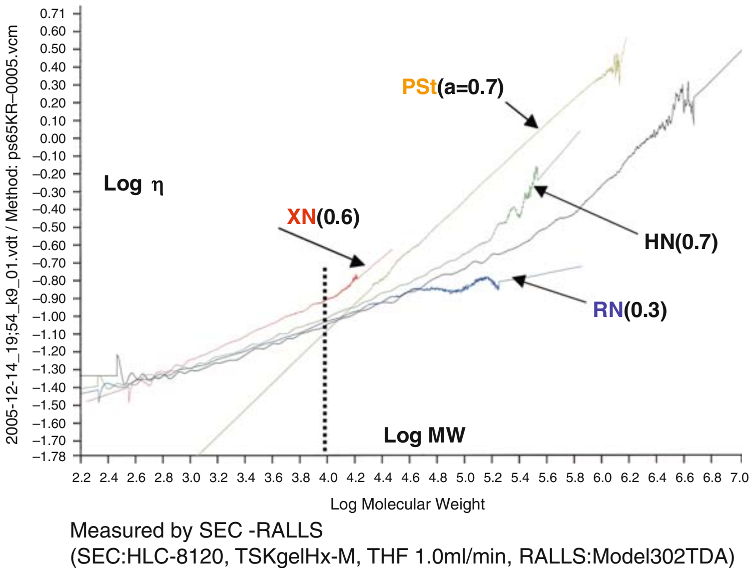


Fig. 4.17 Effect of molecular weight, distribution, and the linkage structure on the torque curve

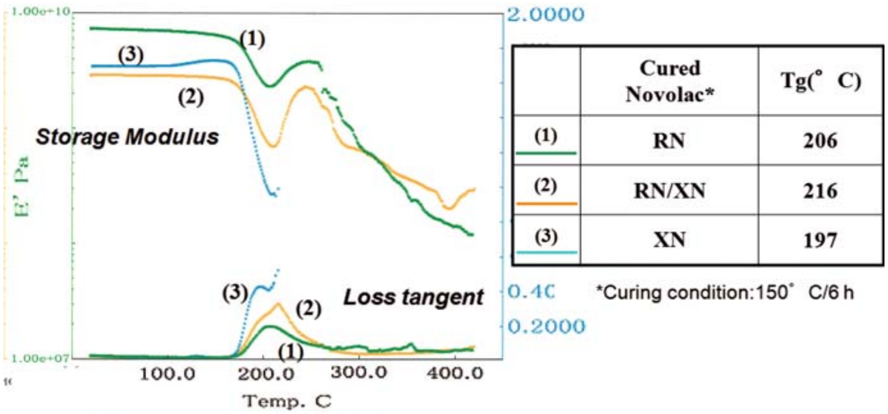


Measured by SEC -RALLS
(SEC:HLC-8120, TSKgelHx-M, THF 1.0ml/min, RALLS:Model302TDA)

Fig. 4.18 MHS's equation logarithmic plot of various novolaks

Measurement of T_g's of novolaks (shown below) such as random (RN), equimixture of random and xylok (RN/XN) , and neat xylok (XN) cured by hexa (6 h at 150°C) demonstrated the same trend as noted in the curelastomer with Xyok mixture exhibiting the highest T_g of 216°C, followed by T_g of 206°C for the random novolak, and lastly a T_g of 197°C for the neat Xylok novolak.

Tg values of novolaks DMA



	Cured Novolac*	Tg(° C)
(1)	RN	206
(2)	RN/XN	216
(3)	XN	197

*Curing condition:150° C/6 h

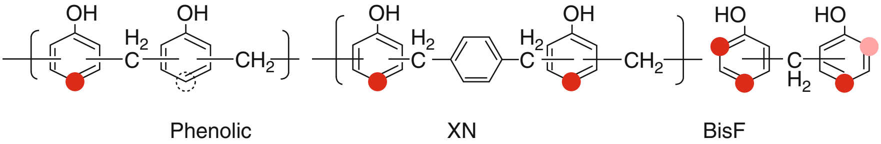
Measured by DMA(SEIKO Instruments DMS6100)
mode:bending, ramp:5° C/min, frequency:10 Hz

Formaldehyde/phenol ratio of cured random (RN) novolak by ^{13}C CP/MAS NMR is about 0.96 with a corresponding value of about 73% for the ortho/para methylene bridge and suggests that the cure of random novolak occurs upto about 70%–80% in spite of excess hexa , high cure temperature of 175°C, and extended cure time of 6 h.

A comparison of the DSC data for heat release (KJ/phenolic ring) of random (phenolic) novolak, high MW (XN) Xylok, low MW (XN) Xylok, and Bisphenol F (lowest MW novolak) indicated that the least amount of heat is released by the random novolak, followed by higher heat release by both Xyloks having approximately the same amount of heat release of 6.8–7.5 KJ, and lastly the bisphenol F showing the highest heat release of 12.8 KJ.

Within the DSC chart, the solid circles show where hexa cure has occurred and the open circles show the absence of cure. A lower heat release value for the random phenolic suggests that there are reactive sites within the random novolak that do not undergo cure and this reduced or lack of cure results in a reduced cross link density and more importantly lower strength and lower mechanical properties.

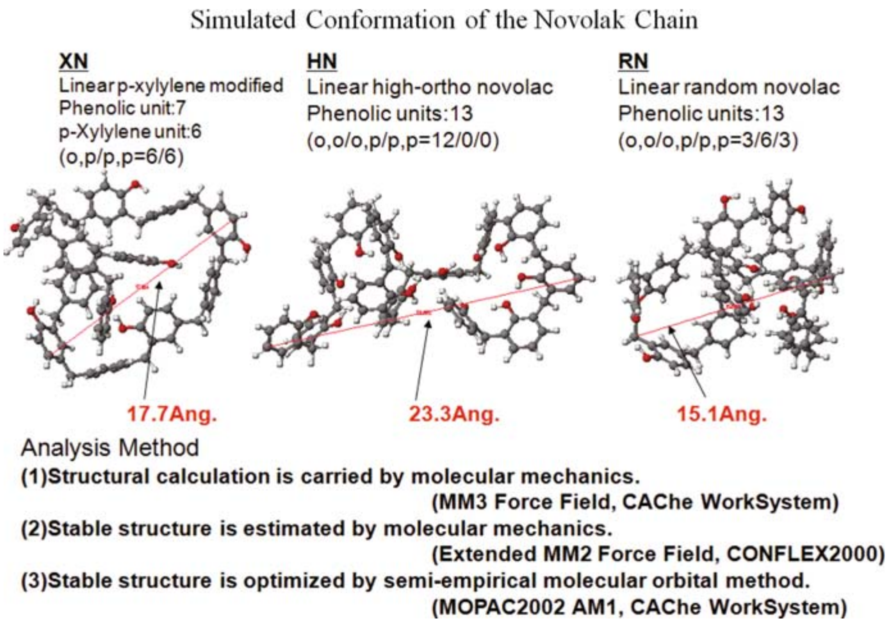
DSC data for heat release



Novolac	MW (Mn)	Peak Temp. (° C)	Heat Release* (KJ/phenolic ring mol)
Phenolic	900	150	3.5
High MW XN	1000	170	7.5
Low MW XN	700	170	6.8
BisF	425	143	12.8

*Calculated by DSC(@10° C/min, resin/HMTA = 100/17.5 w/w)

SB researchers have determined simulated conformation of the novolak chain of XN, HN, and RN by various software methods. These are represented pictorially with comparable phenolic units along with estimated unit chain length in Ångstroms. These simulated models provide further support for linearity and extended length of both XN and HN while RN is coiled and reduced in length.



Analysis Method

(1)Structural calculation is carried by molecular mechanics.
(MM3 Force Field, CAChe WorkSystem)
(2)Stable structure is estimated by molecular mechanics.
(Extended MM2 Force Field, CONFLEX2000)
(3)Stable structure is optimized by semi-empirical molecular orbital method.
(MOPAC2002 AM1, CAChe WorkSystem)

Although the conformation of most novolaks is branched or coiled, a more highly cross linked 3D network structure can be achieved with a “reasonably” linear novolak exhibiting very high T_g, exceptional strength, and performance.

4.9.2 Resole

Due to their mode of preparation, different curing conditions are necessary to crosslink resole resins. Resoles are readily cured by acid, base, or thermal conditions. There are some other special resole curing systems such as carboxylic acid esters, anhydrides, amides, and carbonates which are reported to accelerate the cure of resole resins. The conditions under which these selective systems operate are not completely understood.

Complete cure of phenolic resole leads to a high modulus, high crosslink density, moderately high T_g (~150°C) material exhibiting excellent moisture, and heat resistance. These features coupled with attractive economics are the motivating factors for the use of phenolics, particularly resoles, in many applications. The molar ratio of F to P in resoles can vary from equimolar amounts to greater than 3 moles of F to P, and it will be challenging to examine the curing mechanism of these resoles with varying F/P ratios. With an optimum F/P molar ratio of 2.1, fully cured resole is predominately methylene bridged phenolic ring structures with some hydroxymethyl and methylene ether groups, oxymethylene species, and oxidation products of F. Evidence is also presented for the presence of small amounts of carboxaldehyde and quinone structures as functional end groups or species of the fully cured resin system [13].

4.9.2.1 Latent Curing Agents

A well recognized problem is the difficulty in controlling the reactivity of an acid catalyzed phenolic resin system particularly when considering final product quality and safety. Phenolic resole resins can be highly reactive when mixed with strong acids and result in severe exothermic reactions. The reactivity of a catalyzed resin can be so rapid that the processing becomes virtually impossible to control. A method that has been used to circumvent the hazards of strong acid conditions is the use of a latent acid catalyst system.

A heat activated latent acid is usually a room temperature stable salt formed from combining an acid and a base. The activation is dependent on heating the salt to a temperature at which the salt decomposes with subsequent release of the acid. Usually organic acids such as aryl sulfonic acids are combined with primary or secondary amines such as propylamine, butylamine, and diethylamine to form stable salts which will decompose at elevated temperatures. The problem with the most common latent catalyst salts is that they require too high a temperature to decompose and release the acid. Further weaker basic primary and secondary amines do not associate with strong acids to form a stable enough salt to prevent premature catalysis after several hours.

Bac2, a Southampton, UK based manufacturer of conductive composites based on electronic and ionic conducting phenolic resins for use in electrochemical applications, has developed a novel latent acid system for use in the production of acid cured phenolic composite bipolar plates which are components for fuel cell applications. For compression molding of Bac2's composite bipolar plates, the mix life issues were prevalent. A graphite composite pre-mix consisting of a phenolic resin and a relatively strong acid when mixed together begins to react immediately and within minutes the molding properties are affected.

To overcome this problem, Bac2 [79] developed a latent acid system which enables the storage life of a bipolar plate composite pre-mix formulation comprising graphite, phenolic resole, and a relatively strong acid to be extended from 30 min to over 6 months by the use of hydroxylamine as the selected base to inhibit the acid catalysis reaction. The stable pre-mix formulation can be compression molded after 3 months to produce a plate of similar dimensions and properties of a molding produced after 24 h.

Bac2's system is based on recently filed UK Patent Applications 0902863.0 and 0912267.2 and uses hydroxylamine as the base in association with a relatively strong acid such as phenol sulfonic acid, to give a remarkably stable adduct from which the hydroxylamine component decomposes at temperatures above 117°C producing gaseous ammonia, nitrous oxide, and water vapour leaving the acid completely free to initiate catalysis.

In dry form, hydroxylamine is highly unstable and can decompose violently at ambient temperature in the presence of metallic impurities. On heating it has been shown that hydroxylamine decomposes exothermally in glass cells with an onset temperature of 117°C. In the adduct form the hydroxylamine-acid solution is stable at ambient temperatures but will decompose on heating to temperatures above 117°C. It is the decomposition of hydroxylamine itself rather than the salt, an action which completely releases the acid to initiate resole curing, which gives the hydroxylamine based latent acid longer term stability and a significantly lower activation temperature than other latent catalyst systems. It is important that venting during compression molding, in particular, is increased to allow the gaseous decomposition products to escape.

4.9.3 Non-Hexa Cure of Novolaks

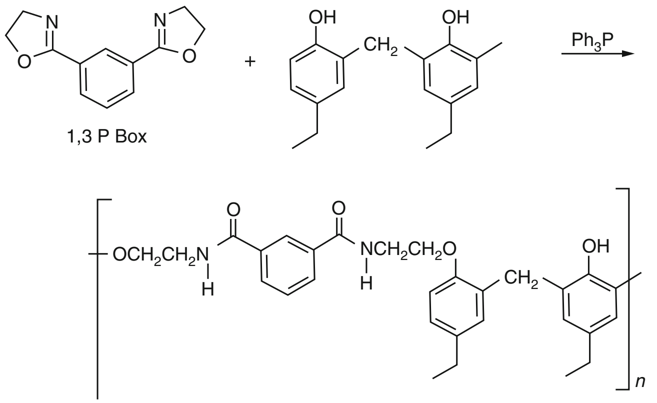
Novolaks require a source of formaldehyde which is usually hexamethylene tetramine (hexa). Other novolak curing agents besides hexa consist of solid resole, bisoxazolines, benzoxazines, and oxazolidines.

4.9.3.1 Solid Resole

Solid resole is a curing agent for novolaks. Special formulations based on solid resole/novolak systems are used in molding compounds for electrical applications and in textile felts for reduced odor in automotive insulation felt applications.

4.9.3.2 Bisoxazolines

The use of bisoxazolines for cure/reaction with novolaks is being revisited with the commercial availability of 1,3 phenylene bisoxazoline (PBO) by Evonik Degussa (Marl, Germany) and Adeka Palmarole (Saint Louis, France). PBO is more formally a co-reactant with novolak rather than a curing agent. Early studies by Ashland [80] and later by Southwest Research Institute [81] established the facile reaction of 1,3 PBO with novolak to yield a high performance polyarylether amide type material with a high $T_g > 200°C$, excellent toughness, and thermal strength (4.12).



(4.12)

Key features of the polyaryl etheramide resin are:

- No volatile by-product(s) emitted
- Low cure exotherm
- Low cure shrinkage
- High neat resin modulus (>500 MPa)
- High compression and shear strength of composites
- Excellent toughness (G_{IC} is five times greater than epoxies, BMI)

The usual cure cycle is 175°C with post cure of 225°C. The glass transition temperature (T_g) increases with increased amount of PBO. Physical, thermal, and mechanical properties are dependent upon the ratio of PBO:novolak with the higher amount of PBO resulting in increased properties. Toughness is optimum at a 60/40 novolak/PBO ratio. This composition is much tougher than those of commercial epoxy systems.

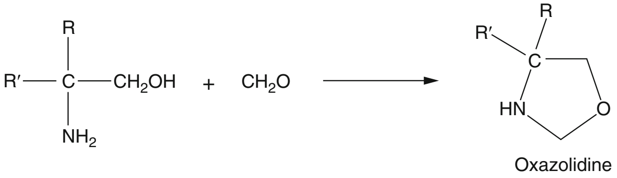
4.9.3.3 Benzoxazines

Benzoxazines co-react with novolaks (see this chapter, Reaction section) and are also recognized as intermediates in the hexa cure of novolaks (see mechanism). The curing behavior between bisbenzoxazine and hexa with novolak has shown that at low cure temperatures, the use of bisbenzoxazines in the cure of novolak does not emit ammonia, and a lower weight loss of the cured product results. Many of the reactions between novolak and BZ actually relate to the use of low amounts of novolak to co-react with BZ for favorable curing conditions of BZ.

4.9.3.4 Oxazolidines

The convenience of using aminoalcohols as formaldehyde scavenging agents through the formation of oxazolidine type materials allows the reversal of the reaction to selectively release formaldehyde from the oxazolidine and bring about the cure of phenolic resins.

Substituted oxazolidines are readily prepared by reacting aminoalcohols with formaldehyde.



(4.13)

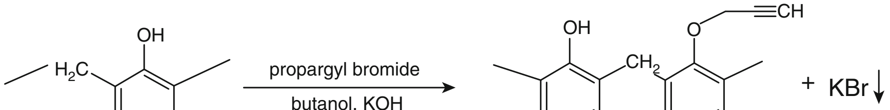
Angus (DOW) Chemical Company commercialized several oxazolidine products as biocides as downstream products emerging from nitroparaffin based chemicals. Wu showed that oxazolidine is able to cure Phenol Resorcinol Formaldehyde resin as a room temperature wood binder [82–84].

Angus (DOW) Chemical Company later [85] introduced a fast cure novolak phenolic system with oxazolidine as curing agent for use in the pultrusion of FST components. The Dow phenolic pultrusion composition is reported to operate with line rates comparable to polyester pultrusion that current phenolics are not able to achieve.

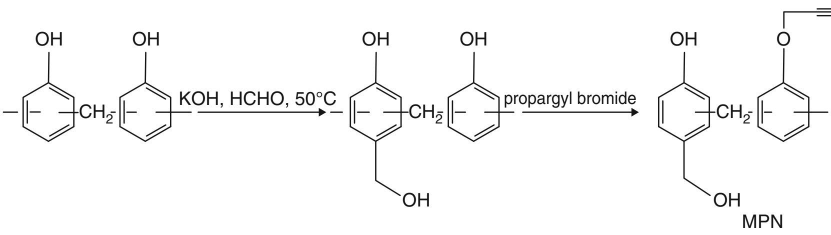
Shea Technology, Reno, NV, has reported high quality fire resistant phenolic composites based on Shea Fireban® phenol resorcinol formaldehyde (PRF) resins [86] that are cured with oxazolidine hardeners. These PRF resins are water based materials that are cured at room temperature with formaldehyde being released from these novel oxazolidine type hardeners. These cured phenolic systems based on oxazolidine are reported to be "formaldehyde free."

4.10 Addition Cure Phenolics

A relatively uncommon method of curing phenolic resin is the use of addition cure conditions. The strategy involving the use of addition chemistry to cure phenolics is an attempt to improve the thermal behavior of cured phenolic and avoid volatile emissions of water (resole) or ammonia (novolak – hexa conditions) during cure. Furthermore these addition cured phenolic materials are relatively catalyst free. A more distant consideration related to the use of these addition cure phenolics was to develop a potential hydrophobic substitute for epoxies in many high performance application areas such as advanced composites, electronics, adhesives, and coatings. A majority of thermoset resins particularly epoxies and BMI, absorb up to 5% moisture and result in low hot/wet mechanical properties. It was speculated that allyl or propargyl ether type phenolic upon cure could minimize these problems. A voluminous review with 239 references on advances in addition-cure phenolic resins was published recently [87]. Addition type functional groups such as allyl or ethynyl groups are appended to the phenolic hydroxyl with either a novolak resin (4.14) or a resole (4.15):



(4.14)



(4.15)

Either of these unsaturated phenolic ethers can be thermally transformed into cured cross linked systems. Allyl derivatives of phenolics have been used for the manufacture of glass FRP and moldings, castings, or impregnation compositions possessing high heat resistance, mechanical strength, and chemical resistance. However achieving complete allyl cure is difficult, requiring prolonged heating, nearly for 6 h at 250°C. Yet allyl type phenols, e.g., bisallyl Bisphenol A, undergo facile Alder-ene reaction with BMI. In a series of publications, Zhao and co-workers [88] have prepared propargyl ether containing novolaks and resoles known as PN (novolak modified with propargyl groups) and MPN (resole modifed with propargyl groups). Both materials possesses low viscosity at elevated

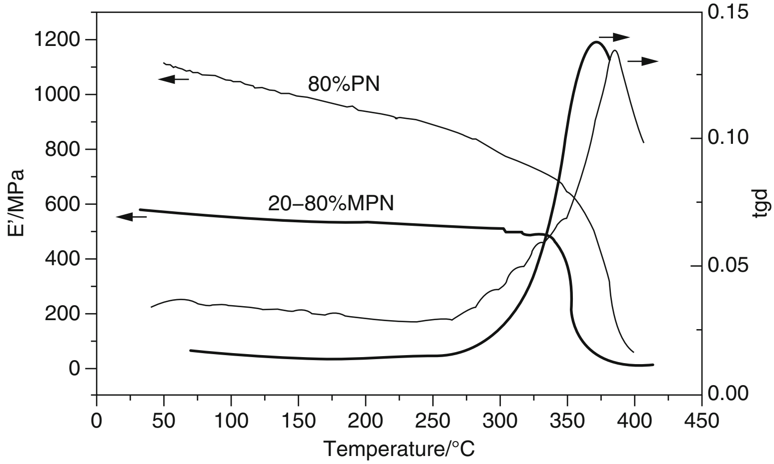


Fig. 4.19 DMA profiles of cured 20%–80% MPN together with cured 80% PN (heating rate 3°C/min, frequency 1 Hz)

temperatures and relatively stable viscosities with a wide processing window for long term shelf life for utilization in compression molding and RTM applications.

The PN cured material exhibited a much higher storage modulus in comparison to the 20%–80% MPN as well as a higher peak temperature of about 375°C (Fig. 4.19).

A similar trend was observed for the cloth laminates as was observed in the neat resins. Silica/80%PN exhibited much higher storage modulus as compared to similar silica cloth with 20%–80% MPN. Glass transition temperature was about 380°C–390°C for MPN laminate composite. It was higher than that of PN composite or 340°C–350°C and considerably higher than silica/novolak control with a T_g of 210°C–230°C (Fig. 4.20).

In Table 4.16 MPN matrix composite showed much better mechanical properties than conventional novolak matrix composite and is indicative of a material that possesses high thermal stability for ultra high performance organic matrix composites.

4.11 Trends

The quest for a more reactive phenolic resin continues to be a key objective for phenolic resin manufacturers. In view of the escalating cost of energy as well as the availability of more reactive competitive formaldehyde containing resins such as urea formaldehyde and melamine formaldehyde resins, studies related to the addition of formaldehyde to phenol solely to prepare highly methylolated phenols (highly reactive phenolic species) via CSTR conditions may be a viable way of improving the reactivity of phenolic resins. These highly methylolated phenols may

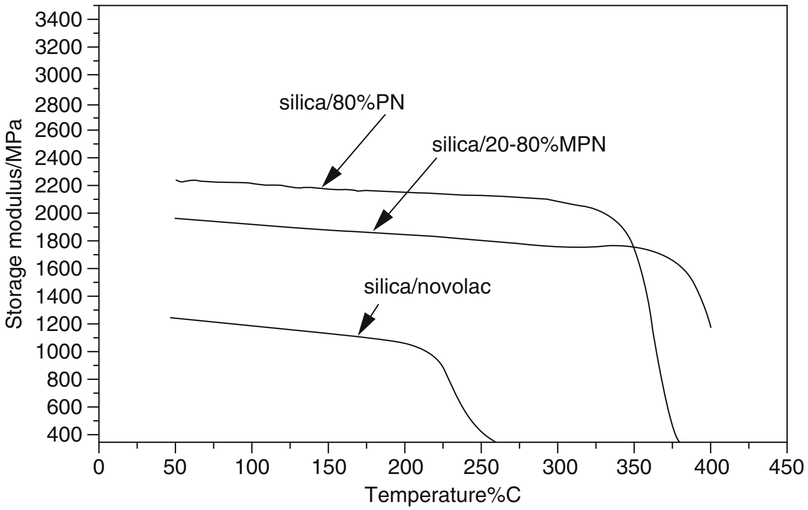


Fig. 4.20 DMA profiles of silica cloth laminates (scanning rate 3°C/min, frequency 1 Hz)

Table 4.16 Mechanical properties of MPN and PN fiber reinforced laminates[a]

Systems	ILSS (MPa) at R.T.	ILSS (MPa) at 380°C	Flexural Strength (MPa) at R.T.	Flexural Modulus (GPa) at R.T.
Silica/20–80% MPN[b]	21.4	9.91	369	24.2
Carbon/20–80%MPN[b]	16.6	9.51	200	21.8
Carbon/80%PN[b]	26.3	7.83	265	22.5
Carbon/Novolak	25	[c]	141	10.5

[a] All laminates with resin content of 36–39%; ILSS sample size is 15 × 5 × 2; flexural sample size is 55 × 15 × 2

[b] Silica/20–80% MPN is Silica-cloth reinforced MPN laminate and carbon/20–80%MPN is carbon-cloth reinforced MPN laminate

[c] Novolak-matrix laminate cannot be tested at 380° due to thermal decomposition

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be suitable as Mineral Wool binders (Chap. 10) or combined with resole, as a bimodal composition for Wood adhesives (Chap. 8).

Bisphenol F continues to be a desirable compound for a variety of areas such as a low viscosity epoxy diluent, monomer component in polycarbonate resin, and high performance epoxy resin matrix. A more streamlined process for Bisphenol F may be possible through the use of the proposed newly developed PAPS novolak process.

Although the PAPS novolak process is in its early developmental stages, PAPS novolaks may offer opportunities in the use of novolak with narrow MWD, lower bulk viscosity, better thermal stability, lower free phenol, and yet lower reactivity with hexa as compared to conventional novolak.

Efforts continue unabated in benzoxazine chemistry due to the favorable characteristics of the BZ structure and resulting resin properties. Besides the introduction of other new BZ type compositions, additional co-reactions of BZ with selected resins such as epoxy, isocyanate, BMI, and BPO are expected and will lead to new materials.

Nanotechnology will contribute to the development of new phenolic and related materials (resole, novolak, BZ, and CE) exhibiting multifunctionality in resin performance with relatively low amounts of nanoparticles added. It is anticipated that nanomodification of phenolic materials used as matrix resins for fuel cells will increase performance of the fuel cells and provide longevity. Seemingly other niche application areas will benefit using the “chemical toolbox” of nanomodification for phenolic resins.

Renewable raw materials cannot be emphasized sufficiently. These renewable materials have been identified with phenolic resins from the early days of phenolic resin commercialization and will continue as a low cost co-reactive component for a diversity of application areas.

Long fiber and carbon fiber containing molding materials represent some exciting newly introduced phenolic reinforced compositions that exhibit significantly higher impact strength and high mechanical strength at high temperatures for further displacement of metals and ceramics by these newly developed materials.

Yet network novolak cure studies suggest more resin structure design is warranted to achieve a complete cure for novolak and ultimate mechanical properties performance. Whether a fully linear novolak with little or no branching can be achieved commercially and cured with hexa for maximum properties remains to be accomplished.

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Chapter 5
Analyses/Testing

David Valdez and Ellen Nagy

Abstract The characterization of phenolic resins by modern analytical techniques is detailed. Common wet chemical and ISO methods are referenced, yet the chapter's emphasis resides in the numerous advances in instrumental techniques. For instance, the authors make a special effort to illustrate the use of GC×GC, MALLS detector in GPC, and some LC-MS and TOF-MS applications. Larger sections on NMR and IR indicate the power of these tools for analysis and also contain peak position tables. Thermal analysis techniques, including rheometry, are discussed with experimental procedures and applications. Finally, microscopy, both optical, and SEM/X-ray, with sample preparation insights, are discussed. The chapter cites 115 papers using analytical chemistry techniques in the examination of phenolic polymers.

Abbreviations

AA	Atomic absorption
ABES	Automated bonding evaluation system
AFM	Atomic force microscopy
APT	Attached proton test
CI	Chemical ionization
CP-MAS	Cross polarization magic angle spinning
CSCM	Chemical shift correlation maps
DEA	Dielectric analysis
DEPT	Distortionless enhancement by polarization transfer
DMA	Dynamic mechanical analysis

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DNPH	Dinitrophenylhydrazine
DQF COSY	Double quantum filtered correlated spectroscopy
DSC	Differential scanning calorimetry
EI	Electron ionization
FIB	Focused ion beam
G'	Storage modulus
G''	Loss modulus
GC	Gas chromatograph(y)
GC-MS	Gas chromatography mass spectrometry
GPC	Gel permeation chromatography
HILIC	Hydrophobic interaction liquid chromatography
HPLC	High pressure liquid chromatograph(y)
HS-GC	Headspace gas chromatography
HS-GC-MS	Headspace gas chromatography mass spectrometry
INEPT	Insensitive nuclei enhancement by polarization transfer
IR	Infrared
KAS	Kissinger–Akahira–Sunose
LPF	Lignin–phenol–formaldehyde
MALDI-TOF-MS	Matrix assisted laser desorption ionization-time of flight mass spectrometry
MALLS	Multi-angle laser light scattering
MDF	Medium density fiberboard
M_n	Number average molecular weight
M_w	Weight average molecular weight
M_z	Z-average molecular weight
NIR	Near-infrared
NMR	Nuclear magnetic resonance
NPLC	Normal phase liquid chromatography
OSB	Oriented strand board
PES	Plasma emission spectrometer
PUF	Phenol–urea–formaldehyde
RI	Refractive index
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
$T\mathrm{g}$	Glass transition temperature
TGA	Thermogravimetric analysis
TLC	Thin layer chromatography
TMA	Thermal mechanical analysis
TOCSY	Total correlation spectroscopy
TOF-MS	Time of flight mass spectrometry
UV	Ultraviolet
VOC	Volatile organic compound

5.1 Introduction

Significant advances in materials characterization have made the field of analytical chemistry both exciting and revolutionary. Basic tests such as viscosity, appearance, density, and cure temperature continue to be an important staple in the analytical toolbox, but changes that have been made to the analytical landscape have been monumental. Instruments such as electron microscopes, infrared (IR) and near-infrared (NIR) spectrometers, nuclear magnetic resonance (NMR) spectrometers, gas and high pressure liquid chromatographs (GC, HPLC), plasma emission spectrometers (PES), and thermal analysis techniques are just a few of the amazing tools available.

The advent of microprocessors and computers coupled to this basic instrumentation has led to the next quantum leap in analytical chemistry generating faster analyses, greater sensitivities, better resolution/visualization, and greater data reduction. The implementation of fast Fourier transforms into NMR and IR, principal component analysis into NIR, various spectral prediction software, statistical control charting, chromatographic simulations, etc., have cemented the computer into the analytical laboratory.

These changes in analytical instrumentation have led to a significant discovery into the three basic stages of thermosets and the transitions between the stages. These stages are defined for reference due to their importance in understanding thermoset chemistry and the analyses applied to these stages and their transitions.

5.1.1 A-Stage, B-Stage, C-Stage, Transitions

Thermosets are generally categorized in terms of three stages: A-stage, B-stage, and C-stage. The initial monomer mixture is generally not considered a stage. This is due to the transient nature of the state and the varying order of raw material additions. Nevertheless, initial analyses of charged ingredients are often performed by weight and refractive index (RI), while its transition to the A-stage is often process monitored via viscosity and by in-situ probes such as NIR. This will be covered in greater detail later in the chapter.

Upon mixing of the reaction monomers, principally phenol (cresol, resorcinol, etc.) and formaldehyde, in the presence of catalyst and heat, a highly exothermic reaction ensues which is quenched by cooling and/or neutralization. The A-stage prepolymer has the lowest molecular weight of the three stages but can range from several hundred to thousands of daltons. Generally, this prepolymer is found solubilized in a solvent, but if presented as a solid, it will free flow upon heating indicating no evidence of cross-linking.

Several areas are of particular interest in A-stage resins. The level and type of solvent, as well as the amounts of free monomers and dimers, are of particular interest, as compliance with volatile organic compound (VOC) is a mandatory issue of existence. The monomers, in addition to the higher polymeric components of the resin, play an extremely important role in the efficacy of the resin application.

Techniques such as gel permeation chromatography (GPC), NMR, RI, and chromatography play a large role in determining whether distributions of components are within specified parameters.

Upon heating, A-stage resins are converted to B-stage resins where some cross-linking between polymeric strands has occurred, yet there still remains appreciable thermoplastic behavior. The resin softens upon heating and swells upon exposure to certain liquids. The moldable characteristic of the resin at this stage lends itself to post-forming applications. The gel point generally occurs as the A-stage resin is transitioned to a B-stage resin. Its accurate determination is of renewed interest with newer rheometric instruments. B-staged resins are often formed on a substrate such as cellulose, glass, or carbon. Solubilization can be difficult but is often done to perform analysis by high-pressure liquid chromatography (HPLC), NMR, IR, or GPC.

Further heating of the B-stage resin to C-stage resin results in high levels of cross-linking, rendering an insoluble and infusible state. Completion of the reaction to C-stage results in a solid three-dimensional networked resin. Techniques that are generally used to characterize the resin are IR spectroscopy, atomic absorption (AA) or PES, solid state NMR, optical microscopy, and scanning electron microscopy (SEM). In this stage, there is particular interest in the application of the material in composite form or as a binder.

Each of the three stages can be regarded as a paused set point awaiting shipping, application, forming, etc. It is at these points that most characterizations take place determining the constitution of the resin. Nevertheless, the phenolic resin is dynamic in nature, and studying the transitions between stages is extremely important in understanding the basic processes the resin will undergo. Typically, in the analytical laboratory, these transitions require carefully administered heat cycles while monitoring a response over time.

Changes that occur may be measured through chemical and mechanical means as materials are transitioned from A-stage to C-stage. Typically, thermodynamic experiments measure exotherms, endotherms, and dimensional and mechanical dynamics. Transitions can also be monitored through RI changes, mid- and near-IR, and viscometric changes.

As we begin exploring the analytical techniques applied to phenolic resins, it is not our intention to necessarily bring you up to date on the latest developments in each area, as this would undoubtedly be old news to many in the scientific community. Instead, the goal is to present salient observations in each technique to help the reader benefit in areas of unfamiliarity, enabling chemists to constructively evaluate these techniques and their application to their respective professional areas.

5.2 Raw Materials

Phenol, formaldehyde, and catalyst represent the simplest ingredients of phenolic resins. The importance of cresols, *t*-butyl phenols, bisphenol-A, resorcinol, and alkylated phenols should not be diminished since they represent classes of phenolics that impart different characteristics such as plasticity, chemical resistance, film adhesion, and even taste preference in food containers! Additionally, the ratio of these monomers and the mode of polymerization yield unique properties specific to their application.

5.2.1 Wet Chemical Methods (RI, pH, Titration)

Testing of incoming raw materials is often limited in industry due to performance-based qualification procedures and the over-reliance upon certificate of analyses. By performance-based, it is meant that the efficacy of raw materials is based upon successful formulation or reaction. Nevertheless, the need is high for rapid identification techniques to satisfy limited time for analyses prior to the acceptance of raw materials in the production facility. Typically, the tests that are used are RI, viscosity, acid–base titrations, and pH. The future lies in the greater use of instruments such as handheld IR and Raman spectrometers capable of being taken to the incoming raw material with data transmitted to a central computer for raw material verification.

5.2.2 Formaldehyde

Formaldehyde, as a raw material, is generally produced as a 37% or 50% product in aqueous solution. Generally, methanol is added to enhance solution stability and prevent paraformaldehyde formation, resulting in precipitation. The analysis of formaldehyde concentration is performed by tests such as the sulfite method [1]. The use of standardized solutions and autotitrators provide excellent results.

Residual formaldehyde in resins can be measured by numerous methods, including hydroxylamine, modified sulfite, and KCN methodology (ISO 11 402). Samples in complex matrices containing moderate to low levels of formaldehyde are often analyzed utilizing EPA method 8315A [2]. The analysis is more complicated, as it utilizes the formation of dinitrophenylhydrazine (DNPH) derivatives and subsequent analysis by HPLC. Interferences are minimized by this method, as excellent chromatographic separation is made from other derivatives and due to the high ultraviolet (UV) wavelength imparted by the derivative. Collection of formaldehyde from impinger solutions can also be analyzed utilizing the DNPH method.

NMR analysis of formaldehyde illustrates the complex nature of formaldehyde in solution. Formaldehyde, as a gas, is the simplest of all aldehydes, but in aqueous solution, it forms polyoxymethylene adducts (see 5.1). Valdez and Mounts [3] assigned peaks in the ^{13}C NMR spectrum to the formal and hemiformal components of formaldehyde. The assignments are shown in Tables 5.1 and 5.2, and Fig. 5.1 shows the NMR spectral range of 80–100 ppm.

$$\begin{aligned} HCHO + H_2O &\leftrightarrow HOCH_2 - OH \\ &\leftrightarrow HO - CH_2 - (O - CH_2)_N - OH \text{ where } N \geq 1 \end{aligned} \tag{5.1}$$

Table 5.1 ^{13}C NMR peak assignments of formal

Letter ID[a]	PPM	Molecular formula
F1A	83.2	HO–$\underline{C}H_2$–OH
F2A	86.7	HO–$\underline{C}H_2$–O– $\underline{C}H_2$–OH
F3A	87.2	HO–$\underline{C}H_2$–O–CH_2–O–$\underline{C}H_2$–OH
F3B	89.9	HO–CH_2–O–$\underline{C}H_2$–O–CH_2–OH
F4A	87.4	HO–$\underline{C}H_2$–O–CH_2–O–CH_2–O–$\underline{C}H_2$–OH
F4B	90.4	HO–CH_2–O–$\underline{C}H_2$–O–$\underline{C}H_2$–O–CH_2–OH
F5A	87.4	HO–$\underline{C}H_2$–O–CH_2–O–CH_2–O–CH_2–O–$\underline{C}H_2$–OH
F5B	90.5	HO–CH_2–O–$\underline{C}H_2$–O–CH_2–O–$\underline{C}H_2$–O–CH_2–OH
F5C	91.0	HO–CH_2–O–CH_2–O–$\underline{C}H_2$–O–CH_2–O–CH_2–OH
F6A	87.4	HO–$\underline{C}H_2$–O–CH_2–O–CH_2–O–CH_2–O–CH_2–O–$\underline{C}H_2$–OH
F6B	90.8	HO–CH_2–O–$\underline{C}H_2$–O–CH_2–O–CH_2–O–$\underline{C}H_2$–O–CH_2–OH
F6C	91.2	HO–CH_2–O–CH_2–O–$\underline{C}H_2$–O–$\underline{C}H_2$–O–CH_2–O–CH_2–OH

[a] "Letter ID" refers to Formal or Hemiformal, total number of carbons, and the location in the sequence

Table 5.2 ^{13}C NMR peak assignments of methanol hemiformal

Letter ID	PPM	Molecular formula
H-0	50.1	$\underline{C}H_3OH$
H-1	55.5	$\underline{C}H_3$–O–CH_2–OH
H-2	56.2	$\underline{C}H_3$–O–CH_2–O–CH_2–OH
H-3	56.39	$\underline{C}H_3$–O–CH_2–O–CH_2–O–CH_2–OH
H-4	56.44	$\underline{C}H_3$–O–CH_2–O–CH_2–O–CH_2– O–CH_2-OH
H1A	90.7	CH_3–O–$\underline{C}H_2$–OH
H2A	94.2	CH_3–O–$\underline{C}H_2$–O–CH_2–OH
H2B	87.1	CH_3–O–CH_2–O–$\underline{C}H_2$–OH
H3A	94.7	CH_3–O–$\underline{C}H_2$–O–CH_2–O–CH_2–OH
H3B	90.2	CH_3–O–CH_2–O–$\underline{C}H_2$–O–CH_2–OH
H3C	87.36	CH_3–O–CH_2–O–CH_2–O–$\underline{C}H_2$–OH
H4A	94.9	CH_3–O–$\underline{C}H_2$–O–CH_2–O–CH_2–O–CH_2–OH
H4B	[a]	CH_3–O–CH_2–O–$\underline{C}H_2$–O–CH_2–O–CH_2–OH
H4C	[a]	CH_3–O–CH_2–O–CH_2–O–$\underline{C}H_2$–O–CH_2–OH
H4D	[a]	CH_3–O–CH_2–O–CH_2–O–CH_2–O–$\underline{C}H_2$–OH

[a] Indistinguishable from formal counterparts found in Table 5.1

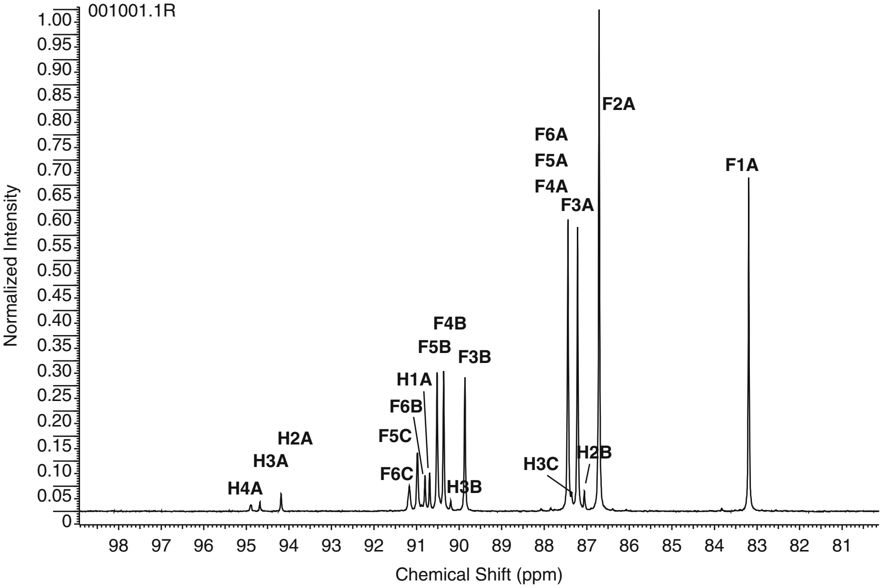


Fig. 5.1 C-13 NMR spectrum of formaldehyde (80–99 ppm)

5.3 Standard Physical and Quality Control Methods – ISO Methods

Physical testing of phenolic materials remains an important aspect of property determination, particularly at manufacturing sites and at the bench while monitoring the progress of reaction. ISO 10082 covers most methods and their significance. Tests that are generally used include pH, RI, specific gravity, melting point, viscosity, gel time, inclined plate flow, water miscibility, and particle size.

Additionally, ISO methods cover Keldahl methods, GPC, gas chromatography (GC), and thin layer chromatography (TLC). The methods given in Table 5.3 provide a great basis for the initial investigation and analysis of phenolic resins.

5.4 Instrumental Analysis

5.4.1 GPC

GPC or size exclusion chromatography (SEC) remains one of the standard characterization tools for phenolic resins. The basic equipment is comprised of a solvent pump, a column(s) containing packing material with pores in the general size of the

Table 5.3 ISO methods

ISO standard	Test method description
Thermal methods	
11409	DSC – endothermic, exothermic heats of reaction
9396	Gel time of resoles using automatic apparatus
8987	Gel time determination on a hot plate
9771	Peak temperature measurement upon acid addition
Chromatographic methods	
8984	Free phenol determination by GC
11401	Method A – GPC of resoles and novolaks
	Method B – HPLC of novolaks on a polar column
	Method C – HPLC of resoles on a nonpolar column
Chemical methods	
8619	Inclined plate flow of prepared tablet
8618	Nonvolatile determination by oven drying
8988	Hexamethylenetetramine by Kjeldahl and perchloric acid
11402	Free formaldehyde determination by hydroxylamine, sulfite, and KCN methods
Physical methods	
8975	Determination of pH
2811	Density of liquid resin by pycnometer
3675	Density of liquid resin by hydrometer
60	Bulk density – weighing a fixed volume of powdered resin
8620	Sieve analysis of powder by air jet screen
13320	Particle size distribution of powder by laser
3146	Melting point in a capillary
9944	Electrical conductivity of solubilized resin
8989	Miscibility of resin with water
2555	Viscosity utilizing Brookfield viscometer
3219	Viscosity utilizing defined velocity gradient
12058	Viscosity by falling ball viscometer

molecules, and a detection system. Polymer samples are solvated in an appropriate solvent, generally tetrahydrofuran, dimethylformamide, or dimethylsulfoxide, and injected into a chromatographic system containing a column with pores larger but of the same general magnitude as the gyrated molecular radii of the molecules in solution. Elution of the resin components is based on entropic terms as the molecules differentially diffuse into the pores of column packing material, and thus, the elution order is from larger to smaller hydrodynamic volumes of the gyrated molecules. Figure 5.2 illustrates typical GPC curves of a phenolic resin with the larger components eluting first. Samples were taken during the progress of the reaction and labeled A–D [4].

GPC values are expressed in terms of molecular weights, specifically M_n, M_w, M_z, and polydispersity (d), where M_n is number average, M_w is weight average, and M_z is the z-average. These terms are calculated based on segmented integrated areas and their relation to the elution time of calibrated standards. These terms are further defined in (5.2–5.5).

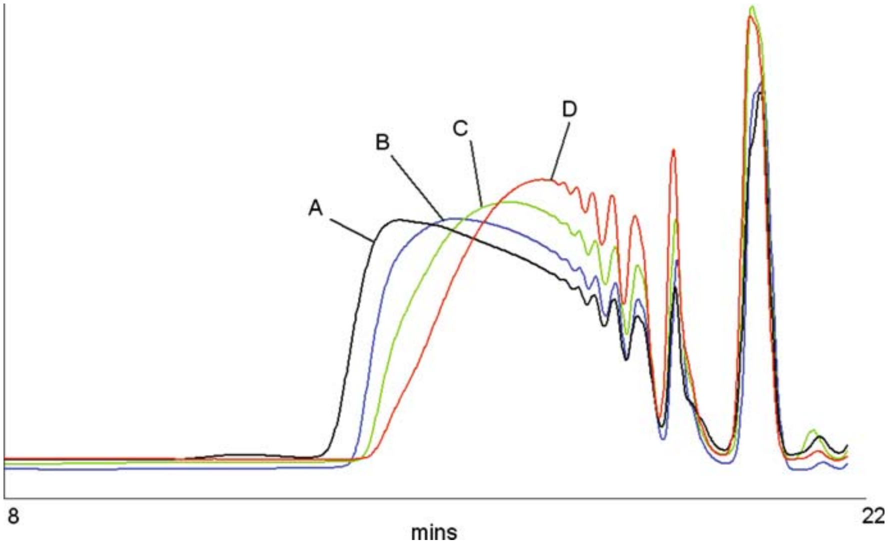


Fig. 5.2 GPC overlays of reaction progress of a phenolic resin, with D being the least advanced and A being the most advanced in molecular weight. Courtesy: Varian Polymer Labs

$$M_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{\sum W_i}{\sum (W_i/M_i)} \tag{5.2}$$

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum W_i M_i}{\sum W_i} \tag{5.3}$$

$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} = \frac{\sum W_i M_i^2}{\sum W_i M_i} \tag{5.4}$$

$$d = M_w/M_n \tag{5.5}$$

N_i and W_i are the number and weight of molecules of the molecular weight M_i. In terms of GPC curves, the area or height of the segment at the *i*th retention volume can be substituted for W and calculations can be readily made.

Often, due to the lack of monodisperse standards of the resins, polystyrene or polyoxymethylene calibration standards are used. These standards have different solvated molecular radii than the resin molecules of identical molecular weight. Nevertheless, these *relative* or *apparent molecular weights,* although skewed from the true molecular weights, provide an excellent basis for comparison of resin families.

To compensate for the lack of true standards, several companies and research groups have utilized viscometry, triple detection, and laser light scattering as a detection tool for the determination of exact molecular weights. These tools incorporate mathematical equations, such as the Mark Houwink, Flory-Fox, and Pittsyn-Eizenner equations, to relate hydrodynamic volumes to molecular weight and branching levels. Mbachu et al. [5] demonstrated the value of a triple detection system in the determination of molecular weights of phenolics.

Dargaville et al. [6] determined number – and weight–average molecular weights of a high ortho novolak resin. Numerous novolak standards having 2–12 methylene-bridged phenolic units were used. In comparison to proton NMR, the GPC data showed similar values for the number average molecular weights. The GPC analysis using an RI detector underestimated the weight average molecular weights when using polystyrene standards.

Similarly, in a GPC study of a phenol–cresol resin, the determined molecular weights obtained from an RI detector and multi-angle laser light scattering (MALLS) were compared by Petrella [7]. The data in Table 5.4 outline a resin synthesis by taking aliquots at predetermined intervals. Comparing GPC-RI vs. GPC-MALLS results, the initial molecular weights appear similar (within ~10% error), and both GPC and MALLS results show the expected increase in molecular weight as the reaction proceeds. MALLS shows that GPC-RI overestimates Mn and underestimates Mw and Mz for this resin. As the resin advances, the molecular weight increases with Mz being significantly higher in the MALLS data. These results suggest that conformational or configurational phenomena of the resin in solution lead to underestimation of the molecular weight by GPC-RI. Increases in molecular weight generally correspond to the increase of nonpolar methylene bridges at the expense of polar methylols or methylene ethers. Thus, differences in solute–solvent interactions result in conformational changes in solution as the molecular weight builds.

Reuther et al. [8] coupled GPC with matrix-assisted laser desorption ionization – time of flight mass spectrometry (MALDI-TOF-MS) in order to characterize novolak resins. By segmenting the eluent into discrete time fractions, droplets taken at these stages could be introduced in the TOF-MS and exact masses obtained. A calibration curve was then constructed utilizing the determined molecular weight vs. time.

5.4.2 GC and GC-Mass Spectrometry

For resins containing volatile and semivolatile components, GC and GC-mass spectrometry (GC-MS) are regularly used for the determination of monomers such as phenol, cresol, butanol, and methanol. An analysis of the monomers typically

Table 5.4 Molecular weight of phenol/cresol resin by refractive index and multi-angle laser light scattering

Sample	Molecular weight by RI			Molecular weight by MALLS		
Interval	M_n	M_w	M_z	M_n	M_w	M_z
1	454	815	1,423	387	865	1,669
2	511	1,004	1,887	424	1,120	2,370
3	578	1,255	2,531	518	1,542	3,453
4	610	1,405	2,929	515	1,753	4,166
5	654	1,635	3,599	575	2,218	5,496
6	681	1,734	3,816	664	2,688	5,802

utilizes internal standard methodology on an instrument with a capillary column and a flame ionization detector. More comprehensive analyses are obtained by the utilization of either an ion trap or quadrupole mass spectrometer as the detector. The ability to speciate unknown components by interpreting electron ionization or chemical ionization mass spectra has been an important advancement. Since standards are often unavailable for the compounds identified, surrogate standards have helped to provide meaningful results when actual standards are not present.

The use of headspace-GC (HS-GC) or HS-GC-MS has also been helpful in the identification of odors in phenolic insulation resins. Bir [9] utilized HS-GC-MS to determine the levels of trimethylamine that resulted due to an interaction of the resin, the glass, and water.

Though other techniques may have surpassed the overall utility of GC, there yet may be a renaissance in this area, particularly in the use of hyphenated techniques. In the examination of phenolic can coatings, Biedermann and Grob [10, 11] used GC-MS, GC×GC, normal phase liquid chromatography–GC (NPLC-GC), and SEC to speciate numerous compounds in resins based on phenolic and cresol/phenol mixtures. The resoles were silylated with BSTFA (N,O-bis-(trimethylsilyl)-trifluoroacetamide), to enhance volatility. GC×GC was found to provide the best visualization of sample composition while NPLC-GC provided the most complete analysis.

Figure 5.3 shows a GCxGC chromatogram where the first dimension shows the typical GC peaks. The second dimension enables further separation of complex mixtures that are normally nonresolved. In GCxGC, the eluent of the first chromatogram is modulated as the eluent is refocused (trapped) at discrete intervals and

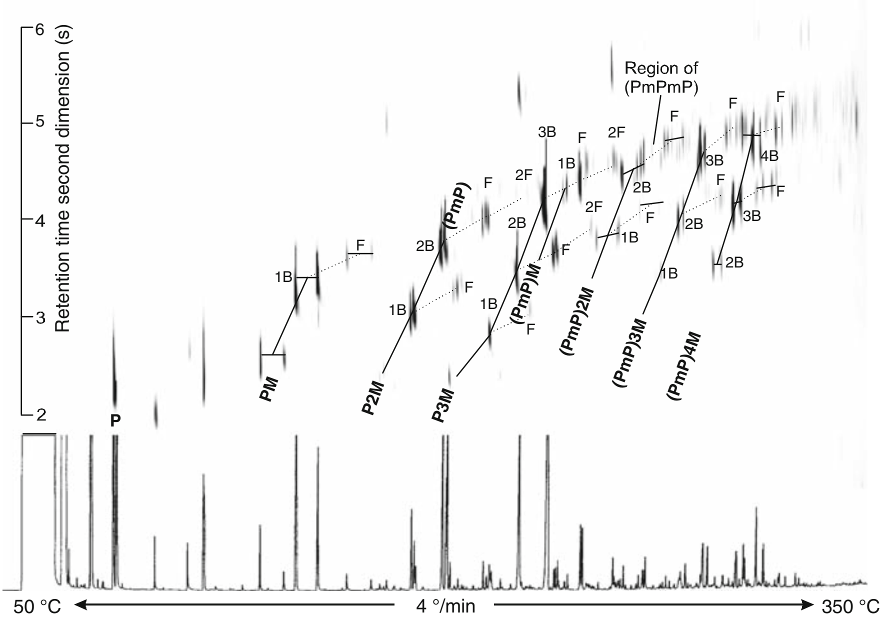


Fig. 5.3 GC×GC chromatograph of phenolic-based resole for can coating

diverted into a second column (dimension) of very different polarity. The second column is generally much shorter than the first column as the second dimension chromatogram retention is equal to the modulation time (seconds). Although the total chromatographic time can be very long, the chromatograms yield a major increase in peak capacity and thus total resolution. It has been shown in biodiesel samples that as many as 30,000 peaks can be resolved.

Recent improvements in Time of Flight mass spectrometers have enabled these instruments to be used as detectors for GC and, especially, GCxGC. Early instrumentation was not sufficiently stable to provide quantitative results. TOF detectors can combine quantitation capabilities with a 500 Hz sampling rate. The additional molecular weight data can be used to deconvolve overlapping peaks. An added benefit is that sample analysis times can be substantially reduced, as the importance of peak resolution is much less due to the efficient mass spectral deconvolution.

5.4.3 Pyrolysis GC

Pyrolysis GC has found a unique application into the fate of foundry sand resins. Pyrolysis GC differs from conventional GC by the use of an injector capable of high temperature heating (750°C–900°C). The injectors vary as to the rate of heating and the length of time at the temperature set point. In the casting process for foundry products, the process of applying molten metal into the cores and cavities of the mold subjects resin binders to rapid heat ramps. The organic binders undergo thermal decomposition and become a source of environmental pollution. Pyrolysis GC coupled with MS provides an excellent tool to investigate the decomposition of the sand core binders.

Dungan and Reeves [12] determined the major thermal decomposition products from novolak, phenolic urethane, and furan resins by pyrolysis GC-MS. The novolak analysis produced over 50 gas chromatographic peaks with 28 of them being identified. The peaks of greatest concentration were found in decreasing order to be *o*-cresol, 3,5-dimethylphenol, 3-methylphenol, phenol, 2,3 dimethylphenol, and 2,4,6 trimethylphenol. Wang et al. [13] utilized analytical pyrolysis techniques as a preliminary screening tool for comparative emissions of alternative core binder systems. Using a Curie-point pyrolyzer at 920°C with a heating rate of 3,000°C/second, they identified and quantified 21 different compounds ranging from phenol to naphthalene isomers. In addition to pyrolysis GC, they monitored greenhouse gases (CO and CO_2) utilizing TGA (thermogravimetric analysis) pyrolysis coupled to a mass spectrometer.

5.4.4 Liquid Chromatography and Liquid Chromatography-MS

HPLC is a separation technique that continues to evolve in the workplace. Similar to GC, a diluted sample is injected onto a column and separation occurs as the analytes differentially migrate down the column. Unlike GC, liquid chromatography utilizes solvents such as methanol, acetonitrile, and water as the mobile phase, which are pumped through the injector and column at high pressures. Reverse phase stationary phases (C-18 reacted onto a silica base) are the most common, but normal phase columns are now being used in techniques such as HILIC (hydrophobic interaction liquid chromatography).

UV detection is the most common detector system but other detectors such as evaporative light scattering and the Corona® CAD® (charged aerosol detector) [ESA Scientific, Inc.] are gaining a wider audience. These newer detectors are often promoted as having higher sensitivity, greater dynamic ranges, and greater universal response to analytes. Generally, sensitivity is not an issue with phenolics, but a universal response factor would benefit an analysis of components that do not have standards readily available.

Most commonly, only phenol, the hydroxymethylphenols, and a few selected dimers are run quantitatively due to lack of available standards. Astarloa-Aierbe et al. [14] studied the kinetics of the phenolic resole condensation focusing their study on the hydroxymethylphenol components. In addition to the hydroxymethylphenols, there are extremely large numbers of compounds that are generated during phenolic synthesis. For example, the early work of Mechin et al. [15, 16] showed an excellent resolution in the separation and identification of over 40 compounds. Li et al. [17] characterized phenolic resins by first fractionating the resin using GPC. He also compared acetonitrile and methanol mobile phases using tetrahydrofuran as a mobile phase modifier. Detection systems used in these analyses include UV-diode array, light scattering, ion trap mass spectrometry, and RI.

The newer technologies applied to HPLC revolve around two specific areas; increasing the number of theoretical plates and fundamental changes to column technology. The classic VanDeemter equation relating the number of theoretical plates to flow velocities shows a strong inverse dependence upon particle size. Peak resolution can be dramatically improved by using smaller particle size ($\leq 2\ \mu$) columns. This mandates changes in injectors, tubing inside diameters, flow cell volumes, etc. Furthermore, the higher back pressures also require new types of pumps and equipment capable of withstanding much higher pressures (10–15,000 psi). Several manufacturers now offer ultra-high pressure systems. In terms of changing the selectivity of analytes, diverse column packings have dramatically changed chromatographic capabilities. Column types, such as polar embedded reverse-phase, monolithic, solid core particle columns, and HILIC, now give chromatographers a much larger choice. Our full expectation is to see some dramatic improvements in this area, particularly when direct coupling to MS and NMR become commonplace in the typical R&D laboratory.

LC-MS is becoming more common in the industrial R&D laboratory. The improvements gained in separation technology are further enhanced by the ability to obtain interpretable mass spectra. A choice of mass spectrometric detectors, ion trap, or dual/triple quadrupole, is available based on whether MS^n or detector sensitivity is the primary criterion. Lindquist et al. [18] separated 44 compounds of a phenolic resin by LC-MS and identified the components in terms of phenolic resin molecular weights and structures. The terms CH_2O can be either a

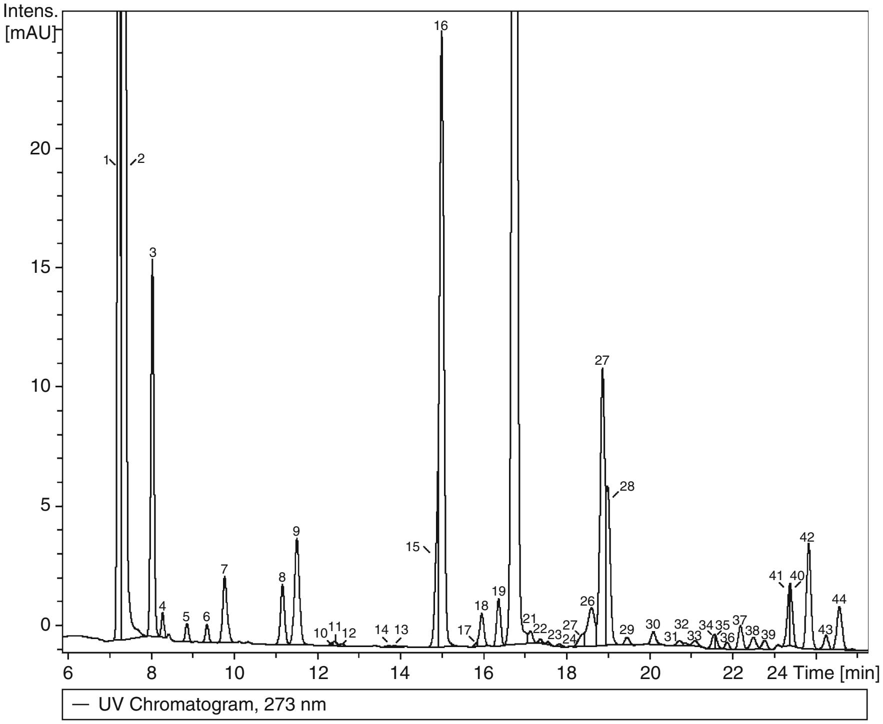


Fig. 5.4 HPLC of standard phenolic resin

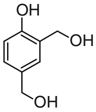
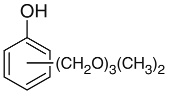
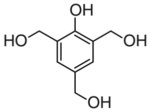
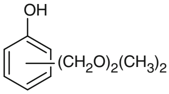
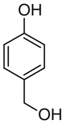
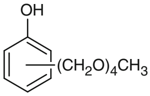
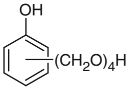
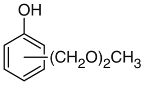
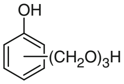
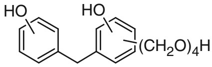
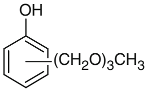
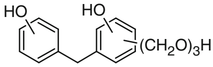
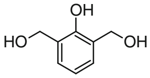
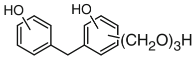
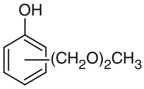
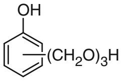
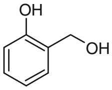
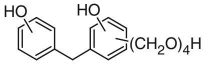
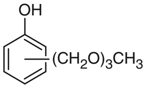
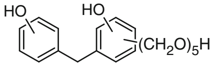
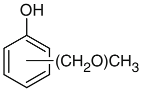
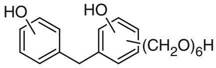
hydroxymethyl group, methylene ether, or a hemiformal, whereas a CH_3 is due to a terminal methyl ether. Further identification can be made by further MS^n analysis. The LC chromatogram from their work is shown in Fig. 5.4 and the peak identification is found in Table 5.5.

5.4.5 *IR Spectroscopy*

IR spectroscopy is a well-established analytical tool for the characterization of phenolic resins. A typical IR spectrum of an A-staged phenolic resole is shown in Fig. 5.5. Numerous authors have summarized the band assignments for the phenolic resin IR bands [19–23]. Table 5.6 lists the typical band assignments for a resole. Depending on the pH and/or additives present, these bands can shift slightly up or down field. Phenolic novolaks are easily distinguishable from the phenolic resoles by the absence of the hydroxymethyl and ether bands.

While NMR may be the preferred method of analysis for the A-staged liquid resin, IR is the simplest and fastest technique for doing an analysis of the cured resin.

Table 5.5 Peak Identification of a Phenolic Insulation Resin

Peak no	[M–H]–	Structure	Peak no	[M–H]–	Structure
1	153		12	211	
2	183		13	181	
3	123		14	227	
4	213		15	167	
5	183		16	319	
6	197		17	289	
7	153		18	289	
8	167		19	183	
9	123		20	319	
10	197		21	349	
11	137		22	379	

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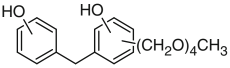
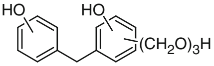
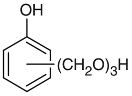
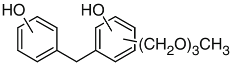
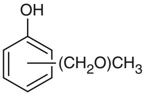
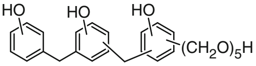
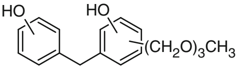
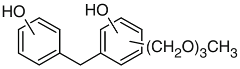
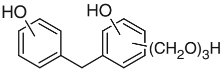
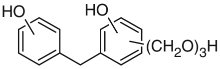
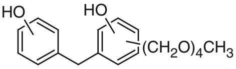
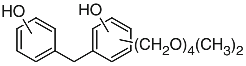
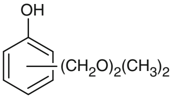
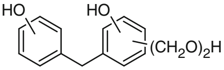
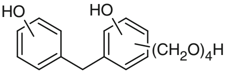
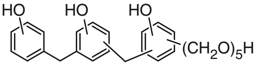
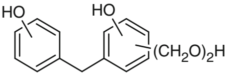
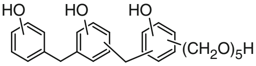
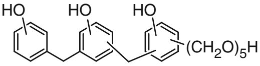
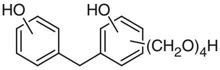
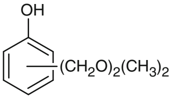
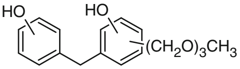
23	333		34	289	
24	183		35	303	
25	137		36	455	
26	303		37	303	
27	289		38	289	
28	333		39	347	
29	181		40	259	
30	319		41	455	
31	259		42	455	
32	455		43	319	
33	181		44	303	

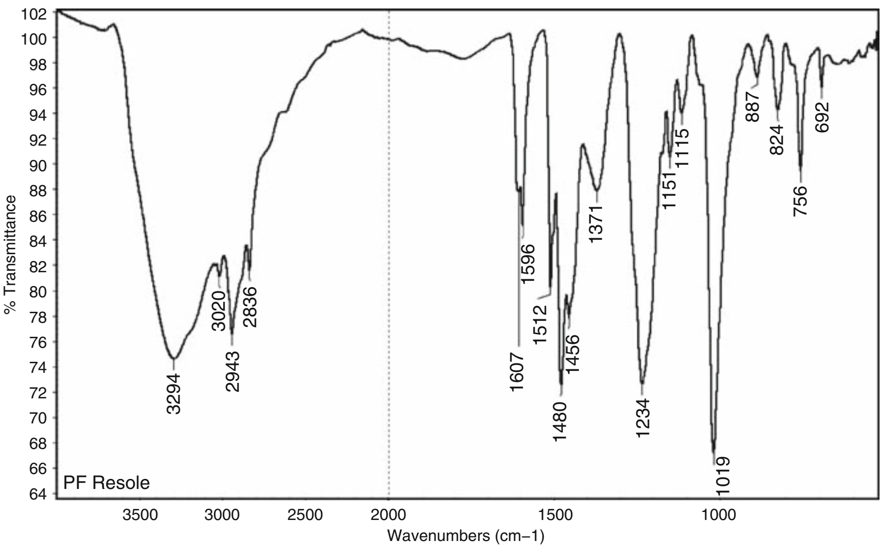


Fig. 5.5 IR spectrum of phenolic resole

Table 5.6 IR Band Assignments for a Phenolic Resole

IR band (cm^{-1})	Chemical functional group
3,600–3,100	OH stretch from phenol and hydroxymethyl
3,010	Aromatic C–H stretch
2,980–2,820	Aliphatic C–H stretch (in plane and out of plane)
1,610	C=C stretch for phenolic ring
1,500	C=C stretch for phenolic ring
1,480	CH2 bending
1,370	Phenolic OH in plane deformation
1,235	Phenolic C–O stretch
1,160	Aromatic C–H in plane deformation
1,120–1,080	Aromatic C–H in plane deformation and ether C-O-C
1,020	Hydroxymethyl C–O stretch
880	*o,p* substituted phenol and *o,o*′, p substituted phenol
820	Phenol with 2 adjacent free H atoms (*p*-substituted)
790	Phenol with 3 adjacent free H atoms (*o,o*′-substituted)
760	Phenol with 4 adjacent free H atoms (*o*-substituted)
690	Phenol with 5 adjacent free H atoms

With the availability of IR microscopes and attenuated total reflectance (ATR) sampling accessories, spectra can be obtained of the resin isolated from the substrate, such as from a plywood glue line, or of the resin in the presence of the substrate, such as resin saturated fibers. The software on the modern IR spectrometer allows for spectral subtraction of substrates and/or additives, making it easier to interpret the spectra obtained. Even the water from an aqueous solution can be spectrally subtracted to provide a usable spectrum of the phenolic resin.

Much of the IR work done today involves studying the changes in the IR bands with changes in reaction parameters. The aromatic substitution bands can be used to compare the levels of ortho- and para-substitution in both resoles and novolaks. Huang et al. [22] used the 812 and 753 cm^{-1} 1,2,3- and 1,2,4-substitution bands to correlate the degree of ortho- versus para-substitution in novolak resins. Using this method, they were able to study the effect of different catalysts on the production of a high ortho-substituted novolak. Maciejewski [24] used the IR ring substitution bands along with melamine bands to study the reactions to form highly branched melamine-phenolic novolaks. Holopainen [21] used multiple linear regressions to predict the mole ratio and quantitative branching in a series of phenolic resins using NMR as the primary method of analysis. Bouajila [20] used solid state NMR correlated to IR to study cured phenolic resin, heated just below degradation temperatures. He studied the changes in cross-linking with the changes in polymerization heating cycles. Others have studied the changes in the IR bands when phenolic resins, are modified with other materials, such as cardanol or alkyl groups [25, 26].

As phenolic resins enter the world of nanotechnology, IR has been applied to their characterization. Chiang [27] used IR and ^{29}Si NMR to study the reaction between a silane and a phenolic novolak to form a hybrid organic–inorganic nano-composite. As the reactions are occurring on the phenolic hydroxide, the changes in the hydroxyl band at 3,300 cm^{-1} were used to follow the reaction. In another paper, Zhang [28] was able to synthesize hollow phenolic fibers, using IR to study the cross-linking of the phenolic resin through changes in the methylene bridge at 1,475 cm^{-1}.

One of the more interesting uses of IR is in the area of reaction monitoring. Samples can either be removed from the reactor at set intervals or a reaction probe can be placed in the reactor to collect spectra throughout the reaction. The kinetics of the methylolation step can be followed by monitoring the hydroxymethyl band at 1,020 cm^{-1}, while the condensation reaction can be followed through monitoring of the methylene bridge at 1,480 cm^{-1}. Work done by Nagy et al. [29] focused on the effect of catalyst and temperature on the kinetics of a standard plywood resole sample. The experiment was done with a diamond ATR immersion probe placed in the reaction vessel. Figure 5.6 shows the spectral data collected from one of the experiments. The increased reaction rate with a higher catalyst was obtained through monitoring the C–H bonding band at 1,480 cm^{-1}. Poljansek et al. [23] used an inline probe to follow the synthesis of phenol–urea–formaldehyde (PUF). They looked at the effect of mole ratio, temperature, and pH on the structure of the reaction product. They were able to note dramatic differences in the condensation between phenolic hydroxymethyl and urea, and between the acidic and alkaline reaction conditions.

The newest addition to IR is the introduction of array detectors. These detectors allow for the spatial collection of IR spectra across an x–y plane without manually moving across the sample. The array detectors are used in conjunction with IR microscopy. Labbe [30] has used this technology to obtain spectra across a plywood glue line and in a wood/plastic composite. Although their work was not done specifically with phenolic resins, the technology is applicable to phenolic-based composites.

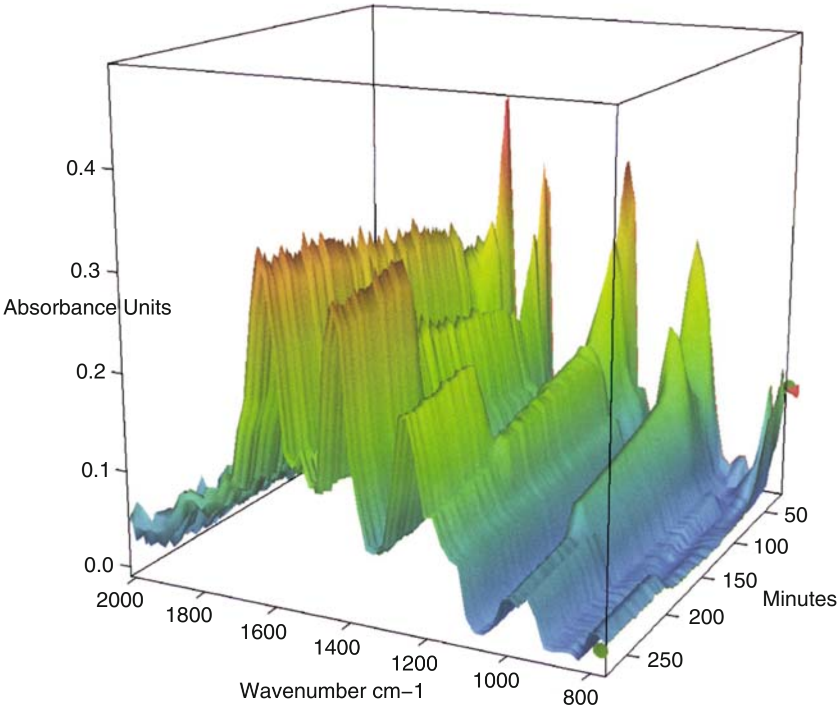


Fig. 5.6 IR spectra from phenol – formaldehyde reaction

5.4.6 *Raman Spectroscopy*

Raman spectroscopy is a complementary technique to IR for obtaining structural information on phenolic resins. Raman spectroscopy has become much more user-friendly over the last decade. Improvements in lasers and detectors have also increased the speed to obtain useful spectra. Water does not produce strong Raman bands, as it does in IR. This makes Raman a useful tool to study aqueous resin solutions.

The biggest area of research currently using Raman spectroscopy is in the study of the chemical changes occurring during the curing and pyrolysis of phenolic resins. Ottenbourgs et al. [31] studied the curing of novolak resins. In IR, as the resin cures, the absorption bands become broad and overlap with each other, resulting in a decrease in usable structural data. As Raman examines the polarization changes that occur during vibrational motion, it does not exhibit the broadening as the polymer cures. With the lack of many reference spectra in the literature, they obtained spectra for numerous reference compounds as part of their experiments. Their paper contains the band assignments for both the model compounds and the experimental samples they analyzed. Through changes in the intensities of these bands, they were able to follow the structural changes occurring during the curing of the novolak resins examined. Correlation of the Raman results with solid state NMR results was also done.

Monni et al. [32] used Raman spectroscopy for on-line reaction monitoring of the synthesis and curing of phenolic resoles. Utilizing a fiber optic probe focused on a quartz window in the reactor, spectral data were collected during both the methylolation and condensation reactions. Utilizing model compounds, the Raman bands for both the starting materials and the reaction intermediates were assigned. Raman was demonstrated to be a good method for monitoring phenolic reactions.

Phenolic resins are used as precursors in carbon–carbon composites due to their high carbon yield. During the high temperature pyrolysis, low molecular weight species and unreacted monomer evolve from the matrix, resulting in shrinkage and voids in the structure. Raman spectroscopy has been used by Ko et al. [33, 34] to study the changes in the microstructure of the phenolic resin during carbonization and graphitization. The Raman bands for the carbon–carbon bonds formed during pyrolysis were examined. They were able to show differences in the bands between ordered and disordered carbon–carbon structures.

5.4.7 NIR Spectroscopy and Other Process Control Instruments

NIR spectroscopy has seen a rapid growth in popularity for both raw material qualification and process monitoring over the last several years. There are many good review books on the theory of NIR for process control [35]. Therefore, only an overview of NIR theory is presented here. In the electromagnetic spectrum, the NIR regions fall in the frequency range of 12,500 cm^{-1}–4,000 cm^{-1}. It occurs between the visible and mid-IR regions. The NIR spectral bands are typically broad, overlapping, and not useful for identification. The NIR bands are the overtones and combination bands of the fundamental vibrations found in the stretching region of the mid-IR. The bands detectable in the NIR are the C–H, N–H, O–H, S–H, C=O, and C=C.

Unlike mid-IR, which is primarily used for identification and quantification in the analytical laboratory, NIR is used primarily for quantification in the production facility. NIR is known as a secondary technique for quantification. The NIR must be calibrated against a primary method and can only be as accurate as the primary method that it is calibrated against. In the mid-IR, calibration curves are developed using Beer's Law plots in which the peak height or area of the IR peak of interest is plotted against the desired parameter for a small set of samples in which the desired parameter is known or measured from a primary technique. Using the equation for the line in the linear Beer's Law plot, the spectra from additional samples can be analyzed to determine the desired parameter. With NIR, there is no single band to correlate to a desired parameter. Chemometric mathematics, utilizing partial least square (PLS) algorithms, are used to correlate the entire NIR spectrum to the desired parameter. The calibration set typically contains over 100 samples.

Although the development of NIR methods is very labor-intensive, once developed, utilizing the techniques to obtain the desired parameter is relatively easy.

Utilizing fiber-optical cables to connect the sampling probes to the spectrometer, the spectrometer can be placed away from the reactors and/or production line. Either transmission probes or surface probes can be used to collect data from the reactors, while specular reflectance or diffuse reflectance, noncontact probes are used with production line monitoring.

The literature contains very few references for NIR process monitoring for phenolic-based resin production. Unlike the pharmaceutical and food industry, the chemical industry tends not to publish their NIR work, keeping it proprietary. Jiang, Huang, and associates at the Harbin Institute of Technology in China have published papers utilizing NIR for process monitoring of glass/phenolic resin prepregs [36] and cloth/phenolic resin prepregs [37]. They were able to successfully develop NIR methods for resin and volatile content in both the glass and cloth prepregs. They used a diffuse reflectance probe placed over the production line between the dry tower and the take-up mechanism. The primary test for calibration utilizes weighing samples before and after heating (160°C for volatiles, 600°C for resin content). Although the method is easy to do, samples must be cut from the production roll and analyzed in a relatively slow process. Obtaining the information during production ensures that problems are identified more quickly and resolved more quickly to produce a more consistent, high-quality product. The Harbin group has also listed the band assignments in the NIR, which can be helpful in choosing the spectral ranges to include in the development of the calibration method. The bands are summarized in Table 5.7.

NIR methods have been developed by Nagy et al. [38] to determine the percentages of wax, resin, and water in a single component phenolic resin/wax adhesive system. A surface contact probe was used to collect the data. The calibration set contained samples with known weights of resin binder and wax dispersion. The percent volatiles were used to calculate the percent water in both the resin binder and wax dispersion.

Mbachu et al. [39] developed NIR methods for percent resin, moisture, and wax on wood substrates during board production. Their methods were developed for particleboard, medium density fiberboard (MDF), oriented strand board (OSB), and plywood. They patented many of their methods for monitoring the resin-loading

Table 5.7 NIR Band Assignments for Phenolic Resin

NIR band (cm^{-1})	Chemical functional group
8,731	Benzene C–H stretch second overtone
7,339	Methyl and methylene combination of C–H stretch and C–H deformation
6,908	Water OH stretch first overtone
6,356	Alcohol OH stretch first overtone
5,922	Benzene C–H stretch first overtone
5,658	Methyl and methylene C–H stretch first overtone
5,257	Water combination OH stretch and deformation
4,796	OH stretch and deformation (alcohol, phenol, and methylol)
4,637	Benzene combination of C–H stretch C–H deformation
4,358	Methyl and methylene combination of C–H stretch and C–H deformation

during the production of engineered wood, veneers, and composite wood panels [40–44]. Calibration curves were developed for the various products with known resin-loading. The calibration curves were then used to monitor and adjust resin-loading during production to maintain consistent resin-loading and optimized resin usage. Feedback loops were used to make continuous adjustments for resin application rate to maintain resin-loading within specific ranges. Through changes in the wavelengths used, the method developed for wood–veneer resin coatings was made specific to each of several different hardwood and softwood veneers. All of the methods utilize reflectance in which the source radiation reflects off the sample and is then collected by the detector. This allows the NIR probes to be positioned above the moving samples with no direct contact between the probe and the sample. They have also patented a similar method for monitoring binder loading on fiberglass mats [45]. Husted et al. [46] at J. M. Huber also patented their method for using NIR to monitor the percent resin solids in the resin composition feed stream and controlling and adjusting the percentages through adjustments of the resin/wood proportions.

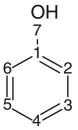
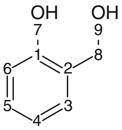
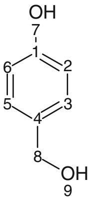
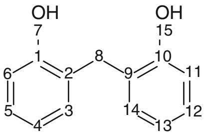
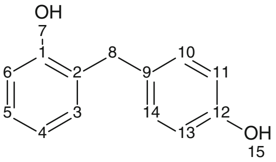
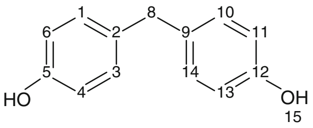
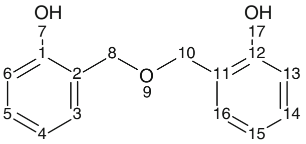
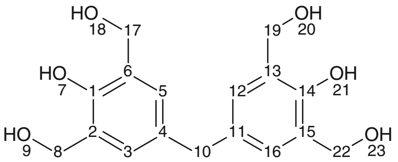
Although NIR has proven to be a useful tool for in-line monitoring during the production of phenolic resins and phenolic resin containing finished products, it is not the only tool being used for process control. In-line viscometers, refractometers, and pH probes are commonly used during the production of phenolic resins. The ability to monitor viscosity, RI, and pH during a production without the requirement to remove the sample from the reaction vessel translates to more consistent products and a substantial decrease in an out-of-specification product.

5.4.8 NMR Spectroscopy

NMR spectroscopy has taken a significant role in resin analysis, as illustrated by the high number of publications. NMR spectroscopy can be broken down into several areas such as high field NMR inclusive of 1D and 2D applications, solid state NMR, and low field NMR. ^{13}C NMR has taken a more important role than proton NMR due to the larger chemical shift region, enabling better assignments of the molecular structure to the spectra. Nevertheless, proton NMR has been used for a detailed analysis of most phenolic resins such as phenol–resorcinol–formaldehyde resins [47].

One-dimensional applications of NMR have been extremely important because of the ease of acquiring spectra, the vast amount of interpretive information, and the ability to quantify peaks of interest. Spectral assignments have been an ongoing process since the inception of NMR. Numerous authors [48–54] have made model compounds and have made excellent peak assignment tables of the PF, RF, PUF, MUF, and benzylphenols. Modestly confounding these assignments are chemical shift dependence upon solvent and pH. Furthermore, since TMS is not always used as a chemical shift reference, differences in the chemical shift can be dependent upon the deutero-solvent peak used. These differences are minor, acknowledged, and then generally neglected. Table 5.8 gives typical band assignments for some model phenolic compounds with their average resonance positions noted.

Table 5.8 Typical NMR Assignments for Model Compounds

	Carbon	PPM	Carbon	PPM
	1 2,6	159 116	3,5 4	130 121
	1 2 3 4	156 128 128.5 121	5 6 8	128.8 116 161
	1 2,6 3,5	158 116 129	4 8	134 64
	1,10 2,9 3,14	155 129 132	5,12 6,11 8	128 116 31
	1 2 3 4 5 6	155 129 131 121 128 116	8 9 10,14 11,13 12	36 133 131 116 156
	1,3,10,14 2,9 4,6,11,13	131 133 116	5,12 8	156 41
	1,12 2,11 3,16 4,15	157 122 130 121	5,14 6,13 8,10	128 117 69
	1,14 2,6,13,15 3,5,12,16	153 128 127	4,11 8,17,19,22 10	133 62 41

Solvent choice is an important consideration when running ^{13}C NMR experiments. For example, DMSO can obscure the *o–o* methylene bridge region and acetone can obscure the *p–p* methylene region, rendering important parts of phenolic resin analysis unavailable. For most phenolic resins, methanol is a good solvent which does not show spectral interferences. The use of variable temperatures in the probe can have several additional effects. Peaks that are superimposed may sufficiently shift or narrow to distinguish them with the additional benefit of better signal-to-noise. Peak narrowing is generally due to viscosity reduction changing the rotational correlation time.

A recent paper delineates the spectral assignments of the 18 possible methylol derivatives of the 2,4′- and 4,4′-dihydroxydiphenylmethanes [49]. Less referenced, but in the NMR toolbox, are experiments which identify the number of protons attached to carbon such as APT (attached proton test) and the series of DEPT (distortionless enhancement by polarization transfer) experiments. Computerized spectral assignments are of significant importance, as several companies offer excellent carbon-13 prediction software. Structures are transformed into spectra utilizing mathematical algorithms and model compounds. Figure 5.7 represents a predicted ^{13}C NMR spectrum of a *t*-butylphenol derivative utilizing software from Advanced Chemistry Development, Inc. (ACD/Labs Toronto, Ontario). Further enhancements can be typically made with these types of software by building user libraries.

Quantitation of NMR peaks provides details of the resins, including features such as mole ratio, degree of condensation, molecular weights, levels of unreacted para and ortho positions of phenol, etc [55, 56]. Accurate quantitation can be obtained using the inverse gated heteronuclear decoupling experiment. Determination of the longest relaxation time that is necessary, generally, five times the spin-lattice

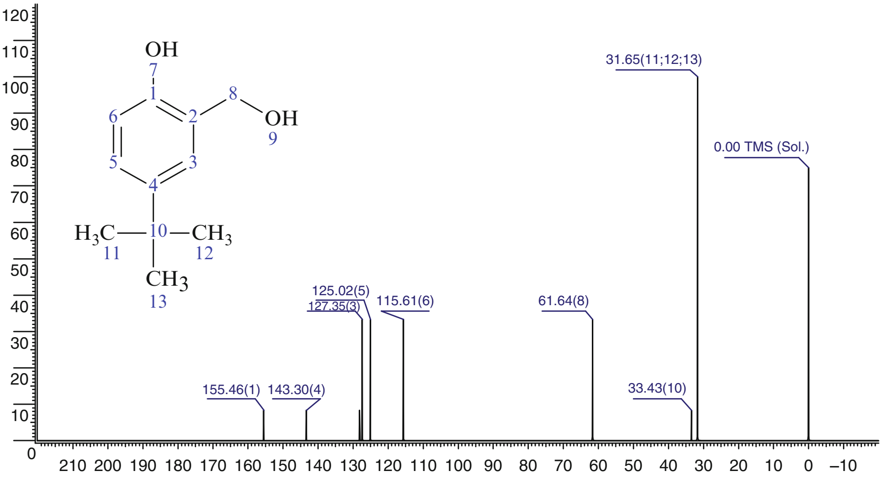


Fig. 5.7 Predicted spectrum of 4-tert-2-(hydroxymethyl)phenol (ACD/CNMR predictor software, version 11.01)

relaxation time, has resulted in times reported to range from 2 to 120 s between each scan. This has led to experiments that take up to 10–12 h.

The addition of paramagnetic reagents to resin–solvent mixtures has led to a pronounced reduction in spin-lattice relaxation times. The use of $Cr(acac)_3$ at 20 mM concentrations reduces the experimental time to under 2 h [55, 57]. The use of a 10 mm probe vs. the standard 5 mm probe can facilitate the same time reduction, as fewer scans are necessitated to achieve the same signal-to-noise. The use of cryoprobes will also produce shorter experimental times as noise is further reduced in the acquisition signal. The dependence of signal-to-noise, correct phasing, and baseline correction on optimal quantitation has been demonstrated by Valdez [56]. Excellent discussions can be found in the literature detailing theoretical and experimental considerations for quantitatively assessing NMR peak areas [58].

Mechanisms of reaction and curing have been well examined by NMR spectroscopy. The use of hexamethylenetetramine as a curing agent in novolak resins has shown intermediates, such as benzoxazines and benzylamines, which can generate methylene linkages while various side products such as imines, amides, and imides are noted [59, 60].

Application of NMR methodologies to lithographic positive and negative photoresists was made utilizing INEPT (insensitive nuclei enhancement by polarization transfer), DEPT, and 2D experiments [61]. The determination of substitution (S_n) and unsubstitution (U_n) indices provided information on the linearity of novolaks and subsequent correlation to lithographic performance.

Further 2D NMR experiments on resoles by Fisher et al. [62] have utilized DQF COSY (double quantum filtered correlated spectroscopy) and CSCM (chemical shift correlation maps) to provide qualitative identification of major phenolic components in a group of PF resins. DQF COSY and TOCSY (total correlation spectroscopy) have been used to calculate and improve the U_n value and the degree of linearity [63]. The paper also describes a deconvolution program used for Lorentzian line shapes and then quantitation of the deconvoluted areas.

Cured phenolic solids have been examined by NMR using CP-MAS (cross polarization magic angle spinning). The fate of formaldehyde in fully cured resins was investigated in terms of methylene bridges, ether bridges across the C-1 phenolic carbon, and residuals. Lower mole ratios in the solid resin than the initial liquid resin constitution indicated higher levels of carbonic matter (carbonate, bicarbonate, and formate) formed than was determined by NMR [64]. Solid State NMR of bond lines has proven useful for determining the degree of cure [65, 66]. Laborie and Frazier [67] compared a cured PF resin to a cured yellow poplar powder phenolic composite. The study suggested secondary interactions of the wood constituents with the resin hydroxyls.

Andriaensens [68] utilized wideline NMR experiments to determine resin cure kinetics by monitoring the relaxation decay curve. As a result of rapid spin diffusion, the proton spin lattice relaxation times yield information on the degree of cure, mobile end groups, and side-chain branches. The high frequency motions of the end groups and branches at temperatures below the glass transition give rise to the higher rotational correlation times. Additionally, the plots of proton spin lattice relaxation measurements as a function of temperature indicated that the predominant relaxation pathways result from branches and end groups. The authors indicated the possibility of at-line or on-line NMR relaxometry studies.

5.4.9 Time of Flight Mass Spectroscopy

The general operation of a mass spectrometer is to create gas phase ions, separate them in space or time based on their mass–charge ratio, and then quantify the ions of each mass–charge ratio. For our discussion, two areas have differentiated MS; the introduction of the analyte and the type of mass spectrometer used. Analyte introduction has typically utilized various sources such as a gas chromatograph, liquid chromatography, and direct injection techniques. Mass spectrometers generally in use today are magnetic sector, quadrupole, ion-trap, and time of flight.

Time of flight MS measures an ion's travel time from the ion source to the detector. The time of travel is dependent on the kinetic energy imparted to an ion, the charge on the ion, and the length of the flight tube where,

$$t = L(m/2eV)^{1/2} \tag{5.6}$$

t = time, L = length, m = mass of the ion, e = the charge on the ion, and V = applied accelerating voltage.

The utility of the technique is the high mass range and the high mass resolution. Numerous articles have been published delineating structures of phenol–formaldehyde resins and their counterparts such as phenol–urea–formaldehyde (PUF) and phenol–resorcinol–formaldehyde [69, 70], and melamine–urea–formaldehyde [48]. In a wood panel adhesive application, Lei et al. [71] used MALDI TOF-MS in conjunction with NMR and GPC to identify labile anhydride intermediates when using ester accelerators.

Analysis of a novolak reacted with ethylene carbonate demonstrates the power of this technique. Bir et al. [72] found three distinct polymeric distributions in a glycolated phenolic resin. In Fig. 5.8, the first distribution is that typically found in novolaks (199, 305, 411 daltons etc.). Two further distributions are easily noted containing novolaks that are singularly and doubly glycolated. The exact position of glycolation along the chain is not known. The structures in the table of molecular weights only indicate the number of glycol units, not the position (Table 5.9).

5.4.10 PES, Atomic Absorption Spectroscopy

The inorganic analysis of resins by plasma emission or atomic absorption spectroscopy is well established. Analyses for calcium, sodium, potassium, etc. often give

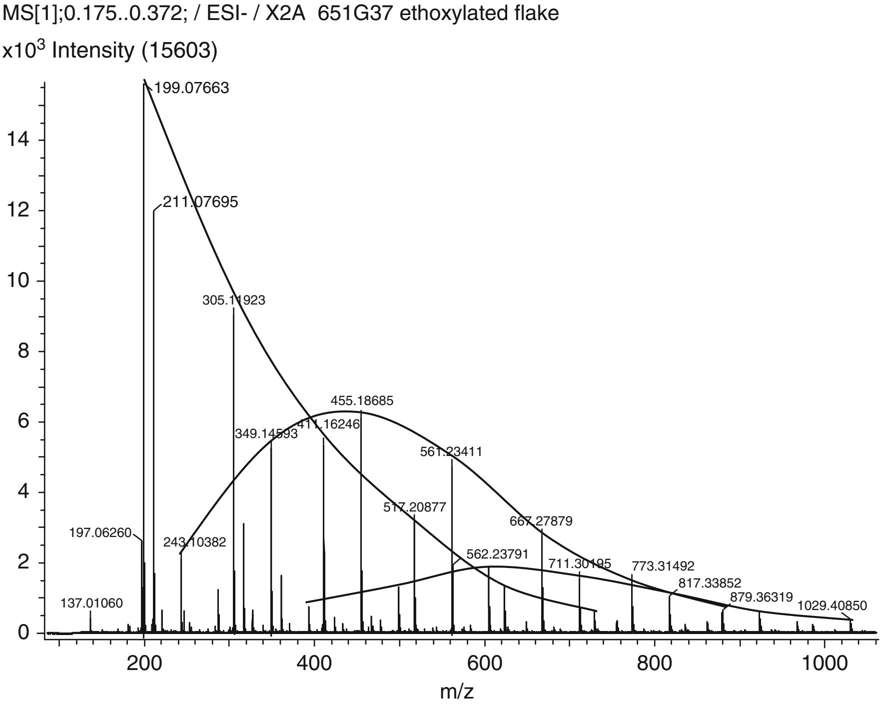


Fig. 5.8 TOF-MS of glycolated Novolak

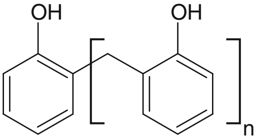
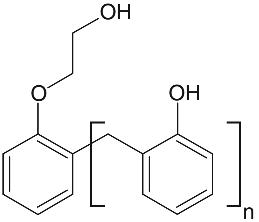
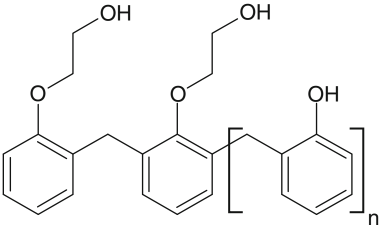
strong evidence of the types of catalysts used in the polymerization process. Samples are digested using strong acids, often nitric and sulfuric acids, along with hydrogen peroxide to ensure complete digestion of the samples. The samples are then aspirated into a flame or plasma depending on the technique used. In the case of AA, the samples are analyzed for individual elements taking considerable amount of time if multiple element analysis is required. In PES, the sample is aspirated into a high temperature argon plasma whereby the elements present become emitters of energy whose frequencies are unique to each element. Simultaneous measurement for multiple elements is easily achieved.

Ormondroyd and Grisby [73] described their use of PES in the analysis of sodium in wood panels. The panels contained sodium as result of the resin loading onto the panels. Relationships were developed between the determined levels of sodium and the percent resin loading on the panels.

5.4.11 Thermal Analysis

Thermal analysis techniques are standard techniques for studying the thermal behavior of phenolic resins. Information on the temperatures of reaction, degree

Table 5.9 Molecular weights of glycolated Novolak calculated and experimental M–H$^+$

	n	Calc mass	Exp. mass
	1	199.076	199.077
	2	305.118	305.119
	3	411.160	411.162
	4	517.202	517.209
	5	623.244	623.257
	1	243.102	243.104
	2	349.144	349.146
	3	455.186	455.187
	4	561.228	561.234
	5	667.270	667.279
	6	773.312	773.315
	7	879.354	879.363
	1	287.128	287.112
	2	393.170	393.168
	3	499.212	499.223
	4	605.254	605.263
	5	711.296	711.302
	6	817.338	817.339
	7	923.380	923.377

of reaction, and thermal stability are only a few of the things routinely attainable by the various thermal techniques commercially available today.

5.4.11.1 Thermogravimetric Analysis

TGA is one of the simplest of the thermal analysis techniques. TGA measures weight change as a function of temperature and/or time. The technique is used to determine thermal stability and the temperature of degradation for materials. TGA can be used to evaluate phenolic resins in their pre-cured state or their fully cured state, both with and without other components. Heating a pre-cured resin to processing temperatures provides information on the amount of volatile materials evolving from the resin during processing. By subtracting the percent water in the sample from the percent volatiles, the percent VOC can be determined. Fully cured composite samples can be analyzed to determine the temperature at which the composite degrades. For wood-based composites, this information is very useful in determining the temperature in which wood structures no longer have structural integrity. TGA weight loss curves for pre-cured phenolic resins typically show a steady weight loss throughout the heating from the loss of water and/or solvents at low temperatures, followed by water loss from the condensation reaction to form the cured resin. The lower molecular weight components of the polymer degrade prior to the higher molecular weight polymer components, resulting in degradation occurring over a broad temperature range.

While TGA provides valuable thermal information, coupling the TGA with IR or mass spectroscopy (MS) allows for the identification of the gases evolving from the sample during heating. Heated transfer lines are typically used to carry the evolving gases from the TGA to either a heated IR gas cell or directly to the MS. The gases from the TGA can also be trapped in absorbent tubes and analyzed through thermodesorption by GC/MS. Changes in the mole ratio of phenol to formaldehyde, catalyst, and reaction temperatures all affect the weight loss profile of the TGA.

Bouajila et al. [74] did a thorough evaluation of the degradation of various phenolic resins in inert and oxidizing atmospheres. They analyzed the resins via TGA/IR and thermogravimetry/thermodesorption/GC/mass spectroscopy (TG/TCT/GC/MS). In an oxidizing atmosphere, phenolics were found to evolve carbon dioxide, carbon monoxide, water, formaldehyde, and methanol. In a nitrogen atmosphere, aromatic compounds are observed along with the low molecular weight gases during degradation.

Kristkova et al. [75] looked at the influence of various metals on the degradation of phenolic resins used in friction composites. They found that copper and iron may catalyze the degradation of phenolic resins and proposed possible mechanisms for the catalytic process. They also found that brass (CuZn) does not have the same effect on degradation.

5.4.11.2 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is used to measure the temperatures and heat flows associated with exothermic and/or endothermic changes that occur during thermal transitions in a material. The main application for phenolic resins is the determination of the temperature of cure and the heat of reaction associated with the cure. The heat of reaction during the cure is related to the degree of cure. The technique is very useful when examining the effect of processing changes on cure. Changes in mole ratio, reaction temperature, catalysts, and additives can affect both the cure temperature and degree of cure. DSC has become a standard technique for evaluating the changes in cure that occur when one or more of these changes occur [76]. Figure 5.9 shows the typical DSC plots for two phenolic resins generated by Fowler [77] on a pressurized DSC. The curves are labeled with the onset of cure, the cure maximum, and the heat of reaction. The “A” resin shows an earlier onset of cure, while the “B” resin is more advanced, with less residual cure remaining.

Sample preparation and experimental conditions are a major consideration when running DSC on phenolic resins. Because phenolic resins contain water and/or solvents, they cannot be run like other non-aqueous thermosetting resins. If run in a

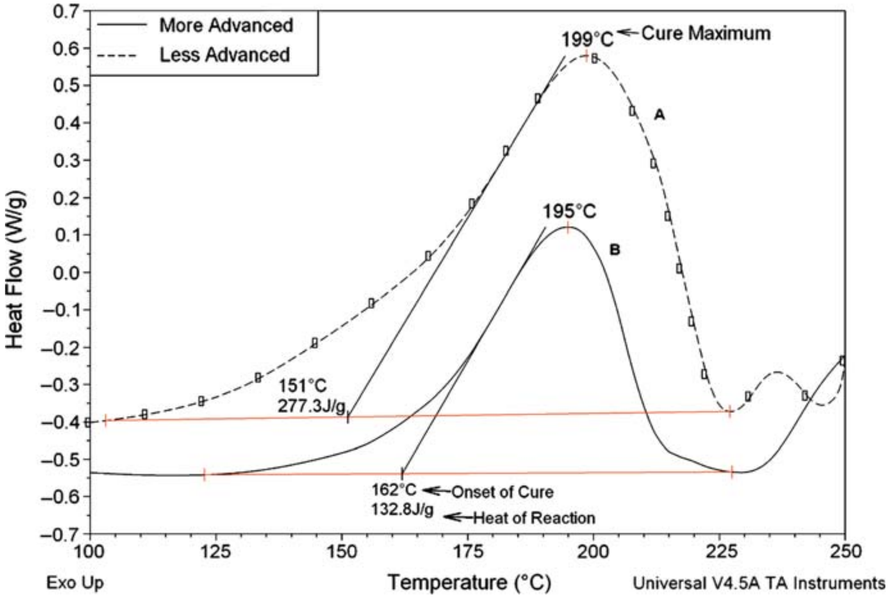


Fig. 5.9 Differential scanning calorimetry plot for two phenolic resins

typical open pan, the signal from the vaporization of water would make it nearly impossible to detect the transitions from the phenolic resins. There are typically three ways to handle samples with water. The first way is to remove the water through a freeze-drying process such that no curing of the phenolic takes place during drying. The second method involves running the system under pressure. While the pressure subdues the water transition, it does not affect the phenolic curing transition. In the third method, the sample is sealed in a closed pan so that pressure is generated as the water vaporization occurs. Although deformation of the pan may occur, making this the least desirable of the three methods, it is the only method that does not require the purchase of either a freeze-dryer or a pressurized DSC. All of these methods have an effect on the cure data. Therefore, one can only compare the results from samples analyzed in the same manner. Sample size and heating rates also have an effect on the results.

Monni, et al. [78] utilized DSC to study the reactivity of phenolic resoles synthesized in a continuous process for the methylolation step prior to a batch process condensation. The DSC results for samples isolated following the first stage (methylolation) of the two-stage synthesis were compared with those of a standard one-step reaction. The curing temperatures were found to be similar between the samples. Correlating the DSC results with the NMR results, they were able to show a linear relationship between reaction enthalpy and the total amount of free aromatic carbons. The enthalpy (released reaction heat) decreased as the total number of available free aromatic carbons decreased.

Obtaining kinetic data from the DSC has been studied by numerous groups. Gabilondo et al. [79] used DSC to study the differences in the curing kinetics of amine and sodium hydroxide-catalyzed resole type phenolic resins and phenolic resins with variations in formaldehyde content. In their work, they applied three different model-free kinetic algorithms for determination of the kinetics and activation energy. They found that the Friedman model was more convenient to use and provided accurate energy values. The Kissinger–Akahira–Sunose (KAS) model was found to be better for dynamic cure prediction. Decreasing the formaldehyde concentration was found to produce an increase in activation energy. Lee et al. [80] also found a correlation between activation energy and mole ratio with low mole ratio resins showing higher activation energies. de Medeiros et al. [81] used DSC to study the kinetics of novolak-type phenolic resins, using the Ozawa method to evaluate the kinetics of the reaction as the heating rates were changed. From their experiments, they concluded that initial curing was controlled by the growth of microgels, while the later curing was controlled by diffusion. Alonso et al. [82] studied the differences between a dynamic model, the Ozawa method, and an isothermal isoconversional fit for predicting the isothermal behavior of cure for phenolic and lignin–phenol–formaldehyde resins (LPF). They showed that the kinetic parameters determined via the Ozawa method were equivalent to those obtained by an isothermal method.

Multiple groups have studied the effect of adding lignin on the cure profile of phenolic resins. Tejado et al. [83] evaluated three different lignins by multiple techniques, including DSC. They compared the glass transition temperatures (T_g) of dried lignin. They found that the T_g values ranged between 90°C and 180°C. Khan and Ashraf [84] found that incorporating lignin into the phenolic changed the thermal behavior of the resin. The presence of the lignin lowered both the curing temperature and the rate of cure.

5.4.11.3 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) is another thermal analysis technique used to obtain information on the curing of materials. While DSC obtains information on the chemical changes occurring in the sample through changes in the heat flow, DMA determines the temperature at which mechanical curing takes place as materials transition between a rubbery state to a glassy state. Both solids and liquids can be analyzed via DMA. For liquid samples, the resin is impregnated onto a fiberglass braid. The resin-impregnated fiberglass braid is placed into the DMA’s single or dual cantilever sampling assembly so that the ends of the braid are held rigid and the center clamp is modulated at a set frequency. The energy required to maintain the modulation is measured to obtain the storage modulus and loss modulus. Tan delta, a ratio of the storage and loss moduli, is also obtained. Solid composites can also be analyzed by forming or cutting them to the specified size for the DMA and analyzing the “bars” in the same apparatus.

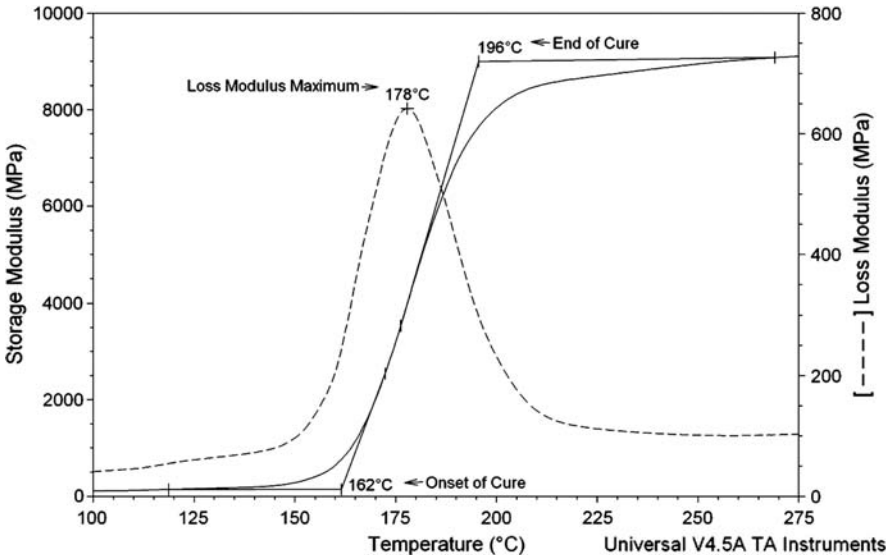


Fig. 5.10 DMA plot for a resole

Examination of the DMA plots provides information on cure temperature, cure time, and residual cure. A typical DMA plot for a resole-based phenolic resin is shown in Fig. 5.10 [77]. The onset of cure and the end of cure are determined from the storage modulus. The maximum temperature of loss modulus is also labeled. DMA provides complementary information to the DSC and is often run along with the DSC.

The use of DMA to study the curing of phenolic resins for wood bonding applications has been studied by He and Yan [85]. They used both tan delta and the storage modulus to determine the effect of molecular weight and wood species on curing. They found that the resin needed both a low and high molecular weight fraction to produce the best curing. They found that the wood species did not significantly affect curing. Recently, Laborie, Salmen, and Frazier [86] used DMA to study the cure differences between low and high molecular weight phenolic resins impregnated into yellow poplar. They were able to attribute the cure differences to the migration of the low molecular weight PF into the cell walls at a nanometer scale, interacting with the lignin present with the wood.

Numerous groups have also studied the effect of modifying phenolic resins on other chemistries. Wang et al. [87] utilized DMA to show that novolak resins functionalized with propargyl had substantially improved thermal mechanical properties when compared to conventional cured phenolic resins. Chiu and Cheng [88] blended resoles with unsaturated polyester resins to form an interpenetration network of the two components. They found that the components were miscible at 80/20 and 60/40 phenolic to polyester, but not at 40/60 or 20/80 phenolic to polyester. They used a combination of DMA and DSC to study the cure and SEM to study the miscibility. He and Yan [89] used a combination of DMA and DSC to study the curing of phenol–urea–formaldehyde resins with various changes in mole ratio and pH. Both gel point and tan delta were affected by pH differently in PUF resins than in PF resins. The lowest gel point was noted at a mid-pH for PUF, while the gel point continued to decrease with increasing pH in PF resins. Urea content was found to have a significant effect on cure.

5.4.11.4 Rheometry

The use of rheometry to study the curing of phenolic resins has seen a dramatic increase in publications [90–97]. Like the DMA, rheometers measure the strain on a system when a stress is applied. The stress/strain data can be used to measure storage and loss moduli, tan delta, and viscosity. As with the DMA, experiments can be run while the temperature is increased or at any set temperature for extended periods of time. A typical rheometer used to analyze phenolic resins uses disposable parallel plates with the resin sandwiched between the plates. Liquids or powders pressed between the plates can both be run using this configuration. The bottom plate is held stationary, while the top plate is either rotated continuously for running viscosity experiments or oscillated at a set distance at a set frequency for curing studies.

Viscosity experiments are typically run as flow experiments in which either the frequency is increased as the temperature is held constant or the temperature is increased as the frequency is held constant. Prior to cure, phenolic resins behave as a non-Newtonian liquid, showing a shear-thinning behavior (decrease in viscosity as the frequency of shearing is increased). As the resin advances toward curing, the viscosity increases. Curing studies are typically run in an oscillatory configuration in which the top plate is oscillated at a set small distance and at a set frequency while the temperature is increased. Time studies can also be done in which the samples are added at an elevated temperature and held at the elevated temperature until curing occurs.

The gel time, t_g, is measured as the time in which the polymer cross-linking has occurred. It is measured in any of the five ways; (1) Maximum peak in tan delta, (2) tangent line to the G′ (storage modulus) curve, (3) crossover between G′ and G″ (loss modulus) curves, (4) when viscosity reaches a pre-set value, and (5)intersection of the tan delta curves over multiple frequencies. The maximum peak in tan delta and the crossover point for G′ and G″ are used more often, as they are easiest to measure. Many authors have studied the changes in gel time versus temperature for phenolic resins [91, 92, 96, 97]. Both novolak and resole resins have been examined at multiple mole ratios. Malkin, et al. [95] did a comparison of multiple methods (IR, DSC, and rheometry) for monitoring the kinetics of the curing reaction. They found that each method reflected different aspects of the curing process so that the curing, as determined from one technique, was different from that of the other techniques. Different equations were needed to fit the cure data from each of the various techniques.

5.4.11.5 Other Thermal Techniques

Other thermal techniques are also used to characterize phenolic resins. Thermal Mechanical Analysis (TMA) is used to study the dimensional changes occurring during temperature and/or force changes. The technique is used to study powdered resins and fully cured solids to determine their softening temperatures, creep, glass transition, and coefficient of linear thermal expansion. Pizzi et al. [98] first used TMA to study the curing of thermosetting resins in 1998, obtaining cross-link density from the TMA data. More recently, Taki, Yoshida, and Yamada [99] used TMA to study the curing behaviors of phenolic resins using a TMA with a small wire spring. They correlated the TMA data to bond failure for the phenolic-based wood adhesives.

Dielectric analysis (DEA) is also used to study the curing of phenolic resins. DEA measures the changes in the dielectric properties of materials as samples are heated or are held at elevated temperatures. As resins cure, there is a change in conductivity and ion mobility. These changes are measured in the DEA. Samples can be analyzed in a traditional laboratory setting or in a process environment with sensors that can be placed with the resin during the processing of resin composites. Sernek and Kamke [100, 101] measured the curing of phenolic resins used in the wood industry via an in-process dielectric sensor. They studied the effect of press temperature and wood moisture. In another work, Sernek, et al. [102] presented the equations for obtaining the degree of cure from the dielectric data.

The automated bonding evaluation system (ABES), developed by Philip Humphrey [103], is a system for evaluating the bonding of adhesive systems to wood substrates. The adhesive bonds are formed in the system with temperature, press loading, and time precisely controlled. Following curing of the bond, the bond is tested to destruction by shearing the wood/adhesive sample. Both the tensile load needed to break the bond and the elongation of the sample are recorded. The system is designed to easily change any of the controlled settings and monitor their effect on the bond strength. Lecourt, Pizzi, and Humprhrey [104] found good correlation between ABES breaking load and TMA modulus of elasticity (MOE).

5.4.12 Microscopy

Although no chemical information is directly obtainable from microscopic techniques, the microscope is a very powerful tool for evaluating the bond between the phenolic resin and a substrate. As many of the other chapters of this book show, phenolic resins are used as the adhesive binder in a wide and diverse number of products. SEM, optical light microscopy, and optical fluorescence microscopy have been successfully used for many years to study the interface between resin and substrate. More recently, atomic force microscopy (AFM) and confocal microscopy have been added to the list of microscopic techniques applied to phenolic resin containing materials.

Sample preparation prior to microscopic examination is the most challenging aspect of microscopy. The phenolic resin composite is one of the more difficult sample types to prepare. In preparing samples, extreme care is needed to not damage or alter the interface between resin and substrate. For samples like wood products, the hard, brittle nature of the phenolic and the soft, elastic nature of wood cells, result in a very challenging undertaking.

For most composite samples, a cross-section of the sample is needed to examine the bonding between resin and substrate. The cross-section can be obtained from one of the following procedures; (1) fracturing (freeze-fracturing or room temperature) the sample, (2) using a microtome to obtain a thin, cross-sectional slice of the composite, (3) using a microtome to obtain a flat cross-sectional surface through the removal of slices of the composite, and (4) rough cutting of the composite, followed by polishing of the cross-sectional surface.

For wood-based composites, obtaining thin microtome slices produces the best images under SEM (see Fig. 5.11). From the microtome slice, a clear view of the wood cells and the resin penetration between the wood cells is more easily observed than with any of the other methods for SEM sample preparation. The slices are best obtained by first hydrating the wood cells with water to prevent their collapse during cutting.

X-ray mapping in the SEM using the energy dispersive X-ray detector adds additional information to the topographical image. By mapping the inorganic cation in the catalyst (for example, sodium), a map of the resin penetration into the wood cells can be obtained. A sodium map from a plywood glue line is shown in Fig. 5.12.

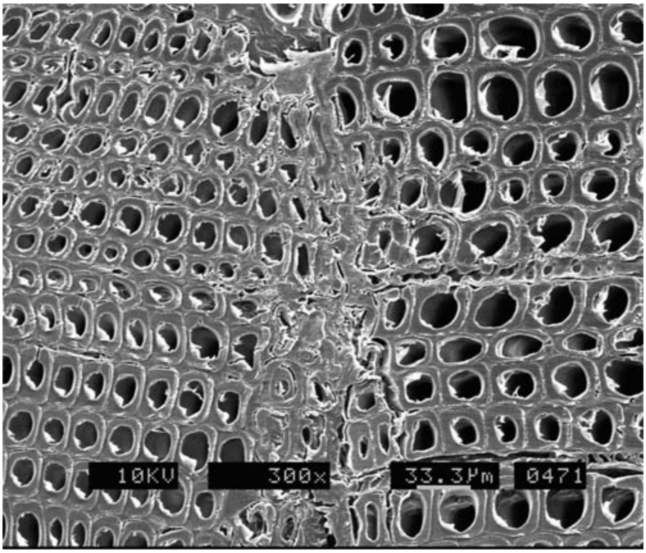


Fig. 5.11 SEM of plywood glue line taken from a microtome thin slice

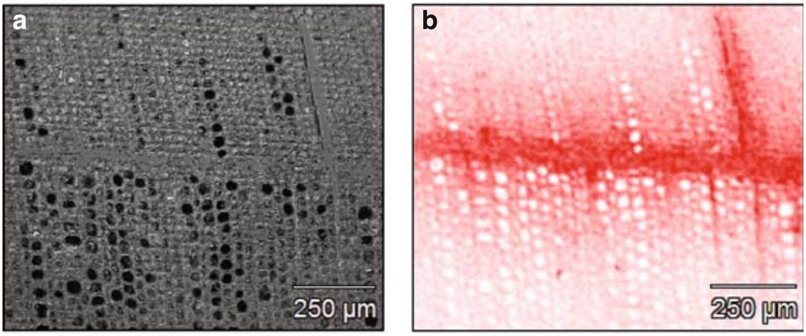


Fig. 5.12 (**a**) SEM micrograph of glue line (**b**) Sodium X-ray map of the same glue line

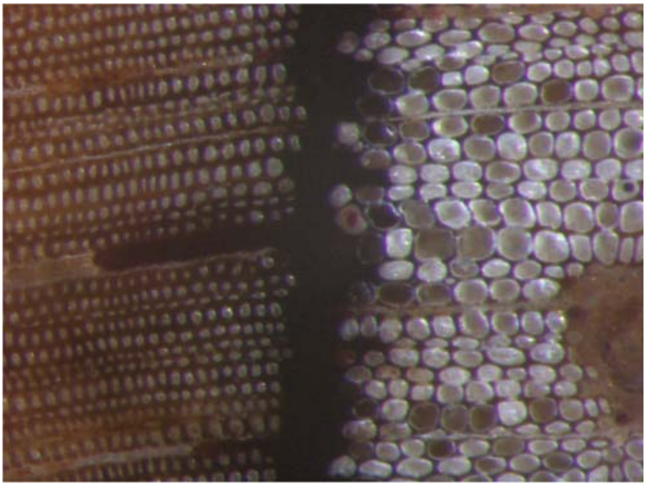


Fig. 5.13 Optical photo of plywood glue line taken from a handpolished sample

For optical microscopy of wood-based composites, polishing the surface in a step-wise fashion with progressively finer sandpaper down to 50 μ grit will produce a high-quality image without the need of the microtome (see Fig. 5.13). With the microtome, the sample size needs to be very small to have success at obtaining usable slices. The sample size can be much larger with the polishing technique, allowing for the examination of larger areas. Both commercial polishers and hand polishing work well at producing a good cross-section.

For glass-resin composites and other inorganic containing composites, freeze-fracturing has been used very successfully to obtain the cross-sectional surface for imaging. The breaking of the sample, either through fracturing or cutting, can pull the glass rods away from the interface with the resin; so a careful examination must be taken to ensure that the lack of a good bond is not from the preparation of the sample. Fracturing or polishing can also be used for frac sand to determine resin thickness on the sand grains. These sample preparation techniques work well for both SEM and optical examinations.

Straight phenolic samples, such as powdered phenolic resins used in OSB or phenolic foams, also need to be cross-sectioned prior to examination. Fracturing is a relatively easy way to examine powdered phenolic resins to determine if the spheres are hollow or solid and to determine the thickness of the walls in hollow spheres. For phenolic foam samples, fracturing and cutting away the surface with the microtome produces reasonably smooth surfaces for analysis.

The literature contains many examples of microscopy being used to examine phenolic containing samples. SEM was used by Jiang [105] to examine phase-change microcapsules with phenolic resin shells and *n*-hexadecane core. The SEM images showed a smooth spherical surface with consistent shell thicknesses. Wang [106] did an extensive study on the mechanism of failure in phenolic composites. They used a hot stage and an optical microscope to observe micro-cracks as they formed during high temperature heating. SEM was then used to study the fractured surfaces. Nigam [107] used SEM to characterize rubber-modified epoxy novolaks. They were able to correlate the microstructure of fractured cross-sections to toughness. When phenolic resins were heated to pyrolysis in the formation of carbon–carbon composites, microscopy was used to study shrinkage, porosity, and the overall microstructure of the resin [33, 108].

Osterle and Bettge [109] did a very interesting study comparing confocal laser scanning microscopy, interference microscopy, SEM, optical microscopy, and focused ion beam (FIB) to study brake lining surfaces made with phenolic composites. Although the FIB was used to obtain the cross-sections for SEM, the FIB, using a very low intensity of ion beam, was able to identify thin frictional layers that were 100 nm thick. Although all the methods they employed gave good images of the stressed brake lining surface, the FIB image provided the most information, as it was able to "see" the 100-nm thick frictional layer that was not detectable by the other techniques.

Frihart and others [110, 111] have been using fluorescence microscopy to study the adhesive penetration in wood products. With or without fluorescence dyes, the resin was much more easily distinguished from the wood cells, making it much easier to determine the degree of penetration of the resin into both the lumen and cell walls of the wood cellulose.

In the past, microscopy was limited to visual examination of materials only. Recently, many "nano" techniques have been developed to not only obtain topographical information on a nanometer scale but to also measure property differences between spatial locations on a nanometer scale. One of these techniques, scanning thermal microscopy, has been used to study adhesive penetration into wood cell walls. Using nanofabricated thermal probes, the surface temperature of adhesives and cell walls were measured. The temperature of the cell walls was found to be different with and without adhesives penetrating into the cell wall structure [112]. Nanoidentation mapping was used to determine the elasticity and hardness of PRF adhesives and wood cell walls. Cell walls in contact with resin were found to have a slight increase in the modulus of elasticity and an increase in hardness when compared with cell walls not in contact with resin [113]. Microthermal analysis was used to determine that the type of wood substrate used has a significant effect on the curing process of the phenolic resin [114].

AFM techniques are also being used to study the surfaces of the curing resins. The force exerted on the cantilever as it is moved across a cast film of cured resin was used to measure the tackiness of the resin. The effects of mole ratio and cure time were then correlated to the determined nano-tack [115]. As with any biological system, such as wood, care must be taken to collect enough data to account for the inherent heterogeneity.

5.5 Conclusion

The advancement of analytical chemistry as recently as the past decade has led to significant discoveries not only in the characterization of phenolic resins during cure but also in the characterization of the finished manufactured materials. As new analytical techniques and methods emerge for the investigation of phenolic resins, we should anticipate incremental understanding of how phenolic resins bond and perform under varying conditions. As a result, we anticipate that researchers will continue to exploit the unique properties of phenolic resins in increasingly new applications.

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Part II
Production

Chapter 6
Resole Production

Jürgen Lang and Marc Cornick

Abstract Resoles are phenol-formaldehyde condensation products prepared with a molar ratio of F:P of $\geq$ 1, basic catalysts, and lead to reactive phenolic resins with methylol functional groups. A wide variety of additives can be added to provide the final resin with the desired properties such as flame retardancy, plasticization, pigmentation, or improve processability by using release agents, wetting agents, and other surfactants. Most resoles are waterborne, but in some certain applications, they can be solvent based with either alcohols or ketones as solvents.

A vast majority of resoles are manufactured by batch conditions, with the reactor size dependent upon the end-use application. Reactors of 50 m^3 are used for large volume applications, such as mineral wool or wood binders, while lesser volume reactors are used for other lower volume uses.

The convenience of "in-line" monitoring allows the determination of resin reaction to progress and whether the resinous material is ready for the next stage of the process or ready to be discharged. Typical "in-line" process tests include pH, viscosity, water tolerance, and gel time.

Raw materials of most modern phenolic resin manufacturers are charged automatically via closed systems using mass flow meters so that there is no contact of the potentially very harmful chemicals with the operator. To ensure the prevention of run-away reactions that may occur from the exothermic reaction of phenol with formaldehyde under basic conditions, formalin (37–52%) is added continuously over an extended period of time. This allows an adequate temperature control and gives the possibility to interrupt formalin addition if the temperature is increasing to fast. An alternate method is the staged addition of catalyst which reduces energy in the system but is generally less effective in the prevention of run-away reaction than the continuous formalin addition method.

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6.1 Production of Resoles

6.1.1 Resoles

Resoles are phenol-formaldehyde condensation products with methylol groups.

In the case of a resole, the molar ratio P:F is >1 and basic catalysts are used.

Resoles are self-curing under the influence of heat, acids, or bases. The latter is used under special conditions. Their shelf life is limited. Normally, they are liquid, manufactured as solutions in water or other solvents but solid resoles are also in use (Fig. 6.1).

The properties of resoles can be quite varied, depending on the particular application they are designed for. These properties can be influenced by:

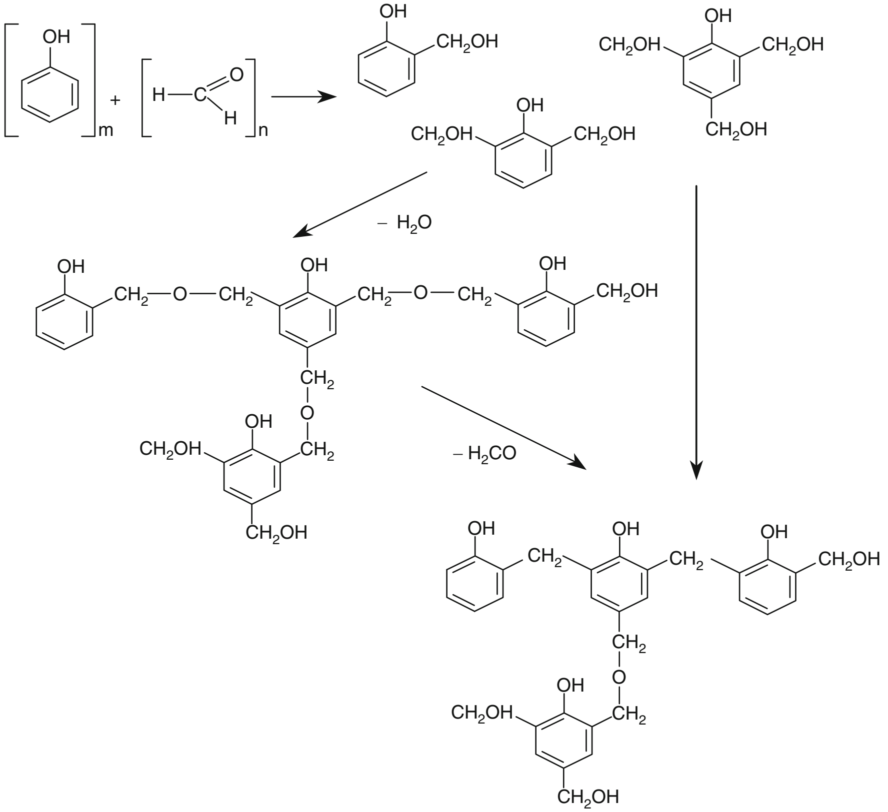

Fig. 6.1 Curing reaction of a resole

6.1.2 *Raw Materials*

- Mainly, phenol is used, but other phenol derivatives, such as cresol, xylenol, alkyl phenols, and resorcinol, or natural poly-phenols such as tannins and cashew nut shell liquid, can also be used.
- The aldehyde component is mainly formaldehyde as Formalin in aqueous solution (37–52%); in some cases, solid paraformaldehyde is also used.
- The most common basic catalyst is sodium hydroxide, but also other hydroxides of alkali or alkaline earth metals are used. Basic amines, such as triethylamine or hexamethylentetramine, can also act as a catalyst.
- There is a wide variety of additives providing the resin and the final product with the desired properties, for example, flame-retardant agents, plasticisers, pigments, etc. Further additives, such as release agents, wetting agents, and other surfactants, can also be used to improve the processibility of the resin.
- For environmental and cost reasons, most of the resoles are waterborne, but for certain industrial applications, solvent-based resins are produced. Solvents can be alcohols such as methanol, ethanol, isopropanol, butanol and furfuryl alcohol, or ketones-like acetone or methyl-ethyl ketone.

6.1.3 *Molar Ratio*

For resoles, the molar ratio P:F can vary between 1:1 and 1:4. The molar ratio exercises a key influence on the structure and density of the resin network, its curing behavior, and residual monomer content.

6.1.4 *Process Parameters*

The temperature/time profile of the reaction has a major impact on the structure of the produced resin, by influencing the competing methylolation – and condensation reaction and the degree of condensation. In some cases, excess water is removed by an additional distillation step.

6.2 Parameters of Resoles

In practice, resoles are characterized by a number of parameters which can vary depending on the application (Table 6.1).

Normally, the specific parameters are agreed between the resole producer and the customer.

Table 6.1 Typical parameters of resoles

Parameter	Standard	Remark
Nonvolatile constituents	DIN EN ISO 3251	Different methods to describe solid content are possible
Viscosity	DIN EN ISO 12058-1	Other methods like rheometer or ford cup possible
pH value	DIN EN ISO 8975	
B-time	DIN EN ISO 8987	B-time at different temperatures, gelation time at 100°C or stroke cure time also possible
Free monomer content phenol	DIN EN ISO 8974	Different methods possible
Free monomer content formaldehyde	DIN EN ISO 11402	Different methods possible

6.3 Production Process

Resoles are normally produced in a batch process. Continuous processes mainly using a kind of cascade process are described in the literature but are not very common.

6.3.1 Principle Steps of the Batch Process

1. Dosing of raw materials
2. Heating to reach condensation temperature
3. Condensation until the desired parameters are reached
4. Distillation of excess water (only if needed)
5. Cooling
6. Adjustment of final parameters
7. Unloading and filtration of the resin (Figs. 6.2 and 6.3)

The production is normally conducted in reactors which can be heated and cooled by jackets or coils. They are equipped with condensers for reflux or distillation and often vacuum can be applied.

In the case of solvent-based resins, explosion proof devices are necessary. The size of the reactor also depends on the application, so for mineral wool resins or binders for wood materials, reactors of 50 m^3 are in use. Due to the corrosive raw materials, the reactor and auxiliary facilities, such as tubes and storage tanks, are made of stainless steel. Modern plants utilize higher concentrated formalin (about 50%) and molten (100%) phenol to save energy cost for heating and distillation and to minimize the amount of wastewater. In this case, the storage facilities and all the tubes and dosing systems have to be heated.

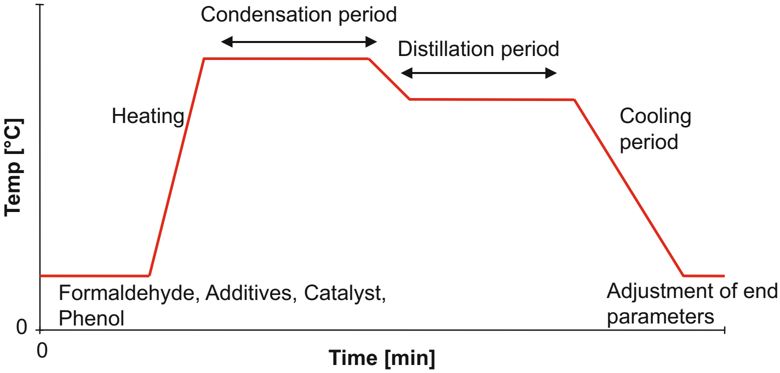

Fig. 6.2 Principle scheme resole production

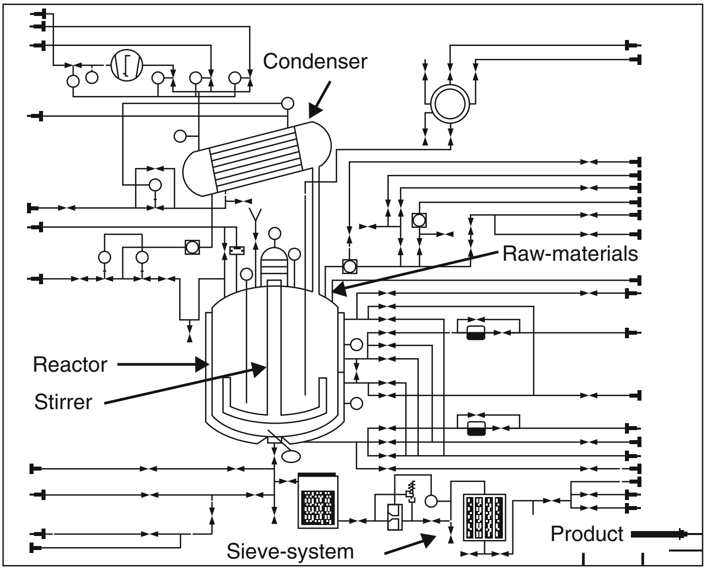

Fig. 6.3 Principle scheme of a reactor for resole production

6.4 Continuous Phenolic Resin Manufacturing Processes

Continuous processes for the production of aqueous resole are also described in the patent literature [1]. This continuous production is generally initiated in multiple reactors of various designs connected in series. Continuous resole synthesis is economically and technically appropriate in situations where large quantities of products exhibiting highly uniform quality are required, for example, in case of binders for chipboard or mineral wool.

6.5 Modern Batch Manufacturing Processes

Continuous manufacturing processes are extremely desirable in certain situations, that is, rapid and reproducible manufacture of simple commodity products. However, their use is rare due to the considerable investment cost involved and also due to the lack of flexibility in making a wide portfolio of highly specified and modified products.

Therefore, batch manufacturing processes are still widely used within the phenolic resins industry. However, the level of technology has advanced considerably from the early resin reactors that required complete manual control, the main advances being in the areas of raw material charging, reactor temperature control, in-line monitoring, and health and safety systems.

6.5.1 Raw Material Charging

In most modern phenolic resin manufacturing plants, all of the main raw materials are charged automatically via closed systems so that the operator has no contact with the potentially very harmful chemicals that are used.

Older charging systems based near weighing tanks are still used in some manufacturing plants, but more modern facilities are generally based around flow meter dosing systems. Early flow meter systems were based on volumetric control, but these have been superseded by systems based on mass flow control.

Mass flow meters function by measuring the coriolis force caused by the liquid flowing through the meter. As the magnitude of the force is directly proportional to the mass of liquid flowing through the flow meter, the mass flow rate can therefore be determined.

Accurate control of raw material charging is paramount to obtain a consistent product, as small changes in catalytic and/or monomer amounts can alter the chemical structure that is formed during the resin manufacturing process and can therefore greatly alter the final properties of the resultant resin.

6.5.2 Temperature Control

As discussed earlier, reactor temperature is usually controlled through jackets and/or heating/cooling coils mounted inside or outside of the reaction vessel. In earlier resin reactors, temperature control was achieved by physical operation of manual valves to circulate steam and/or cooling water into the heating/cooling system.

In modern resin manufacturing plants, the temperature of the reaction vessels is often controlled automatically. Temperature control loops can be of varying complexity, from simple on/off controllers to more advanced and more expensive proportional–integral–derivative (PID) controllers.

As the temperature of the resin manufacturing process can determine which type of reactions take place (e.g., in very general terms, low temperatures tend toward addition reactions and high temperatures tend toward condensation reactions), it is important that the same temperature profile is used from batch-to-batch in order to maintain a consistent product.

6.5.3 In-line Monitoring

Most resin manufacturing processes require that some property of the reaction mixture be tested at intervals to determine how far the reaction has progressed and whether the material is ready for the next stage of the process to start. Typical in-line process tests are:

- pH
- Viscosity
- Water tolerance
- Gel time

This sampling and testing procedure is one of the few stages of the manufacturing processes that brings the operator into direct contact with the harmful chemicals that are being used. In addition, the testing of the "readiness" of the batch can be subject to operator error, and if a misjudgement is made, the clean-up and disposal costs for an "over-cooked" batch of resin can be extremely high.

Therefore, considerable development time has been invested in the investigation of in-line methods of measuring some of these resin properties, the most common being the continuous monitoring of pH and viscosity.

In-line pH measurement is carried out using the same kind of pH electrodes that are used in standard laboratory pH meters. The complicated part of the process is to find an effective method of introducing the resin to the pH probe or vice versa. In-line pH probes can be mounted directly onto the reactor body itself or can be placed externally in a re-circulation loop. The main issue with the use of this kind of pH measuring technique with phenolic resins is how to clean the pH probe and make sure that it does not become contaminated with the material that is under test.

In-line viscosity monitoring is fraught with many of the same issues as In-line pH measurement, that is, how and where to mount the probe and how to ensure that it does not become contaminated through build-up of material such that the results become compromised. In-line viscometry can use a variety of methods of measurement; one common system is to use an oscillating probe that is suspended in the reaction mixture. The viscosity is therefore determined by measuring the response of the probe to a fixed oscillating force or by measuring the power required to maintain a fixed oscillation frequency/amplitude.

The main benefits of using this type of on-line monitoring are:

- Reduction in cycle times as reaction end-points are determined more accurately.
- Better consistency from batch-to-batch due to reaction improved control.
- Reduction in discarded batches due to elimination of operator influence.

6.5.4 Health and Safety Issues

Early manufacturing methods were based around so-called "loaded bomb" systems that effectively involved charging all of the raw materials at once. This is a potentially dangerous situation as the reaction between phenol and formalin is very exothermic (in the presence of catalyst), and if the cooling system fails, this can give rise to a run-away reaction that can result in an explosion in extreme cases.

One way to prevent this kind of run-away reaction is to charge one of the monomers (preferably formalin) via a continuous dosing system over an extended period of time (typically, 30–120 min depending on the molar ratio and/or amount of formalin to be charged). If the temperature of the reactor and the rate of monomer feed are set correctly, then the formalin will effectively be used up almost as soon as it enters the reaction system, thereby preventing any build-up of unreacted material and reducing the potential for run-away to occur. If the temperature appears to be increasing, then the dosing procedure can be interrupted to allow the reaction mixture to cool down before continuing.

An alternative method is to use a staged addition of catalyst, which also reduces the amount of chemical energy in the system, but this is generally less effective in the prevention of run-away than the continuous formalin addition method.

In addition to these measures to control the build-up of exothermic energy during the polymerisation reaction, modern resin reactors are generally equipped with pressure release systems designed to deal with run-away reactions should they occur. These are invariably based around a system involving a rupture disk and a collection tank.

Should a run-away occur and the pressure in the resin reactor builds to an unacceptable level, the rupture disk will fracture, allowing the bulk of the reaction mixture to escape into the collection tank where the exothermic material can be contained and allowed to cool. Although this system prevents a potentially injurious incident from occurring, in such cases, there is still the matter of clean-up and disposal of the reaction mixture. But, this system prevents damage to the resin reactor and therefore, allows the reactor to be back in operation with minimum down-time.

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Chapter 7
Novolak Production

Hiroshi Aiba

Abstract Novolak resins are produced by reacting formaldehyde (30–55% concentration) with phenol under acidic conditions, with oxalic acid as the preferred catalyst and in special conditions, sulfuric acid. Depending on the batch size, all raw material components can be introduced into the reactor, or when there is an increase in the batch size as well as in the reactor volume, the reaction exotherm is controlled by a gradual addition of formaldehyde. Modern novolak production facilities are automated and programmed for reduced operational cost. A flow diagram of a general production line for the manufacture of novolak is shown. Recovery of the novolak is accomplished by the removal of water and devolatilization of crude novolak to molten, low-free phenol novolak resin which can be isolated as flake or pastille or dissolved in appropriate solvents. Novolak is stored either in a solid flake or pastille form or in solution. Most production is conducted under atmospheric conditions, but there are some recent, novel activities such as pressure in a hermetically-closed reactor reaching 0.1–10 MPa by using the heat of reaction without reflux to shorten reaction time, accelerating dehydration time by flash distillation, and providing economic benefit in the cost of novolak production.

Batch production remains as the predominate method of novolak production; however, there persists some mention of continuous processes for novolak production.

7.1 Introduction

The manufacture of novolaks has undergone significant progress as one contrasts the size of Baekeland's tiny reactor (Fig. 7.1) with the current large reactors with capacities of 60 m^3 and larger (Fig. 7.2) [1].

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DOI 10.1007/978-3-642-04714-5_7,

Fig. 7.1 Baekeland's reactor

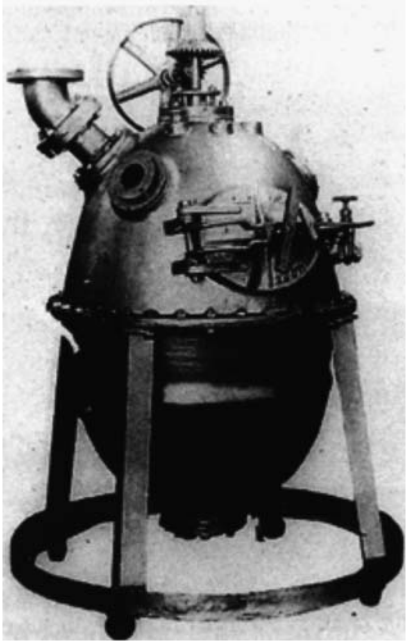

Fig. 7.2 Photo of recent novolak reactor. Sumitomo Bakelite

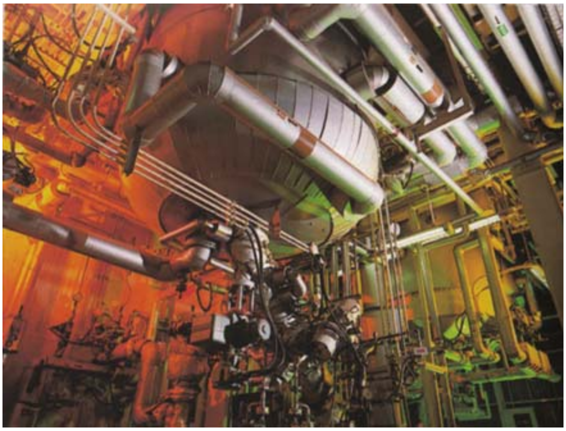

Figure 7.3 shows the flow diagram of a general production line for novolak resin. The production line consists of mainly five parts: raw material tanks, a reactor, a condenser, distillation water tank, and some dischargers.

7.2 Raw Materials

Phenol, formalin (formaldehyde aqueous solutions: formaldehyde concentration is usually 30–55%), and other main raw materials are generally stored in raw material

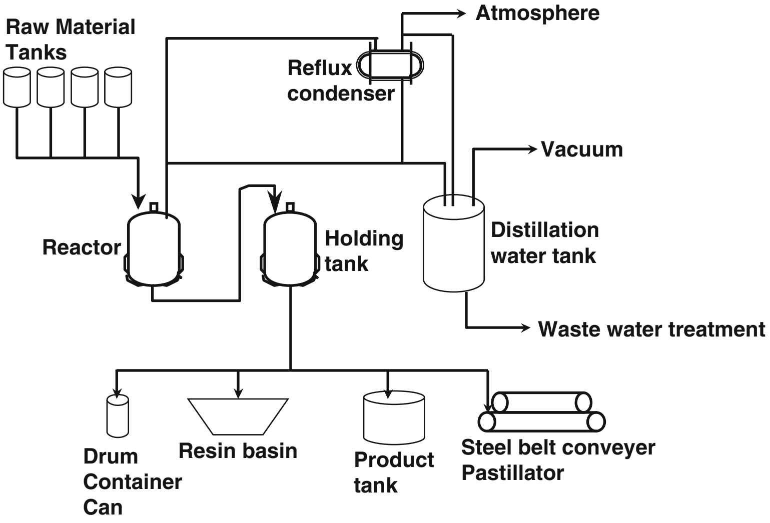

Fig. 7.3 Flow diagram of a general production line of novolak. Sumitomo Bakelite

tanks made of iron and stainless steel. The tanks for some raw materials, whose melting points are higher than room temperature, are heated by various methods such as warm water, steam or hot oil. The tank for formalin is also kept warm (around 50°C) to prevent paraformaldehyde from separating out and preventing formalin from being oxidized to formic acid. From these tanks, raw materials are charged into the reactor. Because the mass affects the mole ratio of phenol to formaldehyde, these components must be managed carefully to control the quality and properties of the novolak. Therefore, in general, phenol, formalin, and other important materials are charged by using a weighing system or a balance or for large reactors mass flow meters guaranteed for their accuracy. A reactor normally has an agitator, heating/cooling jacket, and tubes. A reflux condenser is connected to the reactor.

7.3 Acid Catalysts

Ordinarily, the reaction commences by the addition of an acid catalyst such as oxalic or sulfuric acid in the reactor. Oxalic acid is generally used to catalyze the reaction between formaldehyde and phenol, and loses its acidic activity at elevated temperatures (>180°C) by decomposing into carbon dioxide as the novolak is devolatilized and recovered. Sulfuric acid is typical strong acid and used under special conditions when using raw materials with reduced reactivity.

7.4 Process

During initial reaction, the temperature of the mixture (raw materials and catalyst) in the reactor slowly increases to 100°C through some exothermic heat of reaction of reactants along with some external heating, if necessary. As the reaction continues, additional heat is generated and cooling may be necessary to control reactor temperature. If the heat of reaction cannot be controlled, the reactor will be pressurized due to steam pressure, causing the rupture disc to vent volatile materials or, in extreme cases, the possibility of an explosion.

Depending on the size of the batch, all the raw material components can be introduced into the reactor for reasonable amounts of novolak. As the batch size and the reactor volume increase, it becomes necessary to control the temperature of the reactants by means of a gradual addition of formaldehyde. This gradual addition of formaldehyde may not be possible in some cases to achieve certain characteristics of the desired novolak such as the proper molecular weight distribution. After about 30–60 min, the reaction is under control and maintains a temperature of about 100°C as water is refluxed and returns into the reactor. This combined heating and reflux continues until all the formaldehyde is consumed. The end of the reflux reaction is usually a pre-determined time. Subsequently, "in-line" analytical methods are employed to characterize the crude novolak and consist of tests such as free formaldehyde, viscosity, refractive index, or molecular weight. These samples are taken directly from the reactor.

The water, from aqueous formalin and the amount that is generated by the condensation of phenol and formaldehyde, must be removed to obtain the novolak resin after the reflux reaction is complete. For this reason, a distillation water tank is used to collect the aqueous distillate. Distillation is usually conducted under atmospheric conditions to control the liquid level of the mixture which must be kept below the maximum level of the reactor to avoid boil over into the distillation tank. The novolak liquid level rises due to an increased temperature of $>100°C$ as well as the propensity of novolak resins to foam. Therefore, the liquid level is controlled by heat adjustment, and an antifoam agent may be used to prevent foaming. However, conditions, such as the use of vacuum, can be used to speed up the removal of water. Thus, in some cases, water can be removed via a "rough vacuum" method while controlling the liquid level of the mixture. Vacuum is created in the reactor by a vacuum pump pulling through the condenser. The initially recovered aqueous distillate contains some phenol, so that the aqueous distillate is treated by activated sludge or any other environmentally acceptable methods before being discharged into the environment to meet the required regulatory compliance.

After dehydration, additional phenol monomer is still present in the novolak resin. Therefore, the phenol monomer is removed to desired, low levels by vacuum distillation. In the vacuum distillation process, the ultimate vacuum and temperature depend on the target-free monomer level in the final novolak. This distillation fraction is collected in a distillation tank and is rich in phenol. This fraction can be typically recovered after some treatment and recycled for use in future resin production.

The finished novolak is discharged from the reactor into two types of commercial novolak products: solid novolak and liquid novolak. A solid novolak in the molten state must be cooled and solidified. For this purpose, steel belt conveyers, with belts that are cooled by chilled water, are usually used to solidify the novolak into the shape of a flake. However, the flaked novolak has a tendency to sinter if its melting point is low. In those cases, a pastillator can be used. If the viscosity of the molten novolak is too high to discharge using steel belt conveyers, then the novolak can be discharged into resin basins or trays. Liquid novolaks, which are dissolved in appropriate solvents after distillation, are transferred to storage tanks or directly discharged to drums, containers, or cans after cooling in the reactor.

An overview of a typical novolak production system is presented. In recent years, the novolak production process has become much more complicated by the quality demanded by specialty market requirements for novolak. For example, to obtain certain resin characteristics, different types of auxiliary materials are added during the production of the resin, and the temperature of the mixture must be controlled precisely at the pre-determined temperature to obtain the desired characteristics. Additionally, the productivity and the production rate may require additional improvement. Many production processes are automated and programmed for reducing operational cost. High-pressure reaction can be used to reduce production time. Normally, reaction is conducted in atmospheric conditions so that water is refluxed around 100°C, but for a high-pressure reaction, the pressure in a hermetically closed reactor may rise to 0.1–10 MPa by using the heat of reaction since there is no reflux. This high-pressure reaction can shorten the reaction time up to about 10 min and shorten the dehydration time by flash dehydration from a high-pressure condition to an atmospheric condition. Although most production processes of novolaks are still batch processes, the continuous production process of novolak persists in being examined by Frontini et al. [2], Tochimoto et al. [3], and Inadumi et al. [4]. A balance must be maintained between high quality and high productivity while ensuring safety of these new techniques in the days ahead.

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Part III
Applications

Chapter 8
Wood Composite Adhesives

Jose Gomez-Bueso and Robert Haupt

Abstract The global environment, in which phenolic resins are being used for wood composite manufacture, has changed significantly during the last decade. This chapter reviews trends that are driving the use and consumption of phenolic resins around the world. The review begins with recent data on volume usage and regional trends, followed by an analysis of factors affecting global markets. In a section on environmental factors, the impact of recent formaldehyde emission regulations is discussed. The section on economics introduces wood composite production as it relates to the available adhesive systems, with special emphasis on the technical requirement to improve phenolic reactivity. Advances in composite process technology are introduced, especially in regard to the increased demands the improvements place upon adhesive system performance. The specific requirements for the various wood composite families are considered in the context of adhesive performance needs. The results of research into current chemistries are discussed, with a review of recent findings regarding the mechanisms of phenolic condensation and acceleration. Also, the work regarding alternate natural materials, such as carbohydrates, lignins, tannins, and proteinaceous materials, is presented. Finally, new developments in alternative adhesive technologies are reported.

8.1 Introduction

The past decade has witnessed dramatic changes in the world economy, creating new currents and counter currents. Global energy markets are experiencing unprecedented fluctuation in the prices of the oil and natural gas, the precursors for resin

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raw materials. The emerging markets of developing countries possess competitive advantages for the production of composite wood that until recent years had not exploited those resources. The growing awareness of the environmental impact of the wood consumption and the effects of wood adhesives on living environments is reshaping the manner those materials are used and creating pressure for the reduction of emissions from all adhesive-bonded wood composites. The ever present competitive market pressure upon adhesive suppliers demands that they create new value for their composite manufacturing customers. New processes and equipment technologies for wood composite manufacture sometimes require that adhesives provide exceptional performance tailored to them. And, new designs for engineered wood composites are also putting performance demands on wood adhesives as well as shifting the types of composites that are being manufactured. All these driving forces will impact the way phenol–formaldehyde (PF) resins are used for wood composite adhesives in the coming years.

8.2 Volume and Region Trends

The global consumption of phenolic resins in 2004 was 3,200 thousand metric tons with an average capacity utilization of 70% [1]. North America is and will remain one of the largest markets for phenolic resins. According to the same report, the highest expected growth for 2009 is for "Other regions," which includes China, India, Indonesia, etc. (see Fig. 8.1).

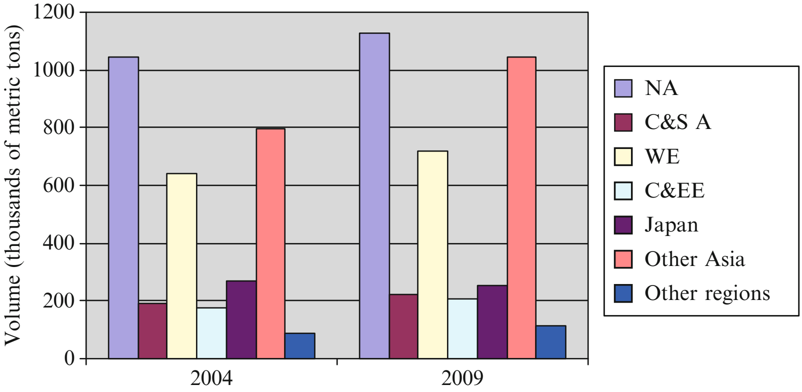

Fig. 8.1 Phenolic resin consumption shown by region for 2004 and expected for 2009 according to figures reported by CEH Marketing Research Report [1]. *NA* North America, *C&SA* Central and South America, *WE* Western Europe, *C&EE* Central and Eastern Europe. Other Asia comprises China, India, Indonesia, the Republic of Korea, Taiwan, Thailand, Malaysia, Singapore, Pakistan, and the Philippines. Other regions comprise Africa, Middle East, and Oceania

Wood adhesives will remain the largest market share and will drive phenolic resin consumption globally (see Fig. 8.2). Since a substantial portion of phenolic resins is used in the wood products industry, the market for phenolic resins in most countries follows housing construction and GDP growth. According to the CEH marketing research report for phenolic resins of September 2005, global PF consumption grew at an annual rate of 3.9% during 2001–2004 while worldwide GDP averaged 3.6%/year [1]. Global phenol–formaldehyde resin consumption, however, grew slowly during 2004–2007. The U.S. housing market slump that began in 2006 and continued through 2008 had a large negative impact on total PF resin consumption during 2004–2007 and an even greater effect in 2008 [2].

According to the CEH report by SHR Consulting for 2008, North America, Western Europe, and Japan accounted for 65% of PF resin consumption in wood adhesive applications during 2007 [2]. An average annual growth rate of 2.8% was expected for total phenolic resin consumption during 2004–2009, with a similar level expected for wood adhesive applications.

North America is the largest market for phenolic resins within the wood adhesives application, with more than 54% of the worldwide consumption (see Fig. 8.3).

In North America, wood adhesive applications account for 60% of phenolic resin consumption, with similar amounts also observed for Central and Eastern Europe (see Fig. 8.4).

Within the wood composite panels segment, the largest markets for phenolic resins are plywood, laminated veneer lumber (LVL), other structural wood products, and oriented strandboard (OSB). In North America, OSB is a serious competitor for many traditional plywood applications and has captured a large proportion of the structural panel market, particularly in housing applications. In 2004, softwood plywood production consumed almost 20% of the U.S. phenolic resin production when compared with 36% in 1986 [1]. In addition, the long-term trend of OSB substitution for plywood will have continued during the last few years (see Fig. 8.5).

The demand for wood composite panels, both structural and nonstructural, is a function of housing demand, which further relates to the income level and

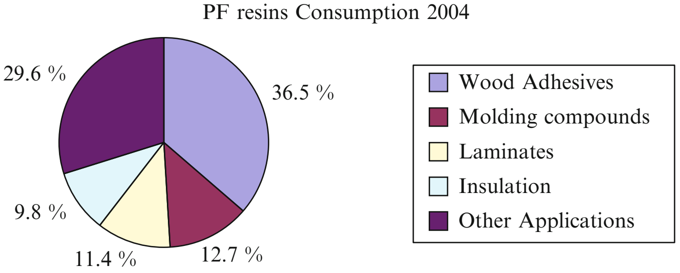

Fig. 8.2 Phenolic resin consumption shown in percent by application for 2004 according to figures reported in CEH Marketing Research Report [1]. Other applications comprise friction materials, foundry materials, abrasives, rubber processing, and protective coating

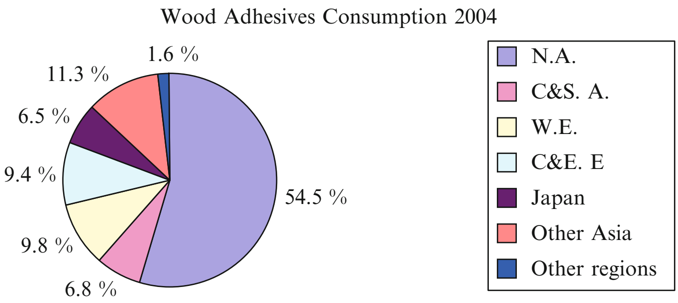

Fig. 8.3 Phenolic resin consumption in wood adhesives shown in percent by regions for 2004 according to figures reported by CEH Marketing Research Report [1]. Other Asia comprises China, India, Indonesia, the Republic of Korea, Taiwan, Thailand, Malaysia, Singapore, Pakistan, and the Philippines. Other regions comprise Africa, Middle East, and Oceania

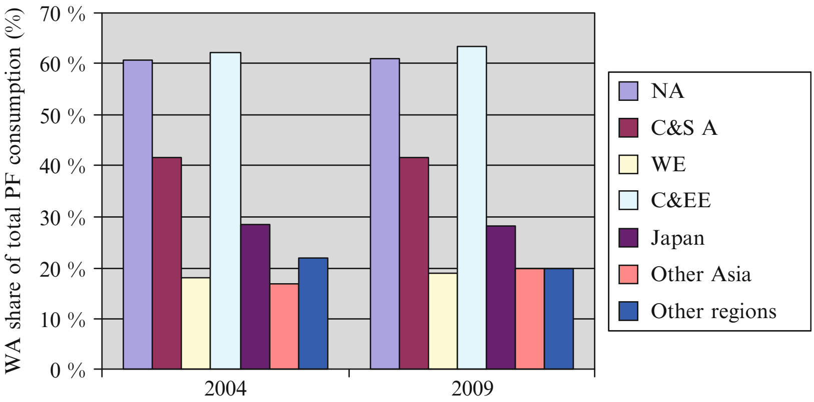

Fig. 8.4 Phenolic resin consumption in wood adhesives shown in percent of actual PF consumption in each region for 2004 and expected consumption for 2009 according to figures reported by CEH Marketing Research Report [1]. Other Asia comprises China, India, Indonesia, the Republic of Korea, Taiwan, Thailand, Malaysia, Singapore, Pakistan, and the Philippines. Other regions comprise Africa, Middle East, and Oceania

population [3]. The consumption of phenolic resins in the wood adhesive application is partly dependent on the housing market and the current worldwide production situation of wood composites. The recent downturn in the construction market has caused consumption of wood composite panels to decline during these last few years [3]. North American wood composite panel demand is not expected to rebound until 2010, and a healthy panel market is expected to return between 2011 and 2013 [4]. The developing regions of Central and South America, Central and Eastern Europe, and Asia (excluding Japan) will experience the largest growth in wood adhesives application according to the same report and a similar report for 2008 [1, 2].

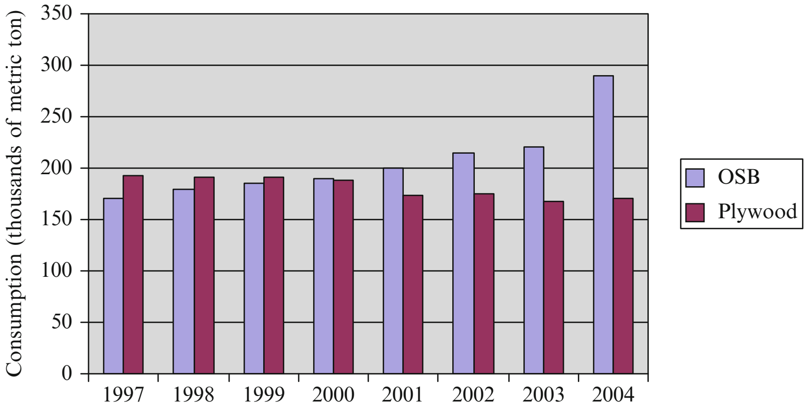

Fig. 8.5 Historical US consumption of phenolic resins in Plywood and OSB
Source: CEH Market Research Report, September 2005

8.3 Global Market Factors

The major cost factors in the production of wood composites include wood fiber, adhesives and chemicals, energy, labor, and production facilities. Several of these costs are directly or indirectly dependent on the cost of oil and natural gas, necessary for the production of resin raw materials. In recent years, the global energy markets have seen substantial price fluctuations, thus impacting the input prices for wood composite commodities and their profitability. In addition, the emergence of new production supply sources for wood-based panels is dramatically altering the industrial landscape. New and existing production facilities in countries, such as Brazil, Russia, India, and China, are changing the nature of competition in the industry. These countries possess various competitive manufacturing advantages in the cost of fiber, labor, and reduced environmental compliance requirements compared to the more established industries in Europe, North America, Oceania, and Japan. As a partial result, this emerging production is causing shifts in resources around the world. High labor cost regions need automated, high-capacity facilities to effectively compete with products from low labor cost regions. Production is shifting toward more efficient fiber utilization, with panel products such as OSB and structural composite lumber (SCL) products such as LVL continuing to supplant plywood. And, where plywood is still manufactured, it is finding its way into value-added niche applications such as concrete shuttering, where its advantageous properties are absolutely necessary. In the recent past, the sharp decline in housing prices in certain global real estate markets has led to a dramatic slump in demand for wood composite building products. Although such declines are a normal part of economic cycles, the weak markets put enormous financial pressures on the manufacturers, most of which would be profitable in stronger markets. Regardless of the location, older and comparatively inefficient mills must either add value and upgrade or be shut down. In addition, the wood composites manufacturing industry faces competition from alternative building materials such as steel and ceramics. As a result, all these factors contribute to a relentless pressure on adhesive suppliers to cut costs, improve productivity and product properties, reduce environmental impact, and to assist their customers in product differentiation.

In the global regions, cultural differences and preferences in the usage of wood composites affect both the mixes of composites used and even the kind of adhesives used to make them. For example, in North America, the preference is for phenol–urea–formaldehyde (PUF) or diphenyl methylene diisocyanate (MDI) resins for OSB and SCL and PF for plywood. There, OSB continues to take market share from plywood for residential sheathing applications, while plywood survives in specialty applications that require its specific superior strength attributes. Some of those specialty applications include overlaid plywood for concrete formwork and paintable panels. Some strand-based specialty applications include paintable overlaid siding and soffit material, and overlaid sheathing for walls and roofs. Specialty OSB grades are made for sub-flooring. When it comes to adhesive selection, OSB is regarded as a variant from plywood and therefore, PF and MDI adhesives have been preferred. Environmental pressure is increasing, but the level of expectations is not nearly the same as in Europe or Japan. In Europe, where OSB is regarded as more of a variant of particleboard, the adhesive preference leans more towards the light-colored amino-formaldehyde resins or MDI, consistent with the historical familiarity and usage of those adhesives and panel applications. Usage of PF wood composite resins has been mostly in plywood and LVL production limited mostly to Scandinavia, with some production emerging in Russia in more recent years. Until recently, the European manufacturers encountered higher environmental regulatory pressures on adhesive requirements than in North America. The Asia-Pacific region has experienced tremendous growth in the manufacture of wood composites for export markets, with plywood providing the bulk of the PF consumption volume. Recent years have seen the shift of plywood production within Asia from Indonesia to China, due to over-logging and reduced access to tropical forests. In regard to environmental regulation, Japan maintains the most stringent formaldehyde emission standard in the world, F**** (see Table 8.1), while most of the other countries are more permissive.

Among the emerging supply nations, each brings varied competitive advantages to the market. Brazil has access to fast-growing trees and low labor costs for the manufacture of plywood and OSB, producing from Eucalyptus in the north and Elliottis pine in the south. With a rapidly improving infrastructure, Brazil offers low-cost production, often with older plant equipment and also with some very modern mills. With its huge fiber resource, Russia is able to produce and deliver substantial volumes of plywood to the rest of Europe in spite of its slower growing climate. As a result of recent investment, it features newer plywood mills offering reasonable labor costs. India has emerged even more recently in the production of wood composites, with its large labor pool also offering low-cost production. Finally, China, which is fast becoming the manufacturing center of the world, has seen very rapid growth in the production of plywood and other wood composites, in

Table 8.1 Existing standards relating to formaldehyde emission requirements according to different methods for particleboard and MDF[a]

Region	Chamber emission (ppm)		Desiccator (mg/L)[b]	Perforator (mg/100 g)[c]
	EN 717-1	ASTM E 1333		
Europe				
E1	**0.10**	–	–	[∼8]
E2	>**0.10**	–	–	[30]
EPF-S[d]	[∼0.05]	–	–	**4 (5)**
Japan				
F****	–	–	**0.3**	[∼2]
F***	–	–	**0.5**	[∼3]
F**	–	–	**1.5**	[∼6.5]
USA				
CARB ‘09	[∼0.13]	**0.18 (0.21)**	–	[∼8]
CARB ‘11	[∼0.07]	**0.09 (0.11)**	–	[∼4]
Dynea AsWood™	–	–	0.08	0.4
Pine[e]	∼3	–	0.08	∼0.3

[a] Figures in **bold** are the standard limits. Figures in (parentheses) are specific for MDF
Figures in [brackets] are estimates based on known correlations
[b] Desiccator test refers to JIS A 1460 and ISO 12460-4
[c] Perforator test refers to EN 120
[d] Voluntarily limits suggested by the European Panel Federation
[e] Samples taken directly from sawmill; not conditioned

part due to its large pool of well educated, but low-cost workers. The country possesses a combination of modern facilities and many labor-intensive low-capital operations. One potential weakness in China is the lack of sufficient wood fiber; as a result, China is somewhat vulnerable to the need to import timber and is forced to use alternative raw materials such as annual plants or bamboo.

8.4 Environmental Factors

The global trend toward greener products and production processes is placing more stringent requirements on adhesive suppliers and wood composite manufacturers. The production phase of composite fabrication will face demands to decrease emissions of volatile organic compounds, nitrous oxides, and any other hazardous air pollutants formed during drying and pressing operations. Although formaldehyde-based adhesives maintain the cost advantage that has made them the historically preferred bonding solution, recent international rulings on the potential health effects of exposure to formaldehyde emitted from wood-based-panels will continue to drive the industry to minimize those emissions. Although urea–formaldehyde (UF)-based adhesives have received the most scrutiny and have seen the most development work related to emissions, the other formaldehyde-based systems will be expected to provide environmental compliance in service. In addition, expectations for PF systems will also include assurances that residual phenol is not present in the panels made with them. Though such improvements will require the commitment of overburdened technical resources, these trends are not going away, and ought to be faced squarely, with a positive advantage going to the best solution providers.

In 1987, the U.S. Environmental Protection Agency (EPA) classified formaldehyde as a probable human carcinogen under conditions of unusually high or prolonged exposure [5]. Studies of industrial workers have suggested that formaldehyde exposure is associated with nasal cancer and nasopharyngeal cancer, and possibly with leukemia. In 1995, the International Agency for Research on Cancer (IARC) concluded that formaldehyde is a probable human carcinogen. In a re-evaluation of existing data in June 2004, however, the IARC reclassified formaldehyde as a known human carcinogen [6].

According to the US EPA [7], medium density fiberboard (MDF) contains a higher resin–wood ratio than any other UF-pressed wood product and is generally recognized as being the highest formaldehyde-emitting pressed wood product. Other pressed wood-based products that contain PF resin generally will emit formaldehyde at considerably lower rates than those containing UF resin.

International standards for formaldehyde emissions have been steadily trending stricter over the last several decades. Currently, the toughest standards are found in Japan, followed by Europe, and then North America. Prudent panel manufacturers wishing to produce in or export to those regions must pay careful attention to the respective formaldehyde emission requirement standards. The Japanese F**** standard is by far the most stringent standard, followed by the European EPF standard, 1/2 E1. In the United States, the California Air Resource Board (CARB) set a new benchmark in 2007, which is likely to have a cascading effect throughout the North American panel industry and among imported wood panel producers (see Table 8.1). Regardless of one's location, the imperative for the development of cost-effective bonding solutions with low emissions is as great as ever. New solution technologies from the adhesive manufacturers will pave the way towards greener in-service panel performance. One such example, the AsWood$^{\text{TM}}$ technology by Dynea, significantly reduces formaldehyde emissions to the near-background levels of wood itself by using a protein-modified PF resin as a binder component for the production of thin high density fiberboard (HDF) panels [8].

The lowest achievable formaldehyde emissions from industrially produced boards are more or less as low as the formaldehyde emissions from raw wood only subjected to a drying process.

8.5 Economic Factors

The ever present competitive market pressures place demands on adhesive suppliers to create added value for their composite manufacturing customers. One example is the usage of liquid versus powder PF adhesives for OSB. Under certain circumstances related to distance from the production site to the mill, liquid resins cost less to process, but more to transport, while powder or spray-dried resins cost more to process but less to transport. While each has certain technical advantages, overall economic and technical values determine usage. Since 2003, the cost of energy had been trending higher until mid 2008, doubly impacting composite productions costs: indirectly through the cost of adhesives and other chemicals and directly through the cost of running dryers and hot presses. Here again, the manufacturer will evaluate how much performance the adhesive delivers at a given cost. One of the technical drawbacks of PF resin compared to the alternatives is its relatively slow cure speed that requires more time and heat to cure it than UF, melamine–urea–formaldehyde (MUF), melamine–formaldehyde (MF), or MDI. The deficiency due to the mediocre PF cure speed is probably considered the single PF resin characteristic most in need of significant improvement.

8.6 Process and Equipment Factors

8.6.1 Continuous Press

The market introduction of continuous presses has probably been the biggest challenge for the PF binders for wood composites in general as well as for LVL in particular. The attainable line speed using continuous presses experiences a significant increase compared to the maximum possible with traditional multi-opening presses. In Europe, PF binder systems for OSB and PB have been almost fully replaced by other binders such as MUpF and pMDI due, among other factors, to their slower cure rate.

8.6.2 Steam–Air Preheater

The introduction into the market of the preheater (such as ContiTherm® from Siempelkamp), positioned in front of a continuous OSB or MDF press, has allowed line speed increases. Most new OSB lines will be fitted with this new type of preheater. In the preheater, wood fibers or flake mats are heated in a double-screen conveyer, and then heat is transferred into the mattress via a steam–air mixture. On the opposite side of the mattress, a vacuum system facilitates rapid heat penetration into the core, increasing the temperature by up to 90°C in 10 s [9]. The preheating temperature can be precisely set by adjusting the amount of steam in the mixture. The rate of steam introduction in the mixture will affect the final moisture content of the mat. The temperature increase in the core of the mat permits production line speed increases of between 20% and 40%. One of the probable disadvantages of preheater usage for OSB is that the moisture content increase in both layers contributes to a reduction of the compaction ratio through less densification of the face layer, thereby affecting the vertical density profile. If the press closing strategy or the overall panel density is not changed in order to compensate for the lower panel surface density, then the panel bending properties may suffer.

8.6.3 Radio Frequency Preheater

One combination of radio frequency (RF) and conventional heating applies RF at the beginning of the process. RF current induces uniform heating of the mass, in this case wood, so that the core is heated as fast and to the same temperature as the surfaces. This process stands in contrast to heating generated by other heat sources such as steam, due to conventional hot platen heating of moisture present in the wood furnish, where the heat diffuses slowly as steam from the top and bottom surfaces to the core. The result is that RF current gives a very fast, uniform temperature rise, and this phenomenon can be used to advantage for certain applications. The electromagnetic radio waves used in RF heating range in frequency from 2 to 30 megacycles, which is slightly above the so-called "broadcast range" of 0.5–1.6 megacycles [10]. RF for preheating or even resin cure is more widely used in structural wood and furniture than on other engineered wood products; however, RF has found its way into the production of LVL, as most of these products range from at least 45 mm to 150 mm-thick billets. As LVL is generally thicker than ordinary plywood, it takes more time to cure inner glue lines with conventional hot-pressing. Because heat transfer occurs in veneer-based wood composites by thermal conductivity from the outer veneers to inner veneers, production efficiency decreases as thickness increases. Thus, achieving the required temperature to cure the inner glue lines near the core veneer almost necessitates the use of high-frequency heating. [11]. The use of RF, however, requires the use of two presses, one where the RF is applied and a second one where the final hot pressing is performed.

8.6.4 Microwave Preheater

Microwave technology [12] has also been applied to the production of mainly thick LVL to preheat the core veneer of thick LVL billets. In contrast to the conventional presses and RF technology, microwave heaters target the core of the LVL wood-adhesive assembly, thereby changing the temperature gradient, thus obtaining a cycle time reduction. This technique may also allow the use of higher moisture content veneers. Microwave technology does not require the use of an extra press as is required with RF. Another difference is that with microwave technology, thinner billets can be produced.

8.6.5 *Dry Blending on MDF*

Almost all MDF produced around the world is based on the use of the blow-line addition for resin application. Phenol–formaldehyde resins are not recommended for MDF production mainly due to two reasons: first, due to a tendency to plug the blow line and second, due to a tendency to cause fire on the site. Very little effort has been made to minimize these problems through resin chemistry. The introduction of a new generation of “Dry Blender” equipment into the market by Siempelkamp and Dieffenbacher [13], however, may open the way for the use of phenol–formaldehyde resins in thin MDF and HDF where amino resins have difficulty in achieving very low formaldehyde emission levels, providing potential opportunity for PF technology. Furthermore, both machinery producers claim to need lower resin loads compared with the blow-line addition, thus also making the use of phenol-based resins more competitive.

8.6.6 *Foam and Liquid Extrusion for Plywood and LVL*

Extruded liquid or foam adhesives provide 20% and 30% reductions, respectively, in glue-mix application compared to other glue-mix application methods (see Table 8.2). Foam extrusion requires more sophisticated glue-mix components than previous application methods. Among the glue-mix components, animal-dried blood powder or blood protein is used as a foaming agent [15]. Some advantages of foam extrusion are the low glue spread required, ease of control, and the ability to glue rough veneer. The foam glue line provides a volume that is six times greater than the one obtained by roller coating. Among the disadvantages of foam extrusion are the investment cost for new equipment and the frequent cleaning required, due to the bacterial growth from microorganisms’ feeding off of blood proteins present in the glue mix.

One main advantage of the liquid extrusion method is the reduced glue-mix amount that is required compared to the traditional application methods. A second main advantage is the ease of upgrading existing machinery from the traditional application equipment, such as spray or curtain coaters, to the liquid extrusion method, with much lower cost as compared to foam extrusion. Furthermore, liquid extrusion is also easily controlled and maintained. Its construction provides

Table 8.2 Typical glue mix rates according to application method[a]

Application	Hardwood (g/m^2)	Softwood (g/m^2)
Foam extruder	115	125
Liquid extruder	140	160
Curtain coater	160	180
Spray	160	180
Roller coater	160	200

[a] According to Raute Corporation, Nastola, Finland [14]

flexibility for glue-spread application, where it is possible to apply varied glue-mix spread rates onto different veneers.

8.7 Application Requirement Factors

The main factors for the use of phenolic resins in structural wood-based composites, such as plywood, OSB, LVL, PSL, Glulam, and those products based on them, have been the requirements for exterior applications and for reasonable productivity expectations. Most of these requirements are based initially on solid sawn lumber performance and on engineered product performance when using phenol–formaldehyde or resorcinol-fortified phenol–formaldehyde (PRF) resins. PF and PRF resin systems are preferred for most of these types of wood-based composites around the world, especially in North America and Japan. In Europe, however, the trend is towards MUF, MUpF (>20% melamine weight on weight), or MF in Glulam and the OSB face layer. Since modern machinery allows faster line speeds, the requirement of quick curing resins has become an issue. Melamine-rich amino systems, such as MUF, MuPF, MF, and MDI resin systems, have been favored, as they can cure in a much shorter time than established systems such as PF. In general, other factors, such as the glue-line color and formaldehyde emissions, are less important compared to the other application requirements, although for the German construction market for OSB in particular, these two factors are of great importance.

8.7.1 Plywood

Plywood is probably the oldest engineered-wood product, dating back to ancient Egyptian civilization. But it is only since the 1930s that plywood could be used as construction material possessing an exterior durable bond with the introduction of PF resins [16]. For interior application, the use of UF or melamine-fortified UF resins is widely favored. In North America, South America, Japan, and Europe, PF resin is the preferred system for plywood. In China and South East Asia, this resin system is less prevalent; instead, MUF resin is the adhesive system of choice, with one of the main reasons being their higher tolerance of veneer moisture content variations. Plywood remains one of the two main wood composites that use phenolic resins, as many of their uses and production methods favor the use of this type of resin.

8.7.2 Laminated Veneer Lumber

The commercial utilization of LVL as a high-grade structural member started around 1971 in North America [16]. With LVL, long-span structural members can be manufactured, thereby increasing architectural design flexibility. Most LVL is bonded with PF resins combined with filler and/or extenders. The bulk of LVL produced is used as flange material for wood I-joists and as beams or headers. In the production of LVL, phenolic resin is the predominant type of resin. Some have started to use resorcinol-reinforced phenolic resin to reduce the pressing time. Like plywood, LVL will continue to be manufactured using these types of resin systems.

8.7.3 Oriented Strand Board

OSB has been available since the early 1980s. OSB is widely used in North America for roof or wall sheathing, siding, subflooring, and as web-stock for wood I-beams. OSB has replaced plywood in all the above-mentioned applications due to its attractive wood utilization economics coupled with decent physical properties. In North America, OSB is mainly glued with PF resins, in liquid or powder form, with a substantial minority of production lines bonding with MDI. As shown in Fig. 8.5 the consumption of phenolic resins in OSB has surpassed that of plywood, becoming the main driver in wood composites. In Europe, in contrast, most OSB production is based on MUpF and MDI as binders for face and core layer, respectively, though some mills use only MDI on both layers for niche products.

8.7.4 Structural Composite Lumber Products

Structural composite lumber products are used as load-bearing wood members and have evolved commercially over the last four decades. These products combine wood veneer, flakes, strands, or other geometries with adhesives to form large-dimension composite lumber, such as LVL, parallel strand lumber (PSL), oriented strand lumber (OSL), Scimber, Glulam, etc. Such engineered wood products originally emerged with the use of glue-laminated beams, the production of which is based on solid sawn lumber. PSL and its related product, OSL, are perhaps the newest members in the category of SCL products that have been commercially available in North America since 1990. PSL gives more design flexibility compared to LVL [16]. Another kind of SCL, Scrimber, taking advantage of scrimmed particle geometry, is in the development phase.

Most of these products were initially manufactured using PF resins, and now in certain applications with PRF resins. PRF is very well suited for Glulam due to the cold-set curing properties required in manufacture. PRF resins will cure at room temperature by the addition of a formaldehyde source such as paraformaldehyde or hexamethylenetetramine. Since PRF was the first glue system used for laminated beams, the standards developed have been based on this resin system. New glue systems have been introduced, but have not always provided the specific performance level of the PRF systems, even though they may have been well suited for the application. This variation in standards and specific performance is one of the main reasons for the different usage trends around the world.

In Europe, MUF or MF resins are used in all climate classes and in all types of constructions, and are by far the most common systems currently in use for laminated beams in Europe. New adhesive systems such as Emulsion Polymer Isocyanate (EPI) and Polyurethane (PUR) have also been introduced, but with a more limited application range. In Japan, PRF and EPI resins are the preferred adhesive systems used for bonding beams. PRF is used for outdoor construction and EPI for indoor construction, while MF is only permitted for finger joints. In the USA, PRF has been and still is the most common glue system for laminated beams. The production equipment is generally not as modern as in Europe. Melamine-based resins were introduced many years ago and then they required 60% MF solids on total solids, but have not really penetrated the market.

8.7.5 Hardboards and Light Fiberboards for Insulation Purposes

The worldwide production of fiber-based panels with densities below 500 kg/m^3 was approximately of seven million cubic meter in 2005 (FAO, 2005). The market for insulation fiberboards started to pick up at the end of the nineties owing to the increased awareness among customers about the ecological aspects. Despite the fact that new dry production processes for insulation fiberboards have been developed, the wet process is still in use. The main European growth is occurring in Eastern Europe. The wet process uses mainly PF resins, with resin loading up to 4%, while the dry processes do not use PF resins [17].

8.7.6 PB/HDF/MDF

The use of PF resins in particle board (PB), MDF, and HDF has been decreasing over the last few decades. Panels produced with phenolic resins have excellent weathering properties, making these resins appropriate for exterior-grade structural panels; however, the use of PB, MDF, and HDF as exterior panels is less common. For interior use, panels made with amino resins are more cost competitive than phenolic resins. However, phenolic resins are still used on these types of panels for certain niche applications. The introduction of the CARB regulation concerning panel formaldehyde emissions will revitalize the use of phenolic resins, as they can be exempted from the continuous testing required when using amino resins.

8.7.7 *Novel Products*

8.7.7.1 Bamboo Fused Parquet

Bamboo fused parquet is a novel product in the market, produced mainly in China and other places in Africa. Bamboo strips are converted into fibers. There are two types of products depending on the color. For light color products, the strips are treated with chemicals to stop discoloration. Alternatively, some material is caramelized, giving the fibers a brown color. Dried fibers are dipped in a solution of PF resin for a few minutes, removed, and then dried until they reach the moisture content of the original bamboo. The resinated fibers are then placed in a three-sided steel mold inside a press, and then subjected to extreme high pressure. The compressed bamboo fibers are then placed in an oven to cure the resin. The fused bamboo block is then removed from the mold and cut up into parquet-like pieces. The product is of very high density possessing great dimensional stability and is useful for flooring [18].

8.7.7.2 Scrimber

Scrimber was invented by J.D. Coleman with CSIRO in Melbourne, Australia in 1975. TimTek, LLC, has acquired the rights to those original ideas and has worked to further develop the process [19]. The TimTek process forms high-strength, engineered lumber using small-diameter trees that are crushed into scrim strands, thereby capitalizing on underutilized first-thinnings from pine plantations in the 3–8 in. (7.5–20 cm) diameter range. Coated with an exterior-type adhesive and dried, the scrim strands are then formed to the desired billet dimensions in a specialized steam-injection hot press. The aim of the scrim-based product is commercially viable engineered lumber wood products, with properties similar to other structural engineered lumber and with the high-strength properties of select-grade sawn timber [20].

8.8 Current Chemistry Solutions

8.8.1 *Standard Phenol–Formaldehyde Systems*

8.8.1.1 Recent Kinetics and Mechanism Research

Since alkaline resole phenol–formaldehyde resins are so important for adhesive wood bonding, much attention has been paid to their chemistry, with focus especially on the kinetics and mechanisms of methylolphenol-condensation reactions. The longer range objective of the research has been to apply this fundamental understanding of PF chemistry to improve the cure speed and reduce the energy needed for resin cure. Even though PF resins have been in use for a 100 years now, understanding of this chemistry is still incomplete and even subject to considerable controversy. Several research groups have attempted to shed new light on the kinetics and mechanisms of PF condensation and acceleration in recent years in the hope that their insights would lead to improved PF reactivity with greater selectivity and reaction control.

8.8.1.2 PF Resole Condensation Chemistry

Researchers in Japan, especially Professors Higuchi and Morita, have conducted extensive work on PF condensation chemistry. Higuchi et al. led studies on condensation kinetics and reaction mechanisms using the model compounds 2- and 4-hydroxymethylphenol (HMP) [21,22], while Morita et al. have done similar work for 2,4-dihydroxymethylphenol (DHMP) and 2,4,6-trihydroxymethylphenol (THMP) [23–25]. The studies investigated condensation of the PF model compounds in aqueous alkaline solutions. The studies demonstrated that the condensation of 2-HMP was truly first order. They also showed that the reaction rate was also dependent on the NaOH/2-HMP molar ratio, with the rate increasing to a maximum at 0.1 and then decreasing thereafter. They attributed the results to the formation of a quinone methide intermediate [21]. In another part of the study, they examined the base-catalyzed self-condensation of 4-HMP and found a fractional reaction order of 1.3, concluding that unimolecular and bimolecular reaction mechanisms were occurring simultaneously. The rate controlling unimolecular reaction was attributed to the formation of quinone methide intermediates. The bimolecular reaction was considered to be the combination of methylolphenol reactions in neutral (φ-OH) and anionic (φ-O^{-}) forms with three possible combinations: φ-OH$\cdot\varphi$-OH, φ-OH$\cdot\varphi$-O^{-}, and φ-O$^{-}\cdot\varphi$-O^{-}. The maximum reaction rate occurred at the NaOH/4-HMP molar ratio of 0.1 for the unimolecular reaction and 0.5 for the bimolecular reaction and is indicative of the multiple reactions occurring. They also found that 2-HMP condenses slower than 4-HMP, attributing the slower rate to intramolecular hydrogen bonding of the 2-HMP hydroxymethyl group with the phenolic hydroxyl [22].

In the research by Kamo et al. with 2,4-DHMP and 2,4,6-THMP, they found that no 2-2′ isomers formed, only 2-4′ and 4-4′ isomers. The reaction rates and products indicated that 4-4′ reactions were more preferred to 2-4′ reactions. The slower condensation of the 2-HMP position was attributed to hydrogen bonding to the phenolic hydroxyl hindering access to reaction. The self-condensation for 2,4-DHMP had a fractional reaction order of 1.1, another indication of multiple mechanisms. Interestingly, the reaction order for self-condensation of 2,4,6-THMP was 2.0 when concentration was greater than 1.5 mol/L, indicative of the bimolecular mechanism. On the other hand, the reaction order varied from 1.2 to 1.6 with NaOH/P molar ratio when the concentration was less than 1.5 mol/L, implying that both unimolecular and bimolecular mechanisms were operative. They concluded that the reaction kinetics changed with species and conditions, that is, the exact reactants, and that concentration affects the rates and mechanism of reaction [23].

In order to better understand these concentration effects, Kamo et al. conducted additional experiments. The condensation rate of THMP showed complex dependence on concentration and on the NaOH/P molar ratio, with a maximum rate at NaOH/P of 0.5 for concentrations above 1.0 mol/L, but decreasing from there to a maximum at about NaOH/P of 0.2 for concentrations below 1.0 mol/L. Perhaps the most interesting conclusion was that the mechanism for self-condensation of THMP changed with concentration, with the unimolecular reaction favored at low concentrations and the bimolecular reaction favored at high concentrations. This interpretation can be rationalized as an effect where, in dilute solutions (i.e. less than 1.0 mol/L), the molecules are separated from one another by the solvent and favor unimolecular mechanisms, while at higher concentrations (i.e. greater than 1.5 mol/L), the molecules overlap sufficiently to favor a bimolecular mechanism, with the concentrations in-between representing a transition region from dilute solution to intermolecular overlap or entanglement. Thus, the unimolecular quinone methide mechanism predominates at lower concentrations, while the bimolecular reactions of dissociated and undissociated methylolphenols are prevalent at higher concentrations [24].

Kamo et al. continued to clarify the nature of the molecular interactions of THMP as a function of concentration and the effect they might have on condensation reactions. They used ^{13}C-NMR spin-lattice relaxation time (T_1) to determine the effect of THMP concentration and reaction temperature on hydrogen bond-related intermolecular associates based on the understanding that the relaxation time is dependent upon the onset of molecular aggregation after being perturbed by the magnetic field. They complemented these results with molecular orbital calculations. Their T_1 measurements decreased linearly with increasing concentration, showing an inflection point near 1.2 mol/L, showing that THMP is present as a single molecule in solution at lower concentrations, but in associated aggregates as concentration increases. They concluded that all hydroxymethyl groups associate more as concentration increased, but that 4-HMP does so more closely than 2-HMP, making their rotation in solution more difficult. They used the molecular orbital calculations to determine the most stable configurations for single molecules and for complexes of two and three molecules. For single molecules, the 2-HMP position rotates with more difficulty, as it exists either in a free state or in an intramolecular hydrogen bond with the phenolic hydroxyl group, while the 4-HMP group is relatively free to rotate. As the molecules associate with increasing concentration, the 4-HMP groups also hydrogen bond and thus, all groups have higher rotational energy. The theoretical calculations were consistent with the ^{13}C-NMR T_1 measurement results [25].

These Morita research group studies were based on the premise that better understanding of the condensation mechanism could result in improved cure speed and control over the product structures formed during the curing reactions. The Morita studies have clarified questions regarding the PF condensation mechanism, showing that the possibility of either unimolecular or bimolecular reactions depends on molar concentrations and molar ratios. These studies also provided insight as to why a hydroxymethyl group in the two positions is not particularly reactive for nonaccelerated reactions, suggesting how acceleration chemistries need to focus on reducing the activation energy of the appropriate intermediates through alteration of the electronic environment.

8.8.1.3 Accelerators for PF Resole Condensation

Research interest in PF condensation accelerators continues to be an area of great technical challenge in recent years in view of the relatively slow PF reactivity as an unresolved problem in industrial chemistry of substantial commercial significance. Although considerable progress has been made through the recent research in understanding the fundamental chemistry of various basic PF intermediates, more comprehensive work is still needed to resolve some of the remaining controversies and to harmonize the disparate results of the various investigating research groups.

Park and Riedl studied the effects of propylene carbonate (PC), sodium carbonate (NC), and potassium carbonate (KC) on cure acceleration of PF resins with differential scanning calorimetry (DSC) and ^{13}C-NMR [26, 27]. From DSC, they found that the relative acceleration rate was PC $>$ NC $>$ KC, although they thought that PC would have too short of a pot life to be handled in wood composite manufacture. The NC and KC showed increased conversion with concentration, while PC did so only up to 4% and then became slower as concentration increased. They interpreted this data as a possible view where the diffusion rate affected reactivity. The PC displayed autocatalytic kinetics above 110°C, while the NC & PC showed both n^{th} order and autocatalytic rate kinetics [26]. From ^{13}C-NMR, they concluded that PC led to increased functionality present on the PF resin, while KC and NC led to the appearance of 2-2′ linkages, in contradiction to some other researchers. Solid state ^{13}C-NMR identified 2-2′ linkages with PC, but peaks were obscured for the NC and KC samples, although caution was suggested with the peak assignment. They also found that all the carbonates gave a more flexible, less rigid resin than the PF control, with the PC being more flexible than NC or KC [27]. Although Park and Riedl were able to demonstrate the cure acceleration effect of organic and inorganic carbonates and hinted at the possibility of 2-2′ linkages, they left questions remaining as to the actual reactions, structures, and mechanisms that were occurring. In addition, they identified a potential drawback of accelerated PF systems for wood adhesives: the lack of reactivity control leading to pot-life problems and the risk of precure.

Kamo et al. also attempted to elucidate the cure acceleration mechanisms of PC with hydroxymethylphenols. The authors compared the effects of PC on HMP condensation reactions with PC hydrolysate, sodium bicarbonate ($NaHCO_3$), and ethyl formate. They found that as PC decomposes to bicarbonate and propylene glycol (Fig. 8.6), it accelerates the formation of 2,4′-diphenylmethane (DPM) from HMP in a manner analogous to ethyl formate. Yet, PC hydrolysate accelerates the formation of 4-4′-DPM from THMP as it is shown by $NaHCO_3$. The PC increases

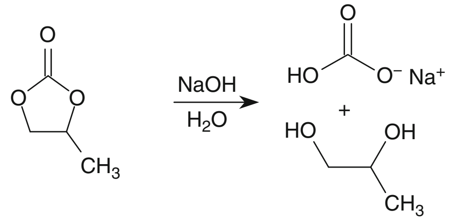

Fig. 8.6 Formation of $NaHCO_3$ and propylene glycol by alkaline hydrolysis of propylene carbonate [28]

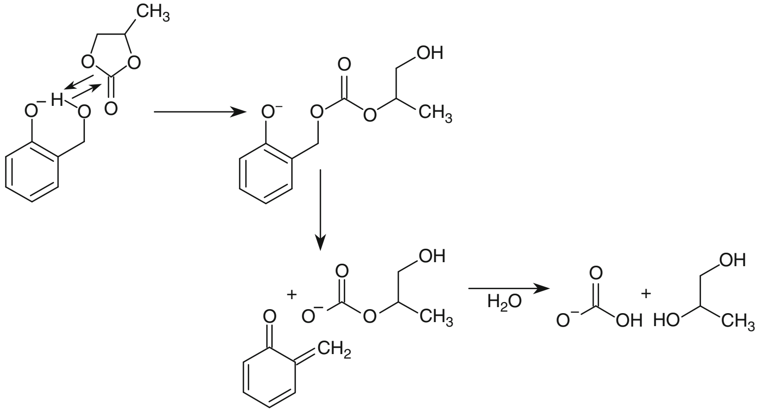

Fig. 8.7 Proposed transesterification reaction of 2-HMP by propylene carbonate to produce 2-quinone methide, bicarbonate, and propylene glycol [28]

the reactivity of the 2-HMP group, while PC hydrolysate and $NaHCO_3$ increase the reactivity of the 4-HMP group. Thus, for THMP, PC would first accelerate the 2-HMP condensation and then accelerate the 4-HMP reaction as hydrolysate. Although they regard transesterification as the mechanism (see Fig. 8.7), they observed no transesterification intermediates [28].

As a follow-up study, the same authors compared the catalytic effects of sodium bicarbonate ($NaHCO_3$) on 2-HMP, 4-HMP, and THMP condensation reactions by measuring the concentration and structural components with HPLC and ^{13}C-NMR. They also performed molecular orbital calculations for the compounds. They concluded that the 4-HMP and bicarbonate (HCO_3^-) facilitate a resonance effect on the dissociation of the HMP phenolic hydroxyl group. Computational models indicated that HCO_3^- forms hydrogen bonds with the two 4-HMP hydroxymethyls or with one 4-HMP hydroxymethyl and a phenolic hydroxyl group. Their proposed mechanism is one of electron delocalization with an electron forming an active species such as a 4-carbocation or 4-quinone methide (see Fig. 8.8) upon interaction of the 4-HMP methylol and the bicarbonate. Bicarbonate did not contribute to the structure of the finished product. Chemical shifts of ^{13}C-NMR indicate a change in the electronic environment on all carbons of the phenolic ring due to the presence of the bicarbonate, with the 4-position gaining higher electron density [29]. These

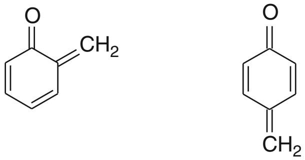

Fig. 8.8 Structure of proposed active species, 2- and 4-quinone methide

studies built on the earlier insight as to why a hydroxymethyl group in the two positions is not particularly reactive for nonaccelerated reactions and pointed out how accelerators may selectively enhance the reactivity of this troublesome functional group. The ultimate hope is that such insights will lead to a breakthrough for enhancing the reactivity of PF resins in industrial wood composites.

Conner et al. investigated accelerated curing reactions of model PF compounds using ethyl formate, PC, γ-butyrolactone, or triacetin. The relative rate of accelerator disappearance followed the order ethyl formate > propylene carbonate > γ-butyrolactone > triacetin, signifying that the accelerators were consumed in the reaction either by alteration or incorporation. Their data suggested that the accelerator was not incorporated into the structure and that the structures formed were consistent with a quinone methide or an S_N2 mechanism. The relative self-condensation rate of 4-HMP was faster than 2-HMP without the accelerator, but slower with it. Both 2-HMP and 4-HMP condense faster with the accelerator, but 2-HMP condenses faster than 4-HMP. Since the accelerator was consumed and the reaction could be resumed with an additional accelerator, the accelerators were not considered to be true catalysts [30].

Lei et al. used triacetin to better understand the mechanism of PF ester cure acceleration, considering PC unusable due to the pot-life consideration. The study involved the use of ^{13}C-NMR spectroscopy, MALDI-TOF mass spectroscopy, and gel permeation chromatography. They reported finding labile intermediates of the reactive species in the resin, attributing them to the diffusion-controlled stage of reaction. They concluded that the reaction mechanism was more complex than previously presented, proposing an anhydride intermediate to explain certain ^{13}C-NMR peaks they found. They also proposed meta substitution and Kolbe–Schmitt reactions [31].

Most of the acceleration studies focused on the relative reaction rates and possible mechanisms. An area that was virtually unexplored is the question of what is the fate of the accelerator after reaction, as those products might provide clues as to what reactions took place. In addition, none of the studies was comprehensive. Some covered PC and inorganic carbonates, others covered PC and inorganic bicarbonates, while others covered organic carbonates and esters. The researchers seemed to have some general agreement (though not complete) as to the possibility of two mechanisms occurring, one for esters and organic carbonates at the 2-HMP position and one for inorganic bicarbonates and carbonates at the 4-HMP position. Further work that is comprehensive in nature is needed to harmonize the available data and provide a clearer overview of PF cure acceleration reaction mechanisms.

8.8.2 *Extenders or Partial Phenol Replacement*

8.8.2.1 Sugar and Other Carbohydrates

Carbohydrates have been widely investigated as a co-reactant with phenol in the production of carbohydrate–phenol–formaldehyde resins. Chang and Kononenko [32] claimed to have developed a resin for plywood application based on the use of sucrose in the preparation of the PF resin. Mudde [33] described the acidic conversion of starch to 5-hydroxymethyl-2-furaldehyde (HMF) for condensing with phenol in a novolak resin. This method has been evaluated for the production of resol with other carbohydrates as starting material. The trial of sugar or other plant-derived carbohydrates as replacement for phenol in PF resins, however, has shown so far that the resins are not suitable for wood composites in exterior exposure, the main application of PF resins [34]. Aqueous solutions of phenol and formaldehyde are stabilized with at least one carbohydrate such as saccharose, glucose, fructose, maltose, starch hydrolysates, or molasses. The solutions are condensable and usable for preparing A-stage phenolic resin [35]. A thermosetting adhesive resin suitable for binding lignocellulosic materials to form products, such as plywood or particle board, is prepared by heating an aqueous sugar or starch solution in the presence of an inorganic acid or its ammonium salt and a metal ion catalyst to obtain a partially polymerized resin which is reacted with an organic acid anhydride just prior to application to the lignocellulosic materials. The adhesive formula contains no formaldehyde and the preferred aqueous solutions are whey or whey byproduct concentrates [36]. Experiments with bonded wood veneers using phenolic resins, in which part of the phenol–formaldehyde was replaced with carbohydrates, showed that the addition of nonreducing carbohydrates and various polyols to PF resol-resins did not adversely affect the dry- or wet-shear strength of 2-ply Douglas-fir panels bonded with those modified resins [37]. An alkyl glycoside, for example, methyl glucoside, is utilized in various ways in the manufacture of an adhesive resin for plywood application, as described by Drury et al. [38, 39]. Results from the use of polyols derived from lactose incorporated in the resin formulation showed no negative effect on the wet shear strength of southern pine plywood bonded with these whey-modified resins [40].

8.8.2.2 Tannins

Tannins have been used mainly as a substitute for phenol in the production of phenol–formaldehyde resins [41] and as an additive to accelerate the curing reaction [42]. Tannins are generally classified in two broad categories; hydrolysable and condensed. Condensed tannins are used the most. The main source is from *Acacia* bark (wattle or mimosa), *Schinopsis* (quebracho), and *Tsuga* (hemlock). Despite the fact that tannins contain many “phenolic or resorcinol”-like subunits, their use as phenol substitutes in standard PF production has not been entirely successful.

The use of tannin-based resins in the wood composite industry has been of more interest in the southern hemisphere than in the northern hemisphere due to the limited raw material supply.

Nonetheless, tannins have been used widely in current commercial resins systems, albeit as hardeners or extenders, and specifically in plywood applications. Tannin-based resins using formaldehyde or the copolymerization of tannins with phenolic or amino resins have been widely reported in the literature [43–48]. The importance of the flavonoid bond cleavage reaction in the preparation of cold set Glulam adhesives was demonstrated by Hemmingway et al. [47].

The use of tannin in the preparation of "Honeymoon"-type resin systems has shown to provide full weather and boil proof properties [49]. The honeymoon systems consist of a separate application system: a synthetic phenol–resorcinol–formaldehyde component with an extra formaldehyde donor to be spread on one of the surfaces and on the matching surface of a tannin sulphonate solution with an alkali catalyst. This system is used for cold-setting of finger joints and laminated beams (glulam). Resins based on plain tannin by auto condensation have been prepared in several laboratories around the world but none has been commercialized. One limiting factor for the use of the tannin-based resins in wood composites is that their high viscosity renders their handling more difficult. To minimize this problem, Pizzi et al. [49] describe different alternatives such as the use of alcohols or controlling the pH, as well as the use of subsequent acid and alkaline treatments of the tannin extract. Tannins of eucalyptus treated in accordance with the method described by Pizzi [49] were used in the preparation of adhesives for manufacturing flake boards with excellent results [50]. Resins containing commercially produced mild-sulfite pine tannin extract have been used as cold-set adhesives for manufacturing finger joints and glulam and have met the specifications of international standards [51].

8.8.2.3 Lignin

Lignin can be used in phenolic resins either as an extender or as a chemical modifier. Lignin use is based on the chemical similarity between phenol and the phenylpropane monomeric unit of the lignin. Lignin-sulfonates, a by-product from the sulfite pulping industry, are used mainly as glue-mix extenders in some wood-based applications. The use of lignin as a phenol substitute in standard phenol–formaldehyde resin production has been widely investigated with limited commercial success [52–57]. Contrary to tannins, lignin from either Kraft liquor or spent sulfite liquor (SSL) pulping processes has no advantage in terms of chemical reactivity or other relevant aspects, except perhaps as a low-cost polymer additive. Much of the difficulty in incorporating lignin into PF resins stems from a lack of beneficial effect on reactivity and consistency as a raw material.

Work by Ren et al. [58] using a modified Kraft lignin demonstrated that modifying white birch lignin with sulfur and sodium hydroxide resulted in a lowering of the methoxyl content, which increases the potential of phenol replacement by Kraft lignin. The bond quality of panels made with the modified lignin–phenol–formaldehyde resin was higher than for the unmodified resin. Vazquez et al. [59] showed through a structural analysis that methylolated lignins are suitable for the production of wood adhesives when studying lignin from a pine acetosolv process. Sellers et al. [60] reported that the use of organosolv lignin could replace up to 40% of the resin solids in a phenol–formaldehyde resin for the production of OSB.

8.8.2.4 Urea

The addition of urea into a finished phenol–formaldehyde resin is usually done to obtain altered physical properties, mainly to reduce the viscosity, with urea functioning as a solid solvent since it reduces the viscosity of the resin by the disruption of hydrogen bonds [61]. Furthermore, urea reduces the PF-free formaldehyde content and it allows a higher degree of resin condensation compared to the unmodified PF resin for the same viscosity. Post-added urea may not co-condense with the phenolic resin, but some researchers have suggested that urea actually may react with the phenolic methylol groups under certain conditions [62]. These authors also claim that co-condensation may occur in the hot press at very high temperatures [63–65]. If urea is regarded as a solvent and not as a resin or a co-reactant, that is, not considered as resin solids, then its use is beneficial for the production of boards since it allows the use of highly condensed PF resins and the use of less water as solvent and allows the use of higher resin loads. Low resorcinol content cold-setting urea–resorcinol–formaldehyde (URF) resins have been also prepared. According to the authors [66], most of these adhesives had water-resistant properties, whereas some also presented weather- and boil-proof adhesive characteristics and performance. Tomita et al. [67–72] have described how co-condensation between phenol and urea could be carried out via two different paths, one by reacting urea with methylol phenol, and the other by the acidic reaction of urea–formaldehyde concentrate (UFC) with phenol followed by an alkaline reaction. These observations by Tomita and co-workers provide some credence to the co-reaction hypothesis for urea with PF resin.

8.8.2.5 Resorcinol

Resorcinol has been used for the preparation of resorcinol–formaldehyde resins and phenol–resorcinol–formaldehyde resins. Phenol–resorcinol–formaldehyde is more commonly used than the pure resorcinol–formaldehyde mainly due to the cost of the resorcinol. These systems are used mostly as cold-setting glues for the production of structural Glulam, finger joints, and exterior structures. Historically, the phenol–resorcinol–formaldehyde resin was prepared by separate polymerization and subsequent blending of the two resins, resorcinol–formaldehyde and phenol–formaldehyde. The most common modern practice is to incorporate the resorcinol into a prepolymerized phenol–formaldehyde resin with low average molecular weight that is rich in methylol content. The resorcinol normally is in excess of the phenol–formaldehyde methylol groups, and allows it to react with the methylol groups, thereby forming a PRF polymer [73]. Phenol–resorcinol formaldehyde resins with a reduced amount of resorcinol can be obtained by the reacting small amounts of urea during resin preparation [73, 74].

8.8.2.6 Wood Pyrolysis Oils

Phenolic-rich pyrolysis oil can be produced by pyrolyzing lignocellulosic material, such as softwood bark waste, at very high temperature and pressure. Such phenolic-rich pyrolysis oils can be directly used in the preparation of phenol–formaldehyde resol resins [75]. Wang claimed that up to 35% of phenol could be replaced in a phenol–formaldehyde resin for OSB application and the panels could fulfill the Canadian Standards CSA O437.0-93 for OSB products [76]. Riedel et al. reported that three-layer panels made with resins having 50% by weight of the phenol replaced by pyrolysis oils on the surface layer resin and 25% by weight of the phenol replaced by pyrolysis oils for the core layer resin, had mechanical properties above the requirements specified by the Canadian Standards CSA O437.0-93 for OSB products [77]. They also found that resins having 25% by weight of the phenol replaced by the pyrolysis oils had similar kinetic curing behavior to the standard resins [78].

8.9 New or Alternative Technologies

8.9.1 Hybrid Systems

An increasing array of hybrid binders are becoming available in the market to meet the new demands being placed on wood composite binders, including various combinations of PF, UF, MF, MDI, and protein-based material due to the variety of raw materials.

8.9.1.1 PF–MDI Adhesive Systems for Wood Composites

Various recent efforts have combined PF and MDI resins to make wood composite adhesives by direct component mixing. US 6214265 outlines a process for binding wood using an adhesive composition comprising a polymethylene polyphenylisocyanate and a solid PF resole. Composites are made by pressing at 350°F for 4.5 min [79]. A related patent, US 6294117, describes a similar process, except using a solid PF novolac instead of a solid resole. Wood composites are made by pressing at 350°F for 4.5 min. Both inventions claim formation of the composite within 2–10 min at temperatures of 120°C–225°C [80]. Another related patent, US 6224800, discloses the use of solid urea or melamine to extend polymethylene polyphenylisocyanate in wood composite binders. In it, particleboard panels are bonded at 350 or 400°F for 4.5 min [81]. In US 6297313, a sprayable adhesive system is described, which is useful for bonding lignocellulosic material at low cost, fast cure, and good performance. The adhesive system is an adhesive composition comprising an aldehyde resin and a polymeric isocyanate. The system can further include a carbonate material, preferably an organic carbonate such as PC, though no examples are given of its use or of its effect on viscosity stability, pot life, and cure speed. The mixed composition of the adhesive system is required to have a viscosity of not more than 500 cps and a pot life of at least 2 h. The preferred system has a Differential Scanning Calorimetry (DSC) onset temperature of 115°C–125°C. The adhesive composition can be mixed prior to application, and can be mixed with an in-line static mixer. In the example, lignocellulosic wafers are pressed with the inventive adhesive system for 120 s at 420°F [82].

Presently, the Frazier research group at Virginia Polytechnical Institute is promoting academic studies into the nature of PF–MDI hybrid adhesive systems. Frazier and co-workers are seeking a fundamental understanding for developing wood binders comprising PF–MDI hybrids, under the assumption that by combining the two resins, the strengths of each could be maximized while minimizing their weaknesses. A key finding was that the two resins formed a two-phase emulsion due to immiscibility of the aqueous PF in the neat MDI. It is believed that the emulsion effect would create a significant obstacle to the industrial application of PF–MDI hybrid adhesives [83]. The Frazier group carried out further follow-up studies of PF–MDI systems with the observation that MDI droplets formed a second separate organic phase in an aqueous PF resin that was preserved in the morphology of cured resins. They also found that MDI accelerated the cure of PF resin continuous phase in DSC studies, but the effect was not observed by dielectric analysis in the bondlines of wood composite during fabrication [84].

Other recent work has combined PF and MDI resins to make wood composite adhesives by chemically modifying or blocking one of the components. JP 10306271 A2 documents an adhesive composition for bonding wood, which cures rapidly at low temperature, by using a water-soluble blocked isocyanate as a cure promoter. This adhesive comprises a PF resole resin, a water-soluble blocked isocyanate, and a water-soluble Lewis acid magnesium complex as a curing agent. An F:P molar ratio of 1.6–3.0 and a temperature of 80°C–100°C are preferred to dissociate the blocked isocyanate [85]. The US patent 6416696 reveals a process for the production of wood composite products of a binder composition comprising an aqueous dispersion of blocked polyisocyanate component and an aqueous solution of a phenolic resin. The invention resolves the problem of the limited pot life of mixtures of aqueous PF and neat MDI resins by blocking the MDI so that it can be dispersed in water. Suitable blocking compounds include certain oximes. In an example, oriented strandboard is prepared by pressing with the inventive composition for 8.5 min at 400°F [86]. US 6478998 provides a hybrid resin formed by mixing an acylated PF resin with a polymeric phenyl isocyanate resin to form a single-phase liquid material having extended shelf stability and yet faster cure than any of its components when used in conventional flakeboard, strandboard, or other board-making processes carried out at elevated temperatures of 125°C–225°C [87].

Some of the latest technological developments are distancing themselves from the traditional adhesives and have suggested the desirability of ambient cure systems for wood composites. In US 2007/0102108 A1, a process is disclosed for making wood laminates using fast-setting adhesives at an ambient temperature ranging from 0.1 to 20 min of pressing. The fast-setting adhesive comprises a compounded emulsion polymer that may be an emulsion polymer isocyanate and a cross-linker that is an isocyanate, an aziradine, or an epoxy compound. The process is useful for bonding surface layers of wood veneer, plastic sheet, metal, or Kraft-paper laminate to a substrate core layer of wood veneer, oriented strandboard, particle board, plywood, or medium density fiberboard [88]. Some researchers are advocating the development of rapid, low-temperature electron beam-curable resin systems for wood adhesives. They estimate that such systems offer potential energy savings to the wood composites industry of 65 trillion BTU/year at full market penetration. The reduction of curing temperatures from 450°F to 250°F is possible with beam-curing systems, and also offers the potential of reducing unit capital costs and doubling throughput. The lower curing temperatures would also decrease process emissions by reducing VOCs. It is stated that "the global objective for this project is to produce new adhesives for wood composites that can be cured at low temperatures, with little drying of raw materials, and virtually instantaneously. This offers tremendous energy savings over more commonly used methods to cure wood adhesives [89]." Another project is focusing on the "development of a novel adhesive for cold-press production of LVL" with the objective of developing novel moisture-curing polyurethane adhesives for the cold-press manufacture of LVL made from high moisture content wood. Realizing the project objective would reduce energy consumption through the elimination of hot pressing and through substantial reduction of wood drying. Reduced wood drying will also curtail VOC production. The project intent is to research 100% organic isocyanate-reactive polyurethanes and reactive latexes cross-linked with polyisocyanates [90].

8.9.1.2 PUF Systems

He and Yan investigated the effects of formulation variables of co-condensed alkaline phenol–urea–formaldehyde (PUF) resol resins on thermal curing properties using Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). They were able to demonstrate a strong pH reactivity dependency and the presence of multiple reactions during cure [91]. He and Yan also investigated the effects of formulation variables of co-condensed alkaline phenol–urea–formaldehyde (PUF) resol resins on their structure, composition, and thermal curing properties. They used liquid ^{13}C-NMR to yield information regarding reaction mechanism, composition, and structure of the uncured PUF resol. Solid state ^{13}C-NMR was conducted to characterize the network structure of the curing or cured PUF resin. They found that urea co-condensed with methylolphenols almost exclusively in the para position to form methylene-bridged structures, while no ortho urea–methylolphenols formed, suggesting that the effect was due to the higher reactivity of the para methylolphenols. Further, the ureas formed ether bridges with other methylol ureas but not with methylolphenols and were absent above pH = 13. They concluded that pH influences the structure and composition of the liquid resin, with the ratios of para to ortho methylolphenols and para–para to ortho–para bridges decreasing with increasing pH. Urea methylene ether bridges were not present in the cured state [92].

8.9.1.3 Proteinaceous Natural Component Modified Phenol–Formaldehyde Resin

European patent application 1318000 A2 describes resin compositions comprising a naturally occurring proteinaceous component, phenol, and formaldehyde, where the naturally occurring component is chemically bound to a PF resin structure to form a protein-modified PF resin. The resin compositions are useful as binders for lignocellulosic or cellulosic materials, providing an excellent combination of low formaldehyde emissions and high strength (see Table 8.3) [93].

8.9.2 Protein-Based Systems

In the United States, Heartland Resource Technologies is developing soy protein-based adhesive technology for use in engineered wood products that is being marketed during 2009 as Soyad®. Product advantages are its environmental friendliness, renewability, reduced formaldehyde usage, and reduced need for petroleum-based materials. They claim that the technology can substitute for phenol formaldehyde adhesive or isocyanate adhesives, with no reduction in performance. Hardwood plywood and oriented strand board (OSB) are target product markets. They also claim that their technology is superior to a cross-linking technology for soy protein developed at Oregon State University (OSU), as described in US Patent 7252735 [94,95]. The OSU technology relies upon an epichlorohydrin adduct with a polyamidoamine resin to cross-link reactive functional groups present in vegetable protein to yield moisture-resistant proteinaceous adhesives.

Table 8.3 Properties of HDF panels produced with EP 1318000 resin system [93]

HDF panel	Units	PF	Protein-PF	UF
Density	kg/m^3	957	938	940
Thickness	mm	2.99	3.14	3.08
IB	MPa	1.39	1.63	1.43
PV	mg/100 g	1.51	0.69	7.77
Resin loading	%	9	9	13
Line speed	mm/s	890	1,020	1,070

US patent 7345136 describes water-resistant vegetable protein-based adhesive dispersion compositions and the methods for preparing them. Typical dispersions are prepared by copolymerizing a denatured vegetable protein that has been functionalized with methylol groups prepared via reaction with formaldehyde with one or more reactive co-monomers based upon phenol, melamine, urea, and/or urea and acidifying the adhesive dispersion. The adhesive dispersions are claimed to provide superior water resistance and can be used to bond wood substrates such as panels or laminates [96]. The US patent 6306997 discloses soybean-based adhesive resins and composite products made from them. The adhesive resin includes soybean flour and a cross-linking agent that is reacted with functional groups in the soybean flour [97].

Columbia Forest Products had implemented the Soyad® technology in seven of its hardwood plywood production plants by 2006 and had trials of the technology in particleboard production. In 2007, they formed the company Columbia Innovations to market Hercules' (currently Ashland Hercules) second generation Soyad® technology to other manufacturers [98]. Soyad® technology development has resulted in a joint venture between Hercules and Heartland Resources since 2007, named H2H Innovations [94, 99].

8.9.3 MUF/MUpF

In Europe, MUpF is the dominant binder preferred for the face layer of OSB in the industry, though some mills in Europe use MDI and PF in the face layer. For moisture-resistant particleboard and MDF, (moisture resistance requires passing the V-100 test, i.e. an internal bond test performed after 2 h in boiling water) MUpF or MUF are the main binders used in Europe and South East Asia. Although MUF/MUpF systems may not be as cost-efficient as MDI, their fast curing properties allow their use in the fast, continuous presses with improved productivity making up for the lost cost-efficiency. Furthermore, these systems do not require the application of release agents on the press platens that MDI requires. A recent patent, US 7422787, describes an MF adhesive resin for OSB which may also contain urea and phenol. The resin is suitable for both the core and face layers of OSB. The adhesive composition requires molar ratios of melamine to formaldehyde in the range of 1:0.8–4.0, with melamine to urea between 1:0 and 2.0, and the molar ratio of melamine to phenol from 1:0 to 2.0. OSB made according to the invention satisfies the requirements of the EN 300 standard for OSB/3 and OSB/4 [100].

8.9.4 MDI

Polymeric MDI is the dominant core layer binder in the OSB industry worldwide. Some mills use MDI in the face layer for all types of products or for certain product applications and markets but they need to add a release agent to protect the press platens. MDI is also used on particleboard and MDF for moisture-resistant applications and in small amounts up to 0.5% on dry wood in the core layer of particle board (PB) and as a strength enhancer allowing faster pressing time. The advantage of using MDI is its cost-efficiency and its excellent mechanical properties.

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Chapter 9
Foam

Marc Cornick

Abstract Phenolic foam is a unique cellular material that can be utilized in either a fully open cell structure or a completely closed cell structure in a diversity of applications such as open cellular material for floral foam, soil propagation media and/or orthopedic use, and closed cell phenolic foam primarily for thermal insulation. Thus, phenolic foam is much more versatile than other competitive organic foams such as polystyrene and polyurethane with the latter materials being more heavily involved in thermal insulation. Foam processing can consider batch, semi-continuous, or continuous conditions, and the features and weaknesses of the appropriate processes are discussed along with continuous mix heads involving high and low pressure conditions.

The use of phenolic foam for thermal insulation is quite active in Europe, particularly in the UK, and is being revisited in North America because of the efforts of a program sponsored by the US Department of Energy leading to proposed neutral pH foam and improved mechanical strength/performance. The latter is accomplished by the introduction of small amounts of chopped cellulose fibers into the resole resin prior to foaming.

New foam areas are described and include the use of foam for air filtration for dust control, carbon foam prepared by carbonization of phenolic foam and then used for high temperature structural composite sandwich panels or for composite tooling, and pultruded phenolic foam. The latter offers an interesting opportunity as a means of preparing sandwich structures continuously by foaming/pultruding between phenolic glass and carbon fiber prepreg face sheets. In a related matter, fiber reinforced pultruded phenolic foam is being developed to possibly replace balsa core currently used by the US Navy in naval ship sandwich panel structures.

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Different test methods are described such as fire testing, insulation efficiency, strength testing, and open/closed cell content. Saturation properties determination for floral foam is detailed.

9.1 Introduction

Phenolic foam is one of several organic polymeric foams that are used for thermal insulation and other foam related application areas. Compared to other organic polymeric foams, it is rather unique and can be used in such distinct applications that require either fully open cell structure for complete water saturation or closed cell structure for thermal insulation.

Organic polymeric foams for thermal insulation consist of phenolic foam, polyisocyanate foam (PUR), and polystyrene (PS) foam. The manufacture of these latter foam materials involves different processing conditions such as gaseous extrusion of molten PS into foam while the reaction of selected diols and diisocyanates with a blowing agent yields PUR. The phenolic foam procedure differs considerably from these other foam systems. The method for preparing phenolic foams requires the use of an oligomeric, heat/acid reactive resole resin which contains an emulsifier and a volatile blowing agent. Upon the addition of the acid catalyst, an exothermic reaction occurs that facilitates the volatilization of the blowing agent into small gas bubbles that become entrapped as the resin is viscoelastically and rapidly transformed from a liquid into a gel and finally into a rigid cross-linked solid thermosetting foam.

9.2 Foam Structure

Depending on the intended application of the polymeric foams, the cellular structure can be open cell foam or closed cell foam, see Fig. 9.1. In entirely open cell foam, the pores are linked together into a continuous interconnected network whereas in closed cell foams the individual pores or cells are not linked but separate from one another. The versatility of utilizing organic polymeric foam as either an open cell or closed cell material is rather unique. Obviously, there are advantages and disadvantages associated with either of these cellular structures and are discussed in this chapter.

All foams generally share the same basic advantage in that they combine a lightweight structure with a moderate degree of mechanical strength. These lightweight structures are often much more cost effective than their solid counterparts and provide additional benefits. In the case of open cell phenolic foams, these materials have a key feature that they can exhibit extremely high absorption properties. In the case of closed cell foams, these materials possess very good thermal insulation properties.

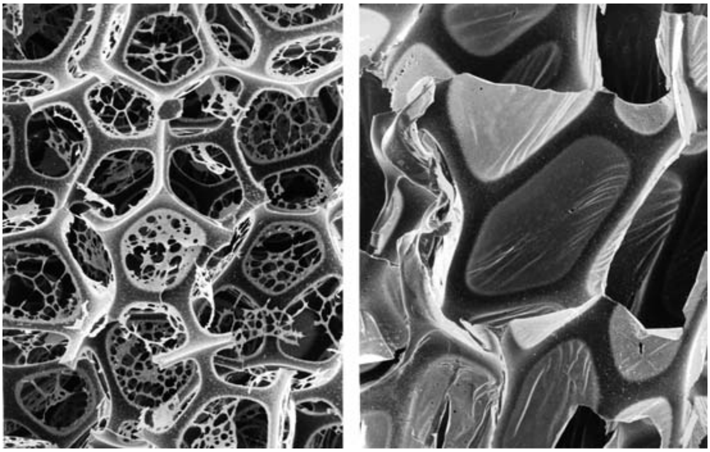

Fig. 9.1 Open and closed cell foams

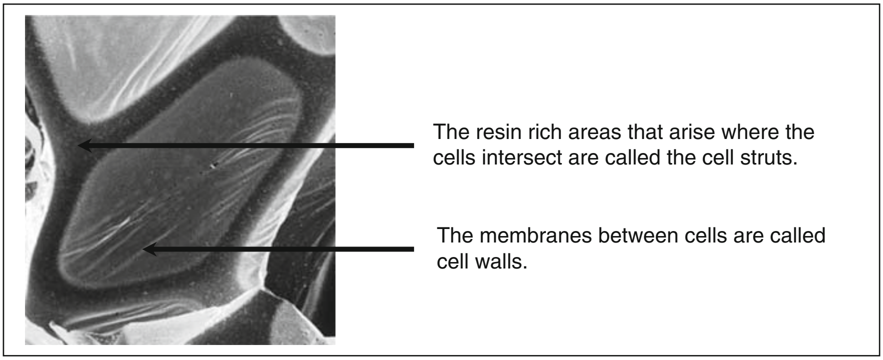

Fig. 9.2 Phenolic foam cell structure

The distribution of material in the cell struts and cell walls (Fig. 9.2) is extremely important in determining the properties of the resultant foam such as its mechanical strength and whether or not it will function as an open or closed cell structure.

The main applications of cellular phenolic materials are in the areas of floral foam, insulation foam, and mining foam which are discussed in the next section.

As end-use applications are widespread, it is difficult to obtain published data for the magnitude of the phenolic foam market; however, several key points can be made on their use:

- The floral foam market is quite well distributed globally, and has a long history in certain markets, that is, Central Europe, North America, and parts of the Asia–Pacific region. The main growth areas for this application are Eastern Europe and China.

- The insulation foam market is concentrated mainly in Europe and particularly in the UK and Ireland due to local building codes and impending legislation regarding the energy efficiency of buildings. There is also growing interest in these products in Eastern Europe and Asia. As will be discussed, there is a resurgence of interest in North America for phenolic foam for thermal insulation as a result of an ongoing program that is sponsored by the US Department of Energy.
- The use of phenolic mining foams is on the decline in most of its traditional market areas due to the general downturn of mining industry in those regions. Some use of these established technologies, however, does exist in Eastern Europe and China, where the mining industry is still relatively strong.

9.3 Foam Applications

9.3.1 Floral Foam

The principal application of open cell phenolic foam is in the manufacture of floral arrangements and tributes with cut flowers. A shaped piece of foam is used as the base for such arrangements and the flowers are pushed into the foam to form the final display.

The important properties of the foam are that it is friable enough to be easily penetrated when the flowers are pushed into it and retains sufficient strength to support the flowers. Further the material will both absorb and retain water so that the flowers remain fresh for the lifetime of the arrangement.

Floral foams can be made continuously on a foaming line or discontinuously in a block molding operation. The foam density for this kind of floral arrangement application is generally in the range of 30–40 kg/m^3.

Polyurethane floral foams are also available, but these are used in different applications to the phenolics. The general rule is that phenolics are used for wettable foams and polyurethanes for dry foams for silk or dry flower arrangements. However, there are some exceptions to these considerations.

A separate but related application area is that of agricultural foam. The foam material is used as a “growing media” or a propagation medium to support young flowers and other plants in the early stages of their growth. Cuttings from “parent” poinsettia plants can be propagated into this phenolic foam “growing media” in the autumn, and within a few weeks, they mature into blossoming poinsettia plants for consumers during the Christmas Holiday Season.

A number of development goals have been ongoing technical programs in the floral foam industry for a number of years such as pH neutral foams and biodegradable foams. Despite a number of patent disclosures that have reported some success for these technologies, their commercial use has not occurred.

In addition to these technological product developments, a great deal of technical effort has been made in the area of improving product quality and consistency through the use of modern mixing techniques and are discussed in further detail in a later section. Note that these equipment developments are also applicable to the area of insulation foams.

9.3.2 Insulation Foam

The phenolic foams used in this application compete with other insulation materials such as mineral wool, polyurethane (including polyisocyanurate) foams, and PS foams. Phenolic foams are more costly and are generally more technically difficult to produce. Therefore, they are only used where their unique combination of properties can offer a key advantage as detailed in Table 9.1. Phenolic foam exhibits favorable thermal insulation and fire resistance and "out-performs" the other organic polymeric foams as well as mineral wool.

It should be noted that for the majority of all phenolic foam insulation applications, the foam density is generally in the range of ca. 40–50 kg/m^3. However, there are some products that are produced at much higher densities. This would include for example, pipe supports for insulated pipework systems, which are mentioned later.

There are two main products in the phenolic foam insulation area and these are:

- Flexible faced panels for wall, floor, and ceiling insulation
- Shaped foam sections for pipe-lagging

Flexible faced phenolic foam panels can be produced continuously on a laminator machine or can be cut from block foamed material. The facing material can vary from application to application and can also be different on the two faces of the board. Common facings include – aluminum foils, paper substrates of different thickness and weight, various types of woven glass tissues, and combinations of these three materials.

A strong bond between the foam and the facing is required in most applications as delamination at this point in the structure of the board can lead to deterioration in key properties such as insulation factor and/or fire resistance.

Note that rigid faced insulation panels, where the facing material is, for example, steel plate, are also available. However, these are generally manufactured with a core of mineral wool or polyurethane foam. They can be manufactured using

Table 9.1 Properties of common insulation materials

	Phenolic foam	Mineral wool	Polyurethane foam	Polystyrene foam
Thermal insulation factor	Good	Poor	Good	Poor
Fire resistance	Good	Good	Poor	Poor

phenolic foam but these are less common. The reason for this is that the extreme rigidity and friability of the phenolic material can lead to delamination when used in conjunction with a facing material such as steel plate. This can cause the problems mentioned above for the same type of failure in flexible faced panels.

The use of phenolic foam for thermal insulation in North America is being revisited mainly due to the efforts of Jan Kosny of Oak Ridge National Laboratories (ORNL, <?xml:namespace prefix = st1 ns = "urn:schemas-microsoft-com:office:smarttags" />Clearwater, FL) and a consortium of collaborators consisting of Kingspan (UK), Kazak Composites (Woburn, MA), University of Southern California (USC) and others. Phenolic foam for thermal insulation was introduced in the 1980s in North America but was withdrawn from the market in 1992 due to corrosion problems occurring from roof decking components caused by relatively low pH (~2.5) foam. The current program sponsored by the US Department of Energy involves a re-examination of the role of acid catalysis of resole resins for foam with the objective of preparing phenolic foam with a pH of ~6 [1] and better foam adhesive and mechanical strength using cellulose fibers (proposed by Kosny) as reinforcing agent in the foam. Some success in increasing the pH of the foam has been achieved by Kingspan and Kazak Composites, members of the ORNL consortium, with insulation phenolic foam possessing a pH of ~5 by using a selective mildly, basic inorganic filler as an additive in the resole formulation [2].

Studies supported by ORNL and conducted at USC involved the introduction of modest amounts of cellulose fiber (1–4%) for fiber reinforced foam with low foam densities of 48–64 kg/m^3. Test values indicated that increased peel strength by up to tenfold, and flexural strength of sandwich beams increased by up to 60% are obtained; yet compressive strength was unaffected. Fractography revealed evidence of extensive bridging, crack deflection, and fiber pullout, reassuring that cellulose fibers provide reinforcement. Various facings (skins) or composite elements do not adequately adhere nor exhibit mechanical integrity (mentioned above) when applied to the unreinforced foam and are possibly not suitable for applications in structural insulated panels (SIPs). Ongoing efforts with Kingspan indicate that in the near future Kingspan may fabricate better fiber reinforced foam that is in full compliance with Structural Insulated Panel Association recommendations. Novel SIPs made with a layer of reinforced phenolic foam sandwiched between two sheets of structural board such as OSB or cement-based composite boards are being evaluated with this newly developed reinforced foam. ORNL is building four zero energy houses with novel configurations of building envelope. One of these houses has a residential roof based on phenolic foam insulation systems from Kingspan.

Pipe lagging is normally manufactured in C-sections and these can also be produced continuously or can be cut from block material. In the continuous method a special type of extruder is used. In this process an "O" shaped foam tube is formed by a moving outer mold and a static inner mandrel. In-line slicing/cutting techniques are used to turn the extrudate into the final C-sections that are required.

Facings are also used in the pipe lagging application and are similar to those mentioned for flexible faced panels above.

One further development of the common pipe-lagging foam product is a material which is used in pipe supports. The material should have a good insulation factor but must also possess high strength to be resistant to the crushing force caused by the supported pipe. The additional strength can be achieved by producing a foam material at a much higher density (ca. 160 kg/m^3 as compared to 40 kg/m^3).

The total sales volume of European insulation industry is about 10 billion euros [3] and although cellular plastics are a relatively niche area presently within this industry they are set to take the majority share of this market by 2011 [4]. It is anticipated that cellular plastics such as PUR, PS, and phenolic foam will possess a majority share.

9.3.3 Mining Foam

This application is rather different to the last two that have been mentioned as this involves the use of an in-situ or spray-in-place system. Phenolic foams are only one of a number of cellular polymers that are used in different applications within the mining industry (Table 9.2).

During mining operation, if the mineworkers break into a void that has the potential for collapse, then the void must be filled in order to eliminate the possibility of an accident. The void is first screened off and then filled with a foaming mixture that will expand and form a plug of foam completely filling the void thereby preventing collapse. The density of the foam material is quite variable as is the open/closed cell content of the foam.

Due to the potential danger that can occur in an underground explosion, these systems cannot use explosive, flammable blowing agents and instead rely on CO_2 (emerging from the reaction of a carbonate with the acid catalyst in the foaming formulation).

9.3.4 New Applications for Phenolic Foams

A number of new application areas have appeared in recent years which, though are using only small volumes of phenolic resins, are generating increasing interest and may become significant in the future. These are listed as follows:

Table 9.2 Applications of mining foam materials

Type of material	Main area of use
Phenolics	Void filling – load bearing applications
Aminoplastics	Void filling – non-load bearing applications
Polyurethanes	Sealing and consolidation
Unsaturated polyesters	Bolt anchoring

- *Air filtration*: Foam panels can be used in heating, ventilation, and air conditioning (HVAC) systems for dust extraction. In this application, the foam has to be an open-cell structure, and should have correct sized openings (pores) to allow free through-flow of air but to arrest solid particles. These products are of particular interest in HVAC systems for use in environments where dust sensitive equipment is present, for example, electrical equipment, electronics, etc.
- *Carbon foams*: These materials are used in the manufacture of structural composite sandwich panels. They have the advantage of combining high strength with low weight, have thermal and acoustic insulation properties, and are resistant to fire and corrosive atmospheres. During the manufacturing process an open cell foam is carbonized over an extended period of time at high temperature. Carbon foams are also used for composite Tooling.
- *Pultruded Phenolic Foam*: A technique to develop unique fire resistant fiber reinforced phenolic foam sandwich systems involving the pultrusion of phenolic foam with glass rovings has been actively pursued in the Far East and in the US. Work at Seoul National University [5] and Nihon University [6] are quite similar involving acid catalyzed resole with methylene chloride blowing agent and glass rovings. Ben and co-workers of Nihon suggest that the pultruded glass reinforced foam product has the potential to be utilized as a natural wood replacement in the construction industry. Later the Nihon investigators [7] reported that thin phenolic glass fabric or phenolic carbon fabric prepregs were used as the pultruded phenolic foam was inserted between these prepreg face sheets and co-cured into a sandwich structure. The pultruded phenolic foam sandwich system is proposed for use in marine vessels and railroad units. In the US, fiber reinforced pultruded phenolic foam is being developed by Kazak Composites (Woburn, MA) to possibly replace balsa core currently used by the US Navy in naval ship sandwich panel structures. While balsa is strong and light in weight, it can be comparatively expensive, sensitive to moisture with widely variable mechanical properties. The pultruded phenolic foam replacement product offers a comparable weight to balsa but is claimed to be less expensive because it is produced from readily available materials and meets all necessary Navy tests such as FST with design tailored to meet specific density and structure property requirements. Further Ebert Composites (Chula Vista, CA) has successfully pultruded an all phenolic "Transonite" sandwich panel. This unique sandwich structure consists of woven glass skins, a phenolic foam core, skin-connecting three-dimensional fiber, and uses a phenolic resin matrix. Ebert plans to apply this new fire resistant panel in the transportation and building materials industries. A similar 3D insertion approach called "Acrosoma" but different from the Ebert method has been developed. The Acrosoma method (www.acrosoma.com) uses 3D sandwich panels to fabricate spars in wind turbine rotor blades and giant assembly fixtures for Airbus wings and for spreader bars to lift the A380 Airbus back on the runway if it skids off the side during landing. Acrosoma reports the use of phenolic foam in their panels but it is not known whether phenolic foam is used for the A380 Airbus or rotor blades applications.

9.4 Foam Manufacturing Process

Foam manufacturing processes represent three basic categories

- Batch
- Continuous
- Semi-continuous

9.4.1 Batch Processes

This is the simplest kind of manufacturing process that can be used in the production of foams. It has the advantage that it requires minimum investment cost, but the disadvantages are that the basic foam quality and quality consistency are lower than in the continuous and semi-continuous processes. In addition, the manual input is also higher for batch processes.

The mixing part of the process is carried out by a simple rotating paddle-type stirrer, which is used to mix the resin and other additives together inside an appropriate container. The mixer can be a permanent installation, that is, based on a fixed mixer fitted within a mixing vessel or can be a temporary set-up. The mixing can be carried out in a number of stages, using different vessels or the whole mix can be made up on a single set-up.

One common system is to have a larger permanent day-tank mixer that is used to make up a master batch containing all of the ingredients required for the mix except the acid catalyst. The master batch is then mixed with the catalyst in a separate smaller mixer just prior to discharge into a mold or container that is used for the foaming process. This has the advantage that the master batch can be mixed longer to give a truly homogenous mixture, thereby improving consistency from shot to shot.

Once the final foaming mix has been prepared, the material is discharged into a block mold. Mold sizes can vary depending on the final size of foam block that is required. The foaming process usually requires some external heat input and there are two ways in which to achieve this: (1) have a solid metal mold that has an integral heating system or (2) use lightweight molds (often made from materials such as wood or aluminum) that can be moved into an oven for foaming and curing to take place.

Foam molding can be carried out with open or closed molds. In open molds the foaming material is allowed to expand in a "free rise" mode. This means that there is no pressure build-up in the mold but the density will vary from block to block and the amount of waste will be higher because the block tends to have a domed surface. With a closed mold there is restriction on the expansion of the foaming material. In this type of process the waste is less and the density can be better controlled but there can be safety issues as the mold can become pressurized and develop high internal temperatures within the foam block.

A further modification of these basic block molding operations is to have a mold fitted with a floating lid. This allows the blocks to be always square so there is less waste and less possibility that excessive pressure can build up inside the mold.

Once the foam has reached the desired level of cure, the blocks can be demolded. For some applications (floral foam) the manufacturing process is complete already at this stage, but for some applications (such as the manufacture of insulation foam), additional drying and post-curing can be required. These additional processes are required because the phenolic curing reaction is quite slow in comparison to that of polyurethane for example and the material requires a number of hours to reach optimum cure in terms of properties. The material would have to stay in the mold for a long time to completely cure and therefore by carrying out these operations in a separate step this improves the productivity of the process. Note that the reaction also generates moisture (water) which must be removed from the foam also in order to achieve maximum performance.

9.4.2 Continuous Processes

The key component of continuous foaming processes is the mixing head. These devices are fed with a continual stream of the components (e.g., resin, blowing agent, and acid) that are needed for the foam formulation and provide a continuous flow of freshly mixed material to the foaming line. The foaming line will normally consist of some kind of conveyor system, with various designs being employed, dependent on the type of foam being produced.

Mixer heads can be selected from two basic designs

- Low pressure dynamic mixing heads
- High pressure static mixing heads

9.4.2.1 Low Pressure Mixing Heads

Low pressure mixing heads are most commonly associated with a type of mechanical mixer called a peg stirrer. This consists of a rotating metal shaft that has a number of pins (or pegs) protruding from it. The shaft is driven by a motor to rotate at high speeds within a barrel that has a corresponding set of pins protruding from it. The design is such that the material is subject to extremely high shear rate during a short residence time within the mixing head, thereby ensuring that homogenous mixing of the various components in the foam formulation is achieved (Fig. 9.3).

9.4.2.2 High Pressure Mixing Heads

High pressure mixing heads operate via the technique of impingement mixing. In this type of mixing head, the components are forced through injectors at high pressure to increase the velocity of the materials mixing together in the small

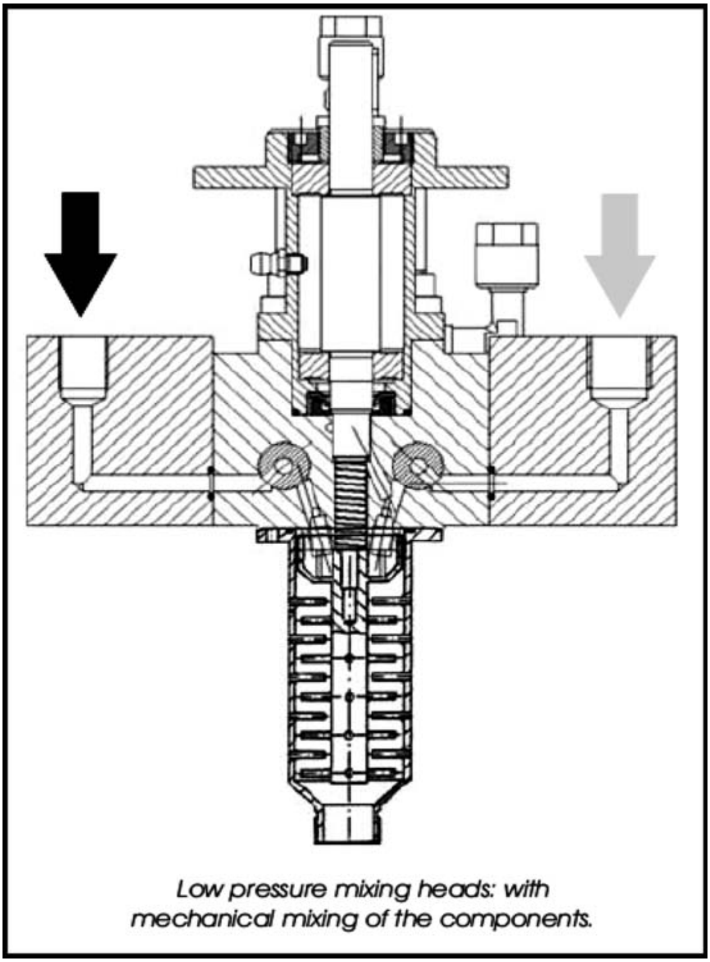

Fig. 9.3 Schematic of a low pressure mixing head [8]

mixing chamber; this high velocity creates the required conditions to ensure homogenous mixing (Fig. 9.4).

Both of these mixer types can effectively fulfill the same role. However, there are a number of advantages and disadvantages with each technique. High pressure mixing heads will produce a more homogenous mixture with a finer cell structure and require minimum cleaning (due to the presence of an extremely low dead volume) but are higher in cost and are not widely proven with phenolic foam systems. The use of low pressure systems is the more widespread; these have lower capital investment cost and give adequate (if not the best) homogeneity in the foam mixture.

For continuous manufacture of floral foam, the foaming mix is laid down onto a single steel belt with side panels and allowed to rise freely. For continuous

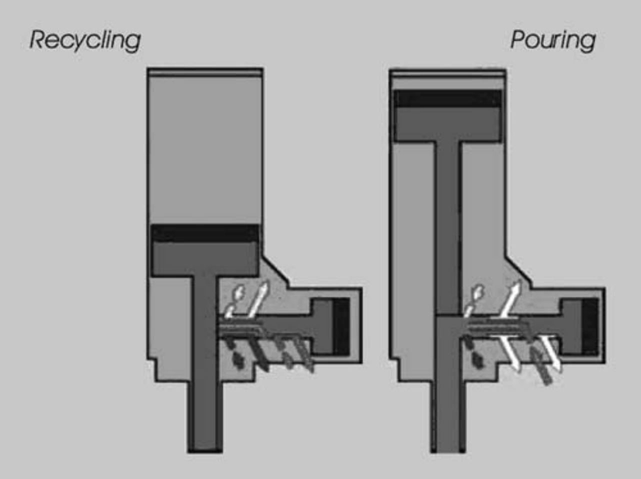

Fig. 9.4 Schematic of a high pressure mixing head [8]

manufacture of insulation boards a machine called a laminator is used and pipe insulation can be continuously manufactured on a special type of extruder.

Semi-continuous processes are half-way options between the two general techniques that have already been described. This type of manufacturing uses a number of block molds, possibly on a conveyor or carousel system so that multiple foam pours can be made sequentially. The mixing is generally carried out using a mixing head, normally of the low pressure type. This type of system is of increasing interest for medium sized companies as this allows them to be able to compete on quality and manufacturing costs without having to bear the burden of the highest initial investment of a continuous foam operation.

Note that in the operation of all of these processes, the appropriate local health, safety, and environmental regulations must be considered. In particular due to the often flammable nature of the blowing agents that are used, equipment must often be rated explosion proof in order to be allowed to operate by the local authority.

9.5 Foam Formulations

The most basic of foam formulations will contain at least four main ingredients; these are listed as:

- Resin
- Emulsifier
- Blowing agent
- (Acid) Catalyst

9.5.1 Foam Resins

The resins for this application are almost exclusively based on resole chemistry. These materials are typically manufactured using a molar ratio $P{:}F$ in the range of 1:1.4–1:2.0 and a basic catalyst such as sodium or barium hydroxide.

These are typically high solids materials (>70%) with moderate to high viscosities (2,000–10,000 mPa s). The high solids content requires that vacuum distillation be used during the manufacturing process, and this is a consideration in the type of resin reactor and ancillary equipment that is used for making these materials. In addition, the high viscosity of the final product requires that lines and transfer pumps also be specially selected for this product.

High solids, high viscosity phenolic resole resins generally age quite rapidly over a period of days resulting in a product that is more viscous and less reactive than when it was prepared. Therefore, insulated and/or cooled storage tanks and transportation vessels are required for these resins in order to minimize the aging effect, and rapid use by the customer is recommended.

The most critical basic parameters of a resin that are used to determine whether it is optimum for a particular foaming application are its viscosity and reactivity. The viscosity is important as this will affect the ease of mixing and can also have an influence on the thickness of the cell walls in the foam as it forms. The reactivity is important as this will affect how the foam will rise and develop over the foaming process cycle. In addition, other properties such as pH, monomer content, water content, etc., will also have an effect.

The specification for a typical floral foam resin from Dynea is given in Table 9.3.

The reactivity is measured by mixing the resin with acid, inserting a thermocouple probe into the mixture, and monitoring the temperature rise with time. A typical reactivity curve is shown in Fig. 9.5. The resin has a specified by a time in minutes and a peak temperature that are related to a mutually agreed arrangement between the customer and resin manufacturer.

It can be noted that the resin can be delivered to the foam manufacturer in an unformulated state or with the emulsifier and (potentially various other additives) already mixed in.

Table 9.4 shows the specification of a typical Dynea insulation resin.

Table 9.3 Specification of Dynea floral foam resin prefere 91 5080V

Resin property	Typical value
Viscosity, 20°C	1,900–2,300 mPa s
pH, 20°C	6.10–6.60
Dry solids content	77.00–81.00%
Free phenol	4.50–6.50%
Free formaldehyde	<1.40%
Reactivity	118°C–122°C

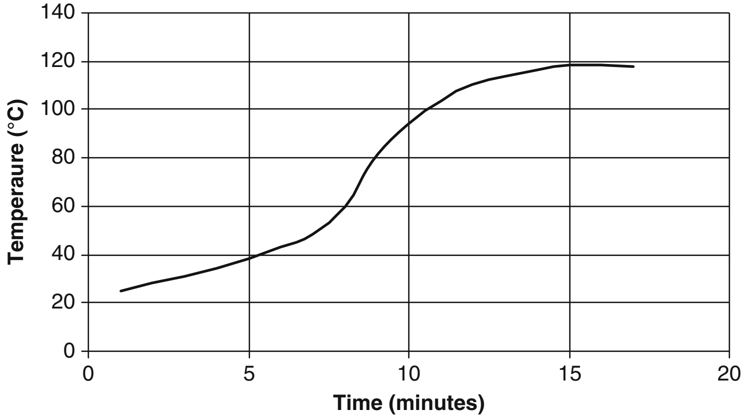

Fig. 9.5 Reactivity curve for Dynea floral foam resin prefere 91 5080V

Table 9.4 Specification of Dynea insulation foam resin prefere 91 5095V

Resin property	Typical value
Viscosity, 20°C	2,000–2,700 mPa s
pH, 20°C	8.50–9.50
Dry solids content	74.00–78.00%
Free phenol	4.00–8.00%
Free formaldehyde	<1.00%
Reactivity	98°C–102°C

9.5.2 Emulsifiers

In order to produce foam from a liquid resin and a liquid hydrocarbon blowing agent, it is critical to form a stable homogenous emulsion between these two materials. As the resole is water soluble and the liquid blowing agent is hydrophobic, the emulsion will be an oil-in-water type.

An emulsifier is used to ensure that the required stability and homogeneity is achieved. Many different kinds of emulsifiers have been examined within the phenolic foam industry over the years but the majority of the applications use ethoxylated ricin (castor) oil materials.

9.5.3 Blowing Agents

Blowing agents fall into two general classes, these are physical blowing agents and chemical blowing agents. Physical blowing agents are low boiling liquids that volatilise during the exothermic reaction between the resin and the acid catalyst. Chemical blowing agents are materials that undergo a chemical reaction (in the case of phenolic foams this reaction is often initiated by the acid catalyst) to evolve one or more gaseous components.

In the case of open cell foams, only the processing properties of the blowing agent are important as it will eventually be replaced by air in the final product.

Table 9.5 Common blowing agents for insulation foams and their lambda values

Blowing agent type	Lambda value (W/m K)
HCFC 141b	0.010
HFC 365mfc	0.011
n-pentane	0.015
i-pentane	0.014
c-pentane	0.012

Therefore, it is generally preferable to use lower cost and volatile hydrocarbon materials such as mixtures of pentane, hexane and/or isomers, or petroleum ethers.

In the case of closed cell insulation foams, however, the lambda value of the final foam is directly related to the lambda value of the blowing agent that is present in the final product as the cell gas. Therefore, the selection of the correct blowing agent is important in determining the insulation properties of the final foam. Table 9.5 gives the lambda values of common blowing agents [9].

A lower lambda value gives a better degree of insulation.

It should be noted that although fluorinated blowing agents were at one stage the material of choice for the insulation industry, these have largely been replaced by pentane blends and other materials due to environmental issues and cost.

Chemical blowing agents are most often found in mining foam formulations today; in these formulations carbonates are used that form carbon dioxide when they react with acid. These materials have been used since the phase-out of CFC type blowing agents.

9.5.4 Acid Catalysts

Almost all phenolic foam formulations use an acid catalyzed curing reaction. This has the effect of both causing the gellation of the resin and providing (at least) part of the energy required for the foam to rise.

Older foam formulations used inorganic acids such as sulphuric acid as the acid catalyst. This generally gives rise to a low pH in the final foam and can cause issues with corrosion. These inorganic acids have therefore largely been replaced by less corrosive organic acids such as *p*-toluene sulphonic acid and phenol sulphonic acid. These organic acids are often used in blends with one another. These blends can contain some small amounts of inorganic acid such as sulphuric or phosphoric acid, which are used in order to boost reaction speed and/or give other benefits.

9.5.5 Other Additives

Due to the extremely rigid nature of cured phenolic resin, phenolic foams can be friable and therefore susceptible to damage in manual handling. Plasticisers are often used in phenolic foam resins in order to try to reduce the level of friability. The most common plasticisers for this purpose are simple glycols such as diethylene or dipropylene glycol. As in other phenolic resin applications, some preliminary work has been carried out in the area of phenolic foams on the plasticisation/toughening of these systems with polymeric additives. Some work published recently suggests that a positive toughening effect can be obtained though the modification of a phenolic insulation foam formulation with polyvinylpyrrolidone [10]; this had the added effect of improving the fire retardancy of the foam.

Although phenolic resins are generally considered to be quite satisfactory in terms of their fire performance, that is, they are highly resistant to burning, self extinguishing and produce little or no smoke. Some applications are so demanding that they require additional flame retardants to be used. There is a wide range of proprietary compounds available that can be used in this role.

In the case of floral foams, other surfactants in addition to the emulsifier are added in order to ensure that the finished product has the correct saturation and water retention properties. Obtaining the correct balance of properties is proprietary, and floral foam manufacturers are very careful in protecting the details of the exact blend of surfactants that are used.

Buffering materials can be added to phenolic foams in an attempt to minimize the impact of the residual acid catalyst that remains in the final foamed product. The use of these materials was more widespread in the past in the areas of both insulation and floral foams but is now on the decrease. By using higher efficiency and more reactive resins and lower acid levels, the final pH of the system can be increased without the need for additional buffering materials.

Thickeners are mainly used in spray foam systems such as those used in the mining industry. If the foam needs to be deployed into a cavern above the head height of the mineworkers, it is important that the material remains where it has been sprayed and there is no chance that the material can fall back down onto any personnel below. In these cases thixotropic thickeners such as fumed silicas are added in order to ensure that the material will remain once it has been sprayed in place.

Fillers can be used in some foams as a way to reduce the cost of the formulation, provide a reinforcing effect, and/or to improve the fire properties of the finished product. Many low cost particulate materials can be used as bulking filler but for reinforcement and fire properties aluminum trihydrate is the most common choice. The major considerations involve the mixing issues that may arise due to the thickening effect that will be seen when the filler is incorporated into the mix. In the case of close-cell foams it is a concern whether the filler will interfere with cell integrity. Recent work with nano-particulate fillers has shown that some positive benefits can be obtained through the use of these materials in foam formulations with respect to both mechanical strength and thermal stability [11].

9.6 Foam Testing

The different types of foam are tested according to varying methods dependent upon the final application.

9.6.1 Fire Testing

This is of great importance in the insulation and mining foam applications but is of no relevance for floral foams. It is very difficult to discuss an industry standard with respect to fire testing since various countries and also groups of countries have adopted different test methods and approaches, which often do not measure the same function, for example, some tests measure flame spread, some are based on heat of burning, some take melting into account whereas others do not, etc.

As the main market for insulation foams is in the UK (as this country is leading the way in promoting more efficient heating and insulation for residential buildings) the main focus will be on UK fire testing; however, other European test methods will also be mentioned.

In order to meet the requirements of UK building regulations (phenolic) insulation foams must be tested according to BS 476, which is a general standard covering fire resistance of building materials/elements. The critical sections of the standard with reference to insulation foam are BS 476-6, which is the method of test for fire propagation of products and BS 476-7, which is the method for determination of flame spread.

The fire propagation test effectively measures the amount of heat released over time by the material when it is subjected to a specific burning regime that involves initial ignition via. A series of gas flame jets and also additional energy from radiant heaters. The result is expressed as an index and is related back to the performance of a non-combustible calibration standard.

The test for flame spread involves suspending a sample of the foam under test vertically and igniting the material at one end. The linear spread of flame along the length of the sample is estimated after a set period of time.

According to literature published by the European Phenolic Foam Association (www.epfa.org.uk) a phenolic foam can meet Class O according to the appropriate UK regulations as laid out above, which means that it meets the highest fire rating of all materials that are tested according to these standards. Although it is difficult to compare European standards, the same publication lists the following as equivalent national standards Dutch NEN 6065/6066 Class 1, Belgian A1, French M1 and German class B1 (DIN 4102).

9.6.2 Insulation Efficiency/Lambda Value

As stated earlier the efficiency of an insulation material is often quoted as its lambda value (also sometimes known as *k*-value). Lambda values of organic foams are listed in Table 9.6. The appropriate British Standard that is applicable in this area is mentioned as BS EN 13166 (Thermal Insulation Products for Buildings – Factory Made Products of Phenolic Foam).

The lambda value is usually measured using a heat flow meter. This apparatus has a test chamber in it in which the foam sample is held between two temperature

Table 9.6 Typical lambda values for insulation foams

Insulation foam type	Lambda value (W/m K)
Phenolic foam	0.018
Polyisocyanurate foam	0.023
Polystyrene foam	0.030

controlled plates. The upper plate (hot plate) is maintained at a higher temperature and the bottom plate (cold plate) is maintained at a lower temperature. This temperature difference creates a flow of heat through the material from the hot plate to the cold plate and this is measured via a thermal flux sensor. If the material provides greater resistance to the flow of heat then it obviously has a higher insulation factor.

For a material to be able to meet the requirements of UK building regulations (phenolic) insulation foams, the lambda value must be tested after a period of aging in order to ensure that the product will still be efficient in the application after a prolonged period of service. Presently there are two acceptable methods of aging:

- Method 1 (slicing) requires that the foam sample be cut into 10 mm slices. These slices are aged at 23°C for up to 90 days (depending on the final thickness of the insulation panels) and then reassembled as a stack prior to testing for lambda value.
- Method 2 (heat aging) requires that the foam sample be aged at 70°C for 175 days prior to testing for lambda value.

According to the method described in this standard all foam samples must be conditioned to a constant weight at 70°C and then are reconditioned at 23°C and 50% humidity for a number of days prior to commencing the tests (as stipulated in British Standard BS EN 12429). The heat aged samples are also reconditioned at 23°C and 50% humidity prior to testing.

9.6.3 Strength Testing

Strength testing is carried out on most foam systems as a part of the manufacturer's in-house quality control process. Strength can be quite critical in some construction and mining applications but even in non-load bearing situations the foam will normally be required to have some minimum mechanical strength in order not to become damaged during any manual handling that is carried out.

Strength testing methods can vary considerably from one application to another and can also differ between different manufacturers who are working in a common field. In the case of insulation foams, the applicable (European) test method is described in British Standard BS EN 826, as this method is well specified and due to the fact that similar strength testing methods are used in other applications also this method is described in some detail.

The test method involves taking a foam sample of known height and compressing it by a factor of 10%, that is, in the case of a sample of thickness 50 mm, this would be compressed by 5 mm to a final thickness of 45 mm. The strength of the foam is then taken as the peak figure that is obtained over the duration of the test; as most phenolic foams will have a brittle failure mode, this peak result is often obtained in the early part of the test, that is, when the degree of deformation is less than 5%.

9.6.4 Determination of Saturation Properties

Saturation tests are only applicable to floral foams and vary greatly from one manufacturer to the other.

All of these tests, however, follow the same basic principle: a standard sized foam brick is placed into a suitable container of water such that as the brick saturates and sinks in the liquid it will not touch the sides of the container. The exact temperature of the water is not critical although it is often conditioned to room temperature as a standard procedure.

The main critical factor is the time taken for the foam brick to become fully saturated with water and this generally forms part of the sales specification for the floral foam product. Additional parameters may also be determined such as how much liquid will drain out of the brick when it is lifted out of the water and the total weight of water that the brick can retain.

9.6.5 Determination of Open/Closed Cell Content

High open cell content is desirable in the case of floral foams and high closed cell content is desirable in the case of insulation foams. Both these properties can be measured by the same instrument and the method of determination is effectively the same. The instrument that is used for this type of analysis is a gas pycnometer and works by measuring both the bulk volume and the specific volume of the sample under test by applying different gas pressures. The closed/open cell content can be expressed as a volume percent by the comparison of these two figures.

In the case of insulation foams, the correct method to be used in the determination of closed cell content is described in EN ISO 4590. This method includes correction factors for additional open-cell content coming from surface cells opened by the cutting of the samples for the test.

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Chapter 10
Mineral Wool Insulation Binders

Stefan Kowatsch

Abstract Mineral wool is considered the best known insulation type among the wide variety of insulation materials. There are three types of mineral wool, and these consist of glass, stone (rock), and slag wool. The overall manufacturing processes, along with features such as specifications and characteristics for each of these types, as well as the role of the binder within the process are described.

Of the variety of mineral wool binders such as sodium silicates, polyesters, melamine urea formaldehyde, polyamides, furane-based resins, and others, phenolic resin-based binders continue to enjoy prominence as the preferred binder for mineral wool.

Optimum conditions are presented for preparing a low viscosity ($<$50 mPas) resole, infinite water dilutability, solids content (SC) between 45 and 55%, low tetradimer content ($\leq$18%), lowfree phenol ($<$0.4%), and adequate storage stability by using a molar ratio of F/P of $\sim$4:1. Various inorganic and organic base catalysts are described along with the strengths and weaknesses of these catalysts. The resulting resole binder contains a high amount of free unreacted formaldehyde and is reduced to zero within a temperature range of 20–40°C by the addition of urea prior to use as a binder. The resulting PFU (phenol-formaldehyde-urea) resin is called "premix" or "prereact."

The formation of the undesirable tetradimer [bis(4-hydroxy-3,5-dimethylolphenol) methane] and several methods to minimize it from crystallizing within the resole are listed. Even some selective base catalysts that are used to prepare the resole binder provide some enhanced stability against tetradimer precipitation.

Gel times or B-Stage of the resole binder is within 5–20 min and is adjusted to coincide with the overall process (from binder spraying to oven cure). A correct set B-stage enables the binder to flow to the junction points of the mineral wool fibers as the material enters the curing oven and cures within the residence time of the

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oven to provide the necessary product properties such as recovery, tensile strength, and resistance against ageing.

The emission of various volatile organic components (VOCs) such as monomethylol phenols, trimethyl amine, ammonia, phenol, and formaldehyde occurs at the site of mineral wool production. The generation of the latter three VOCs is shown to occur by resin cure (formaldehyde), the urea responsible for the generation of ammonia, and free phenol due to an unreacted amount within the resin.

The roles of some of the other components (ammonium hydroxide, ammonium sulfate, silane, emulsifier, de-dusting oil, extenders, and water) that are introduced into the final binder mixture are discussed. Ammonium hydroxide brings the pH of the premix binder to a 9–10 pH value at the site of mineral wool production and "temporarily" stabilizes the higher oligomeric species such as dimers and tetramers from precipitating by maintaining them in solution. Ammonium sulfate (AS) is involved in a multiplicity of roles such as *release of acidity* only at elevated temperature to facilitate resole cure within the curing oven, *regulation of the gel time* of the resole by pH change (guided by a plot of gel time vs pH on the thermal hardening of the resole from the initial spraying, to binder-coated fibers into the collecting chamber, and finally the curing oven), and provides the mineral wool with its *characteristic color* from white to yellow, with an intensity of yellow, due to the amount of AS that is present.. The amount of AS can be 1.03–1.3 mol/mol of the basic catalyst used in resin preparation, and this amount contributes to maximum burst strengths.

10.1 Introduction

In engineering, the term "insulation" refers to minimizing the losses of unwanted energy emissions. Insulation is associated not only with thermal energy but also includes areas such as fire, radiation, sound, electricity, moisture protection, etc. Insulation is one of those ubiquitous techniques that is always present, but hardly noticed. Insulation is a passive product. Once it is installed, it works efficiently, quietly, and continually, usually out of sight, enclosed within a structure or a casing or under cladding. Insulators are a vital component in the building sector: good thermal insulation saves energy associated with heating and cooling and thereby provides a positive contribution to the reduction of carbon dioxide emissions.

The mineral wool producers' industry is strongly driven by energy savings and strives for a more sustainable image.

10.1.1 Global Aspects

In Europe, the industry can be seen as an oligopoly-structure dominated by a few well-known, well-established, and highly consolidated companies like ST. GOBAIN

(ISOVER), ROCKWOOL, KNAUF, PAROC, and URSA with a production footprint all over Europe and Russia. The overall mineral wool production in 2007 was about 40 Mill m^3/a of final mineral wool products. The entire mineral wool production requires about 400,000 tons/year of resin (50% in SC).

Growth in insulation is very much linked to a vibrant activity in the building/construction industry. Nevertheless, drivers such as energy saving, sustainable green houses (and companies), and CO_2-reduction provide the insulation industry with yet another dynamic business opportunity, as compared to other industries. While the western and central part of Europe experienced a modest annual growth in 2006 and 2007, growth is meanwhile stagnating in these regions and even negative in some south European countries. Growth is expected for the next few years in Poland, and the estimates for Russia are still projected to be around 20% growth within the next several years. This remains to be seen, because worldwide there is a huge uncertainty owing to the current economic downturn of 2009 mainly triggered by the construction industry. The outlook is more critical for North America where the housing market has to recover before any growth can be projected.

Typical market trends and requirements are varied and are based on improving Health, Safety, and Environmental (HSE) requirements such as reducing emissions of an entire manufacturing process or product, reclassifying formaldehyde as a potential carcinogen, as recommended by the WHO International Agency for Research on Cancer, and lastly that resin users are very few (above) but consist of very large companies that dominate the insulation industry.

10.1.2 Glossary of Basic Insulation Terms

The understanding of the phenolic resin chemistry is closely coupled with the mineral wool properties and its manufacturing process. Hence, it is necessary to briefly mention typical features of insulation materials, and in particular, mineral wool.

Insulation materials are identified with a glossary of terms such as density (ρ), thermal conductivity (λ), thermal resistance (R), thermal transmittance (U), specific heat capacity (c_p), service temperature, water vapor diffusion resistance (μ), long-term water absorption, tensile strength, compressive strength, dynamic stiffness (s'), air flow resistance, and fire resistance. These terms are used to compare the specifications and characteristics of a variety of insulators (insulation products) with mineral wool products such as mineral wool, glass wool, and stone wool (Tables 10.1 and 10.2). Of importance is fire resistance: in the Euroclass system DIN EN 13501-1, building products are divided into seven classes on the basis of their reaction-to-fire properties: A1, A2, B, and C, D, E, F. The "A" group materials are incombustible. These classifications are extended further according to the smoke development and release of flaming droplets, designated *s* and *d*, respectively. The numbers 0–3 denote the extent of smoke and droplets evolution.

Table 10.1 Specifications of the most common insulation materials

Insulator	Density (kg/m^3)	Thermal conductivity λ (W/m K)	Specific heat capacity (J/kg K)	Limiting short time service temperature (°C)	Limiting long time service temperature (°C)	Water vapour diffusion resistance (μ)	Long-term water absorption (vol%)
Blown perlite (EPB)	90–490	0.045–0.070	1,000	250	110–800	3–5	
Potassium silicate foam	115–300	0.045–0.065	1,000			3–20	
Mineral wool	20–200	0.035–0.045	600–1,000			1–2	3 kg/m^2
Glass wool				600	<500		
Stone wool				1,000	<650		
Phenolic foam	40	0.022–0.040	1,400–1,500	250	150	60	
Polyester fibers	15–20	0.035–0.045	1,500	NA	100	1–2	
Polyethylene foam	50–110	0.033	2,300	NA	−40 to +105	7,000	
Expanded polystyrene (EPS)	15–30	0.035–0.040	1,500	100	80–85	20–100	1–5
Extruded polystyrene foam (XPS)	25–45	0.030–0.040	1,300–1,700	100	75	80–200	0.1–0.3
Polyurethane rigid-foam (PUR)	30–100	0.024–0.030	1,400–1,500	250	−30 to +120	30–200	1.5–3
Foam (cellular) glass	115–220	0.040–0.060	800–1,100	750	−260 to +430	Infinite	0
Expanded vermiculite (EV), mica	70–160	0.046–0.070	800–1,000	NA	700–1,600	3–4	<5
Cellulose fibers	30–80	0.040–0.045	1,700–2,150	NA	60	1–2	

Table 10.2 Characteristic properties of the most common insulation materials

Insulator	Tensile strength perpendicular to the plate surface (kPa)	Compressive strength at 10% deformation (kPa)	Long-term compressive strength (kPa)	Dynamic stiffness (MN/m^3)	Air flow resistance (kPa s/m^2)	Euroclass
Blown perlite (EPB)		150–300	100			C-s1, d0 to D-s1, d0
Potassium silicate foam						–
Mineral wool	3.5–80	15–80				
Glass wool				NA	>5	A1, A2
Stone wool				7–35	6–43	A1
Phenolic foam	60	120				C-s1, d0
Polyester fibers						–
Polyethylene foam						B-s3, d0; D-s2, d0
Expanded polystyrene (EPS)	>100	60–200	20–60	10–40	NA	E
Extruded polystyrene foam (XPS)	>200	150–700	50–250			E
Polyurethane hard-foam (PUR)	40	100–500	20–30			B-s2, d0 to C-s3, d0
Foam (cellular) glass		500–1,700	160–380			A1
Expanded vermiculite (EV), mica		100–450				–
Cellulose fibers		2.5		3–7	43–76	E

10.2 Types of Mineral Wool

Mineral wool is perhaps the most well-known type among the wide range of insulation materials. It is widely used in all sectors of industry, especially transportation and building/construction industries for thermal, acoustic, and fire-protection purposes. There are three types of mineral wool: glass, stone (rock), and slag wool.

10.2.1 Glass Wool

Glass wool, also known as fiberglass or fiberglass wool, is made of sand, limestone, soda, and borax. In recent years, increasingly large amounts of recycled glass are involved in the manufacturing process. The content of the smelter may consist of up to 90% recycled glass, the residual 10% being additives such as sand, limestone, soda, and borax. The manufacturing process starts with the separate silos filled with the necessary raw materials (Fig. 10.1).

The raw materials are then blended in a batch mixer, from which the blend is transported to the smelter. Here, the temperature is adjusted to around 1,100°C – just sufficient to melt the blend into hot lava that is homogenized by stirring (Fig. 10.2).

Sand is introduced from the top of the smelter onto the surface of the lava to create a protective crust. This prevents excessive cooling. From the smelter, the molten glass is poured into a spinner where the fiberizing takes place. The spinner is a rapidly rotating flywheel with more than 2,000 small holes from which the fluid is constrained. Due to centrifugal force, the molten material is spun out of the flywheel (Fig. 10.3).

Since the spinner aperture diameters are in micrometers, only fine fibers are produced. Outside the flywheel, airflow is applied from above to direct the fibers downward to cool them. As the fibers descend, the binder (an aqueous mixture containing thermosetting adhesive) is applied by spraying (Fig. 10.4).

The binder joins the non-woven [1] fibers together at their junction points (Fig. 10.5).

The amount of binder or solid adhesive is adjusted to achieve the required mineral wool criteria. For example, the amount of binder provides the mineral

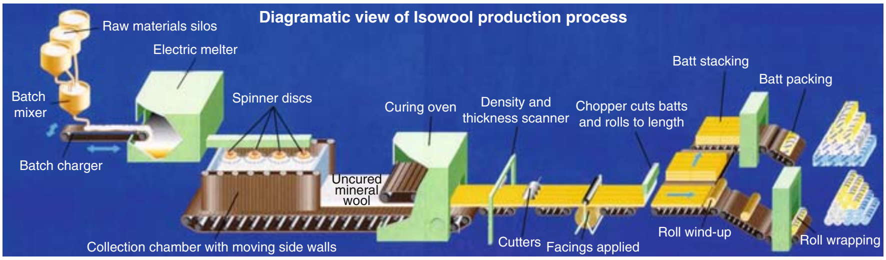


Fig. 10.1 The manufacturing process of glass wool

Fig. 10.2 The furnace where the raw materials are melted

Fig. 10.3 The fiberizing is done in the spinner

wool with its characteristic mechanical properties such as compressive, tensile, and bending strengths. Therefore, flexible glass wool blankets need less binder than rigid slabs. The binder-sprayed glass fibers are white in color, and at this stage, form soft, easily ruptured wool. The wool is then moved along the conveyor belt into the collecting chamber, where most of the water is evaporated at around 80°C. This pre-dried wool then moves into a curing oven equipped with specially arranged conveyor belts (Fig. 10.1). This procedure compresses the soft mineral wool: the distance between the belts controls the mineral wool thickness. In the curing oven

Fig. 10.4 Glass fibers are sprayed with binder

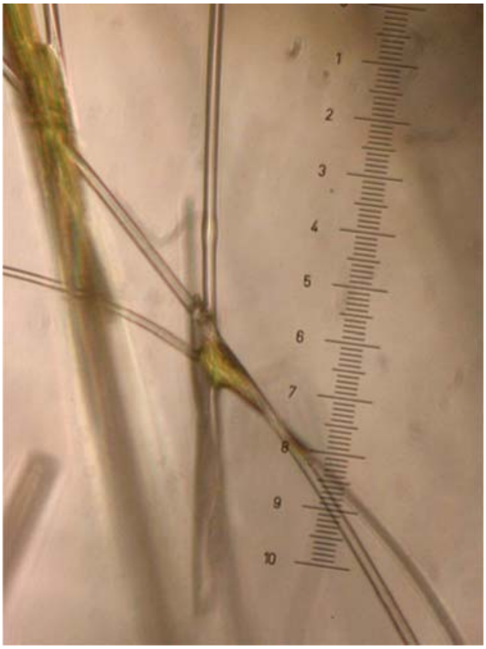


Fig. 10.5 The mineral fibers are bound together by binder at their junction points. The total length of the ruler is 100 µm (Dynea)

(180–250°C), the wool is completely dried, the binder is cured, and the glass wool gets its distinctive yellow color (Fig. 10.6) (see also Sect. 10.3.7 for color development).

The mineral wool exiting the curing oven is almost a complete product with its desired thickness and mechanical properties. As it moves further along the

Fig. 10.6 Curing oven

Fig. 10.7 Edge trimmer

conveyor belt it cools, before being cut to the required size with transverse (length) and edge (width) trimmers (Fig. 10.7).

Facings, such as aluminum foil, may be optionally applied to the wool (Fig. 10.1). In the final step, the wool is packed either into rolls or slabs (mats). To reduce transportation costs, the packing process compresses the wool up to 10% of its original size. However, the rigid adhesion between fibers means that the compressive forces store a potential flexural energy in the wool fibers. This is released on unpacking, leading to almost complete recovery of the original dimensions at its final destination.

10.2.2 Stone Wool

Stone (rock) wool is made from igneous volcanic rocks and blast furnace slag. The most frequently used minerals are basalt, dolomite, sylenite, amphibolite, granite, and diabase. Often, Muskegon sand and borax are added to the blend composition. Apart from an iron blast furnace slag, other sources of slag from copper, lead, and phosphate industries are used.

Crushed rock, limestone, and coke are fed into a cupola furnace, combined with some oxygen from air, the rock is melted at about 1,500°C. The limestone (dolomite) is used as a fluxing agent. The molten lava then runs down channels and cascades onto a train of rotating discs that sling the molten mass as fibers. A high velocity stream of air or steam carries these fibers onto the next stage in the production line (Fig. 10.8).

It is here, as they leave the discs and fall under suction onto the forming conveyor belt that the resin binder is sprayed onto the fibers. From this stage, the wool follows a similar processing sequence as glass wool.

10.2.3 Slag Wool

Slag wool fibers are produced from molten blast furnace slag and other materials such as basalt, in a similar way as the stone wool production. The major chemical components of these fibers are silicon, calcium, magnesium, and aluminum oxides with trace amounts of manganese, iron, and sulfur oxides. Slag wool has similar performance characteristics as stone wool, but is produced less frequently.

10.2.4 Application and Properties of Mineral Wool

Insulation mineral wool is a multipurpose material, and its application is particularly suitable in building as well as industrial insulation sectors. Heating, Ventilating, and Air Conditioning (HVAC) in buildings involves a broad scope of mineral wool products for enhancing air duct insulation. Other important areas in building and construction projects are acoustic/vibration and thermal insulation; especially with regard to attic (roof, loft, ceiling), floor, wall, façades, and sill sealing. Tank wrapping and pipeline sheathing may also be regarded as industrial or technical sector applications. Further, automotive, aircraft, and marine sectors utilize mineral wool insulation.

Each of these application areas employs different mineral wool products. Soft and flexible rolls, sometimes known as mats, felts, blankets, or quilts, can be used in piping insulation. Alternatively, these pipes may be lagged with rigid tubular-shaped mineral wool forms that have a central round aperture. Rigid slabs (also

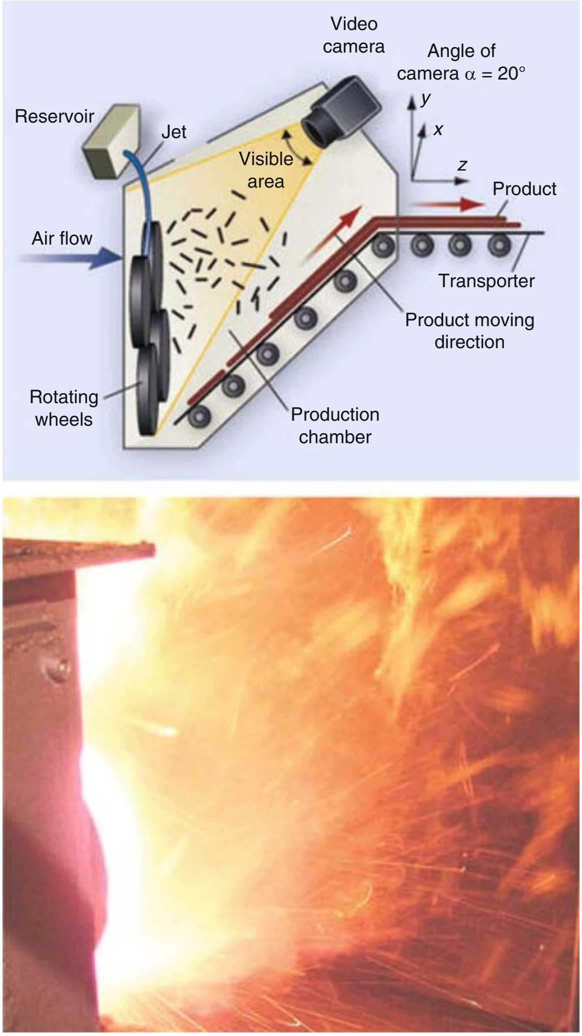


Fig. 10.8 Fiberizing molten rock in the production process of stone wool

known as mats, panels, board, and mattresses) can be built under floating floors. Stitched facings, frequently made of alumina foil, improve the compactness and insulation capability of mineral wool product. Yet, the so-called “blowing” or “pouring wool” comprises mineral fibers rolled up into small fibrous balls, not unlike cotton wool in appearance. This is used for cavity wall insulation where the wool is blown through holes drilled into the wall. “Brown wool” is blowing wool made from stone fiber.

Mineral wool does not necessarily need a binder for its use as an insulation material. The primary glass wool leaving the fiberizing unit, also called “loose white wool", is used in applications where no mechanical strength is required. The market share of the mineral wool without the binder is quite low.

Apart from these mechanical properties that relate to the tensile and compressive strength, the selection of the mineral wool also depends on the use of temperature.

Table 10.3 summarizes characteristic specifications of glass and stone wool.

Mineral wool does not burn and can be classified as fire-resistant according DIN EN 13501-1 as "A class," that is, incombustible. Stone wool can be used up to 900°C and belongs to A1 class. Upon exposure to a direct flame, no smoke or molten droplets are produced – therefore, the material can be used as an excellent fire insulator/barrier in buildings. Glass wool can be used to 450°C, where above this temperature, the wool melts and loses its fire-protecting properties. Glass wool contains more binder than the stone wool (Table 10.3), and upon burning, smoke or droplets will evolve. This reaction of glass wool to fire categorizes the material as "A2 Euroclass". The addition of less binder to the glass wool and/or using a high melting glass source brings the glass wool into "A1 class".

Other noteworthy comments and properties with regard to mineral wool are:

- Under normal condition, the growth of mildew, mold, or bacteria does not occur.
- Stone wool is used for the same applications as glass wool; however, it is denser and has higher tensile and compressive strength. It is better than glass wool for acoustic insulation. Glass wool is lighter, with greater compressibility, and is used more often for thermal insulation of cavity walls and lofts (its thermal performance is generally better for a given weight of material).
- Stone wool provides better fire protection – higher service temperature.

10.3 Binders for Non-Woven Mineral Wool Insulation

The mineral wool fibers are bonded together at the cross-over point by the so-called "BINDER" (Fig. 10.5). This is considered to be the heart of mineral wool insulation product. It is usually a complex aqueous mixture comprising a reactive thermosetting composition. Apart from phenolic resin-based binders; water glass [2] (i.e.,

Table 10.3 Comparison of glass and stone wool properties

	Glass wool	Stone wool
Density (kg/m^3)	15–150	20–200
Thermal conductivity (W/m K)	0.035–0.045	0.035–0.045
Specific heat (J/kg K)	840–1,000	600–840
Fire resistance according to Euroclass classification	A1, A2	A1
Water vapour diffusion resistance	1–2	1–2
Long-term water absorption (kg/m^2)	≤ 3	≤ 3
Service temperature range (°C)	−200 to 450	−200 to 900
Compressive strength at 10% deformation (kPa)	2–15	15–80
Long-term compressive strength (kPa)	3.5	5–20
Air flow resistance (kPa s/m^2)	≥ 5	6–43
Loss on ignition (%)	3–8	0.5–3.5

sodium silicates), polyesters [3–10], melamine–urea–formaldehyde [11], polyamides [12–14], furan-based resin [15], polysiloxane–polyol hybrid organo-inorganic binder [16], and other binders have been reported. To the present date, phenol–formaldehyde resoles or phenol–formaldehyde–urea resins are the most widely used for binding mineral wool. The binder (also known as sizing composition [17], resin preparation [18], binder composition [6], and binder formulation [19]), comprises the following components:

Phenolic resin urea
De-dusting oil
Emulsifier
Dyes
Silanes
Ammonium sulfate
Ammonium hydroxide
Extenders
Water

The binder itself is prepared at the site of mineral wool production, whereas the phenolic resin is manufactured at the resin producer's plant. The addition of urea and extender may take place at either location, but the remaining components are added to form a binder ultimately at the site of the mineral wool manufacturer.

The chemistry and function of the components forming the binder are described in detail in the following sections.

10.3.1 Phenolic Resins for Insulating Mineral Wool

10.3.1.1 Raw Materials for Phenolic Resins

The insulation resins are obtained by the condensation of aromatic hydroxyderivatives and aldehydes. The most common raw materials are phenol and formaldehyde. Formaldehyde is preferably used as a concentrated aqueous solution, that is, formalin. The formaldehyde for commercial purposes has a concentration of about 37%; more concentrated solutions must be stored at an elevated temperature to avoid paraformaldehyde precipitation or be stabilized, for example, by methanol. Some suppliers, such as Dynea, produce their own formaldehyde and therefore can use fresh formalin with a concentration >50% for the subsequent preparation of insulation resins.

10.3.1.2 General Chemistry of Phenolic Resins for Insulating Mineral Wool

Novolak resins are sparingly soluble in water and hence, possess limited applicability as insulation binders. Thus, the application of dispersed novolak-type resins as a binder for mineral wool is rare [20]. Highly water-soluble phenolic resole resins are preferably manufactured for these purposes. A typical phenolic insulation resin is prepared by the condensation of phenol (P) with formaldehyde (F) under alkaline conditions ($pH = 7.5–10$) at an elevated temperature (50–100°C). The P/F ratio is in the range of 2.0–6.0: most commonly, 3.5. The excess formaldehyde favors the formation of monomeric methylolated species, whereas the condensation affording oligomeric or polymeric species is an undesirable side-reaction. This is detrimental to the resin due to the lower water solubility of these oligomeric and polymeric methylolated species, which condense further during the storage of the resin to even less soluble high molecular weight species; thus reducing the water dilutability of the resin. In regard to phenolic insulation resins, the addition of formaldehyde to phenol under basic conditions leads to “methylolation”, that is, “hydroxymethylation at temperatures below 60°C”. Thus, increasing the temperature supports polycondensation, whereas at lower temperatures, methylolation takes place preferentially. Further discussion related to methylolation and condensation of phenol formaldehyde under basic conditions is contained in Chap. 4, Resin Chemistry. An example of the preparation procedure for PF resole resin as used in non-woven insulating mineral wool is provided in Table 10.4 [21]:

Phenol and a 50% formaldehyde solution are mixed in a reaction vessel at a P/F molar ratio of 1:4.25. This mixture is adjusted to 43°C, when 50 wt% sodium hydroxide solution is charged as a catalyst. The quantity of the catalyst charged is 10% of the initial phenol charge. The reaction mixture is then heated to and held at 52°C to obtain a resole with a free phenol content of 0.37 wt%. The resulting phenolic resin was analyzed by high pressure liquid chromatography (HPLC), gel permeation chromatography (GPC), and gas chromatography (GC) (Table 10.4).

As demonstrated by this example, the main component of the final resin is trimethylol phenol . The reaction in the example was transformed to 99.67% phenol conversion and 0.37% free phenol. When this level of phenol is achieved, the reaction mixture is cooled to avoid further condensation. Prolonging reaction times, that is, overcondensation, indeed gives a resin with even lower free phenol. Resins with a low free phenol or better with no free phenol is the desire of every mineral wool producer. This is due to emissions of the phenol to the environment, which may occur during mineral wool manufacture. To date, these emissions cannot be completely eliminated. However, a resin with a very low free phenol

Table 10.4 Composition of the typical PF resole resin for non-wovens insulating mineral wool

Species	Relative GC peak area (%)
Phenol	0.66 (HPLC)
Monomethylol phenol (MMP)	3.93 (GPC)
Dimethylol phenol (DMP)	10.43 (GPC)
Trimethylol phenol (TMP)	57.09 (GPC)
Dimers	25.49 (GPC)
Trimer	2.40 (GPC)
Free phenol[a]	0.37 (GC)

[a] Real content of free unreacted phenol in the final resin based on GC

content (overcondensed), has limited water dilutability [22]. The limited water dilutability in this case would be brought about by competing simultaneous methylolation of the low concentration of the free phenol with an excess of formaldehyde and the polycondensation reaction, which of course leads to an increased amount of dimers and oligomers that have limited solubility. Theoretically, resoles with a very low concentration of phenol, of less than 0.2% and infinite water dilutability, could be achieved by applying a large excess of formaldehyde. For practical reasons, this approach is not followed by the producers of phenolic resins.

The endpoint of the condensation can be determined by an analytical technique such as GC or GPC but is time-consuming. Free phenol value is required quite rapidly while reactants and the product are maintained in the reactor. Hence, a rapid, dynamic free phenol method is necessary. The concentration of the free unreacted phenol is correlated with a method that is both simple and rapid. Titration with salt water [23] is frequently used along with the GC or GPC technique. In this method, an aliquot of the sample is placed in a test tube, and with agitation, titrated with salt water. The end point is the appearance of a permanent white turbidity, which results from the insolubility of the high molecular weight components. An example of this test would be a salt water dilutability of 1:10 (or 1,000% salt water dilutability), which would correspond to a phenol level of 1.2% obtained from GC or GPC. Correlation of salt water test with GC or GPC is a priori established. The salt water dilutability decreases with the condensation time. When the appropriate dilutability is reached, the condensation is terminated by cooling. If there is a reaction procedure that allows the condensation to be terminated at 600% salt water dilutability, then “stop-time” may be predicted by extrapolation from the previous points.

When a series of batches of a standard product is prepared, the time is recorded for each batch. It should be noted that the endpoint of the condensation is not constant for all batches. For example, the general statement that the condensation takes 3 h (corresponding, for example, to 0.7% of free phenol) can only be claimed if the quality of the starting materials and other processing conditions are always the same. This prerequisite, however, is not met in industry, since all batches of phenol, formaldehyde, and catalyst may vary, even if only to a small extent. That is the reason why the condensation of the resins is monitored every time with the indirect checking of the kinetics (conversion of phenol) by the salt water dilutability test or any other simple procedure, which has previously been correlated with an advanced analytical method. Depending on the P/F ratio, the reaction mixture upon condensation contains 5–15% of free unreacted formaldehyde. If this resole resin were to be used (as is) for the manufacture of mineral wool, the free formaldehyde emissions during the production of mineral wool insulation would result in large-scale pollution of the environment. Hence, formaldehyde scavengers are added to the PF resole resin to minimize the free formaldehyde level. Scavengers usually possess amino groups, capable of reacting with free formaldehyde. Frequently used scavengers are ammonia, melamine, and dicyandiamide; but the most common and cost-effective formaldehyde scavenger is urea.

Catalysts

As mentioned earlier in this chapter, resole resins for insulation non-woven mineral wool are prepared by the condensation of phenol with an excess of formaldehyde under alkaline conditions, most commonly at the pH 8–9. If phenol is condensed with an excess of formaldehyde without the catalyst, no reaction takes place, that is, the acidity brought about by phenol and formaldehyde is not sufficient to commence the reaction [24].

Thus, the industrial insulation resins are divided into two groups, classified according to the type of catalyst (C) used: that is, organic and inorganic catalyzed resole resins. The studies on the kinetics and the mechanism of the organic/inorganic catalyzed resole, in general, have been reviewed elsewhere [25–29]. The focus is mainly on the preparation of resins for the manufacture of mineral wool. For insulation resins, a low concentration of catalyst is used, which is sufficient to reach the desired pH level. The small amount of catalyst gives the resin a low viscosity, that is, low condensation grade. The inorganic catalysts for commercial resins are most commonly LiOH, NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$; organic catalysts that are frequently used are tertiary alkylamines such as triethylamine (TEA) and tertiary alkanolamines such as dimethylethanolamine. Primary amines such as ammonia, monoethanolamine, aniline, and polyamines, such as ethylenediamine and diethylenetriamine, are not used, because they undergo a cocondensation reaction, leading to a resin with unsuitable properties for insulation. The amount of catalyst is determined as a mole ratio of the catalyst and phenol. The molar C/P ratio for LiOH, NaOH, and KOH catalyzed resins is usually below 0.1 (10 mol% of catalyst to phenol) which is approximately below 1 wt% related to the PFU resin with 55% SC. Since the alkalinity of the $Ca(OH)_2$, $Ba(OH)_2$, and organic catalysts, such as TEA and triethanolamine, is lower in comparison to alkaline metal hydroxides, a higher amount of catalyst is added ($C/P = 0.1$–0.2, or 1.5–3.5% relative to the resin weight).

Organic Catalyzed Resins

The use of organic catalysts results in an ash-free resin with excellent strengths and moisture resistance. Moreover, the solubility of tetradimer (the role of the dimer is mentioned later) in these resins is enhanced and hence, the organic-catalyzed resins have better storage stability in terms of tetradimer precipitation.

The TEA-catalyzed resin is self-curing, that is, the curing does not require any acid catalyst (vide infa in the Sect. 10.3.7, ammonium sulfate). This is due to the volatility of TEA (b.p. 90°C), which volatilizes during the curing and thus, shifts the pH of the resin into the acidic range (the acidity after the evaporation stems from the phenolic compounds). The toxic TEA emissions pose the only disadvantage of this resin.

The dimethylethanolamine (b.p. 133°C)-catalyzed resin possesses similar properties to the TEA-catalyzed material, but with reduced catalyst emissions.

It has been shown that the resins catalyzed by tertiary alkanolamine, such as 2-dimethylamino-2-methyl-1-propanol and 2-(dimethylamino)-2-(hydroxymethyl)-1,3-propanediol , do not volatilize during the curing [30]. The alkanol group most probably participates in the crosslinking reaction and is, at least partially, covalently bound into the cross-linked resin matrix. Moreover, the presence of the hydroxyl functionality on the amino alcohol molecule may act as a plasticizer and increases the flow of the hot resin melt, thereby increasing the resin efficiency and yielding a stronger bond of the resin with materials such as fiberglass which are integrated with the resin. Further, the chemical bonding of the catalyst to the polymeric matrix also inhibits catalyst emissions in the finished product.

Inorganic Catalysed Resins

The advantage of the catalysis with inorganic hydroxides is their low cost and nonvolatility. These resins are, however, susceptible to tetradimer precipitation (*vide supra*). The catalysts are not volatile and therefore, acidic hardener is required for the curing of the PF urea composition. The hardener, for example, AS or ammonium phosphate, neutralizes the catalyst and once cured, the corresponding alkaline metal or alkaline earth's metal sulfates/phosphates reside in the crosslinked polymer moiety that is bonded to the fibers. All soluble inorganic salts that are present in the cured matrix of the mineral wool fibers cause the tensile strength to deteriorate. The lower the water solubility of the resulting salt, the stronger the tensile strength of the non-woven wool. In this respect, the resins catalyzed by lithium hydroxide exhibit superior wet tensile strengths than those of a corresponding resin catalyzed by the sodium or potassium hydroxides upon curing with AS or phosphate. This is due to the lower water solubility of the lithium sulfate/phosphate in comparison to their sodium or potassium analogs.

Resins catalyzed by $Ca(OH)_2$ or $Ba(OH)_2$ may be used as is, or the catalyst may be precipitated by sulfuric acid or carbon dioxide [31]. The recovered calcium/barium sulfate/carbonate may be subsequently used for other industrial applications.

10.3.2 Urea

Urea serves as a formaldehyde scavenger, fire retardant, coloring agent, and extender. As mentioned above, depending upon the P/F ratio, the condensed reaction mixture of phenol with formaldehyde contains 5–15% of free, unreacted formaldehyde. To reduce the formaldehyde content, urea is subsequently added to scavenge the formaldehyde. Depending on the temperature, time, and the amount of urea used; the level of free formaldehyde may be reduced to zero. The resulting PFU resin is called "premix" or "prereact", and with regard to the addition of urea to PF resin, the industry often refers to it as "*premixing temperature*" and "*premixing time*". The premixing temperature varies in the interval of 20–40°C. Higher temperatures might lead to a simultaneous continuation of the poly-condensation reactions and thus, to limited water dilutability of the premix. The premixing time is in the range of 1–24 h. During this time, methylolation of urea under alkaline conditions takes place, leading to mono-, di- and tri-methylol urea. Tetramethylol urea is apparently not produced, at least not in a detectable quantity. The urea may undergo a cocondensation reaction with methylolated phenol components as well [32, 33]. As mentioned previously in the section concerning the storage stability of the resins, there is one disadvantage of using ready premixed PFU resins. At lower storage temperatures, especially below 10°C, there is a risk of precipitation of free urea or methylolated urea from the premixed PFU resin. The optimal mole ratio of free formaldehyde and urea is in the range of 0.8–1.2. Opacity (the appearance of first nonsoluble particles) increases significantly along with the ammonia emissions if a ratio of less than 0.8 mol is applied. A ratio which is higher than 1.2 leads to increased formaldehyde emissions and the risk of dimethylol urea (DMU) precipitation.

Furthermore, the term "extension level" is defined as a ratio of the concentrations of the PF solid component (% SC(PF)/SC(PFU) and of the concentration of urea (% w(U)/w(PFU) with respect to the SC of the final PFU premix.

Based on the initial molar ratio of the neat PF resin which is preferable between 2.8 and 3.5, commercial PFU premixes have extension levels in the range of 80/20–50/50. The amount of urea used, especially in the PFU premixes, provides the mineral wool with its characteristic physical properties. Thus, premixing with urea improves the bonding strength [31].

The dependence of the bending strengths of sand bars cured with premix with varying amounts of urea has been examined (Chart 10.1).

The study showed that an increase in the PF content in the premix lowered the bending strengths. Urea amounts from 16 to 20% were found to be optimal amounts of urea in the premix, maximizing bending strengths. There is a general rule that too high an amount of free urea within a PFU premix lowers the strength, particularly the wet strength. The drop-in strength when more than 20% of urea is used is probably due to the free urea within the premix.

However, there is a hypothesis where free urea may be incorporated into the cross-linked network of the PF resin during the curing of the binder (Scheme 10.1) [34].

Moreover, the incomplete reaction of urea (i.e., free urea present in the resin) may be responsible for a trimethylamine odor that emerges from the mineral wool [35].

An arbitrary resin was selected for the experimental data of Chart 10.1. It should be noted that the maximum strength values for other resins may be different. Hence, the selection of resin for the correct manufacture of the mineral wool can be viewed as a complex matter, and the detailed characteristics of the resin need to be thoroughly understood before the customer's requirements can be met. The premix may be prepared either at the resin producer's site or at the mineral wool manufacturer's site.

Smoldering or slow, flameless burning is referred to as "punking". Exposing mineral wool to elevated temperatures decomposes the cured binder and ultimately results in the total decomposition of the fiberglass insulating product. The mineral

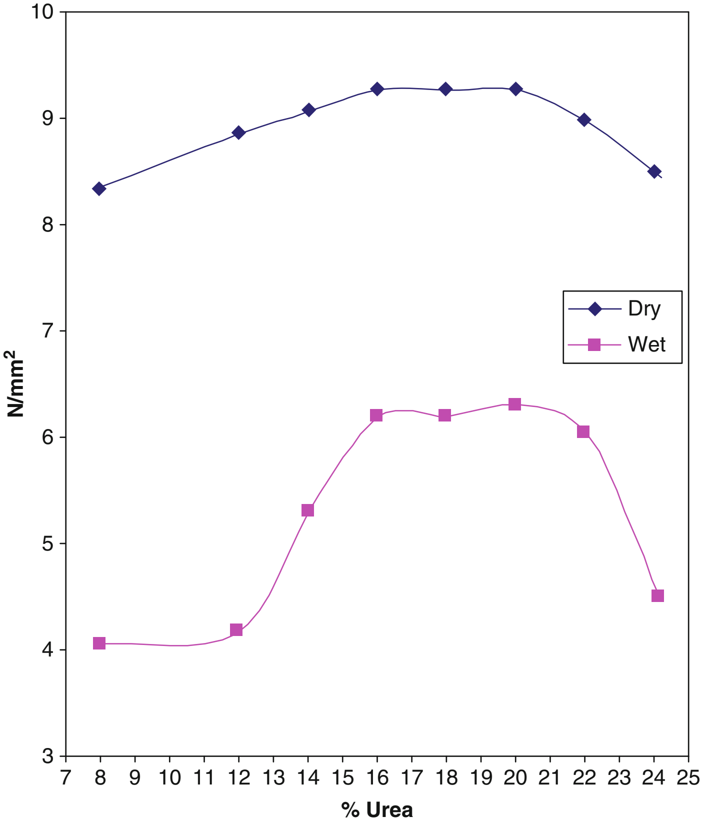
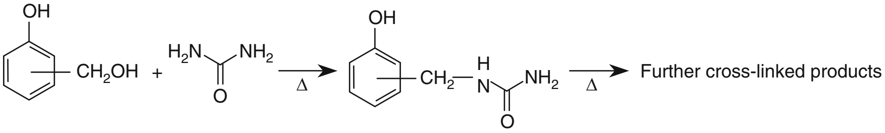


Chart 10.1 The influence of urea amounts in the PFU premix on bending strength of sand bars formed thereof (Dynea)



Scheme 10.1 Reaction of the free urea with methylolated phenol under curing conditions

fiber itself is incombustible, but the punking of the cross-linked phenolic binder contained within the mineral wool may ignite combustible materials in the vicinity such as wood or paint. The addition of urea to the PF resin, however, improves the non-punking properties of the mineral wool [36].

As mentioned earlier, during the condensation of the phenol with formaldehyde, dimers, and other oligomers can be formed and lead to solubility problems. Of great

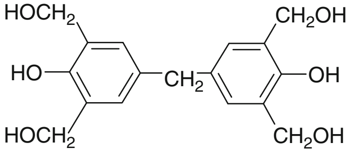


Fig. 10.9 The structure of tetradimer

concern especially is the tetradimer [bis(4-hydroxy-3,5-dimethylolphenol)methane] (Fig. 10.9), which readily crystallizes and precipitates out of the aqueous resin solution.

The concentration (w/w) of the tetradimer in conventional PF resins (50% SC) is generally 10–18% [37]. The excess formaldehyde in the PF resole resin stabilizes the tetradimer from precipitation by solubilization. The problem of tetradimer crystallization may, therefore, occur when the PF resin is extended with urea. Furthermore, when these apparently clear resins solutions are diluted with water during the preparation of a binder composition (particularly if the formaldehyde content is less than 2–3 wt%), the tetradimer may precipitate. Naturally, this can result in precipitation separately in the recesses of tanks, piping, and other binder application equipment, even sprayers. Precipitation of tetradimer may occur at room temperature (22–25°C) and in a time period of 24 h or less. The formation of a visible or quantifiable haze may be observed. Moreover with existing deposited tetradimer, seeding of fresh resin can occur and facilitate the precipitation of dimer within this fresh resin. Since there is an increased effort to reduce formaldehyde concentrations and formaldehyde emissions from such binders, the solution to the problem of tetradimer precipitation represents a technical challenge. There are options for solving the issue of tetradimer precipitation:

(a) The mineral wool manufacturer adds the urea at their sites, thus reducing the premix storage times and hence, the tendency of the tetradimer to precipitate.
(b) The pipes and tanks are regularly cleaned either by mechanical removal of the deposits or by sodium or ammonia hydroxide solutions.
(c) *Sulfite catalyst*: Resins with low concentrations of tetradimer are being developed. For example, a patent describes [37] the use of sulfites as an alkaline catalyst for the resole resin preparation. In an aqueous environment and in the presence of formaldehyde, the alkali metal sulfites have the ability to establish a sufficient level of alkalinity in the reaction mixture for promoting the methylolation and condensation reactions that produce PF resin. The sulfites react with formaldehyde, and one product of this reaction is a salt of the hydroxymethyl sulfonic acid which alters the course of the methylolation and condensation reactions in such a method as to both reduce the generation of tetradimer and to generate other reactive phenolic species having an enhanced aqueous solubility. The concentration of the tetradimer in one example stated in the patent with 50–55% SC was in the low range of 5–7% dimer.
(d) *Borax method*: Another method, patented by Dynea [38] is described, wherein borax is added during the earlier stage of the condensation, yielding a resole resin with reduced tetradimer content and increased storage stability.

(e) The resins are modified such that the tetradimer present in a common concentration range of 10–18% would not precipitate.

For instance, if the condensation is catalyzed by organic catalysts, especially alkanolamines, the resole PFU resin possesses enhanced stability against the tetradimer precipitation [30]. It was discovered that even the simple postaddition of alkanolamines or mono-, or di-saccharides to the resole resin stabilizes the formulation against tetradimer precipitation. Furthermore, these additives also protect against undesirable polycondensation reactions [39].

(f) *Stabilization*: Another discovery is based on the stabilization of the tetradimer against precipitation by the addition of urea–formaldehyde condensate to PF resin [35].

10.3.2.1 Properties of the Insulation Resins

The pH: The pH of the resin can be measured by a meter with a pH-selective electrode. The electrode can be either directly immersed into the resin, or into a diluted resin/water mixture. The latter alternative is preferred to prevent damage (etching) to glass electrodes. The resins for insulation are mostly alkaline (pH 8–9), but acid-neutralized resins (pH 4–8) are also commercially produced.

Appearance: The phenolic resole resins for the insulation are clear, low viscosity, red-colored liquids. The red color is due to the presence of quinones – oxidation products of the phenols. The presence of the quinones is neither detrimental to the mineral wool properties nor does it contribute to the color of the final mineral wool product.

Viscosity: The main components of insulation resole resins are low molecular weight species, resulting in a resin with a low viscosity and not exceeding 50 mPas.

Water dilutability: It is also known as water tolerance (WT). It is the ratio of the weight of resin to the weight of water required to achieve turbidity. For example, a WT of 1:30 means that upon addition of 30 g of water to 1 g of the resin, a persistent white turbidity is seen. The WT can also be reported as a percentage, – that is, 3,000% WT. The cloudiness occurs by the water insolubility of higher molecular weight species such as dimers and trimers. For the processing of the mineral wool manufacture, 1:50 WT is recommended and referred to as infinite water tolerance.

Storage stability: The storage stability of the resin, also known simply as stability, shelf life or pot life, involves two aspects:

(a) The appearance of the resin upon storage over time, that is, no cloudiness or precipitation should occur during the storage.

(b) The water dilutability upon storage over time. During the storage of the resin, the polycondensation of the methylolated species continues – even at storage temperatures of approximately 20°C – leading to higher molecular weight species and reduced WT.

A good quality resin should persist for at least two weeks, often more than a month, depending upon storage temperature. Obviously, the lower the temperature, the higher the stability of the resin. However, at lower temperatures, there is a risk of precipitation of urea or methylolated urea from premixed PFU resin (*vide infra*). The basic prerequisite for the optimal processing of the mineral wool manufacture is to use homogeneous binder solutions or emulsions without any insoluble solid particles present because these may cause clogging of the pipes and sprayers.

Solid content (SC): The commercial resins are aqueous solutions comprising solid material in the concentrations ranging from 45 to 55%. The SC is determined by drying a resin sample at elevated temperature (most frequently, 130–150°C) for 1–2 h. Under these conditions, the VOC such as free phenol, free formaldehyde, and monomethylolated phenol are volatilized together with water. Due to the transportation costs, the 100% resole resin, that is, solid resole, would be ideal, but such a resin has not yet been developed. The producers tend to achieve as high SC as possible, but on the other side, the stability of the resin is reduced. A compromise is then made between the stability of the resin and the SC. SCs <45% would increase the transportation costs to the customer plant.

B-Stage time (min): The curing process of the PF or the PFU resole resins comprises three well-known stages. The liquid resole (A-Stage resin), the gelled (B-Stage) resin, and the fully cross-linked phenolic resin (C-Stage). Differences in polycondensed species and the level of cross-linking makes characterization by the usual methods, such as solubility, melt flow, and swelling behavior, difficult. A more convenient method or Gel time (B-Stage) is determined at 130°C (DIN 16916). The optimal B-Stage times for insulation resins are in the range of 5–20 min. As the sprayed mineral wool moves along the conveyor belt to the entrance of the curing oven, the drops of the binder slide along the fibers to their junction point. Then, once in the oven, the hardening of the resin commences. Shorter B-Stage times would lead to pre-curing before the mineral wool enters the curing oven, that is, the binder would not have enough time to glide into the junction points and would thus cause a poor recovery of the mineral wool. Moreover, the cured raw mineral wool entering the curing oven is not prone to undergo compression to a desired form. On the other hand, if the B-Stage times were too long, incomplete curing could be an issue, that is, the mineral wool's physical properties, such as recovery, tensile strength, and resistance against ageing, would be compromised. Hence, optimal B-Stage times of the resin have to be adjusted in accordance with the production unit of the mineral wool.

The B-time of resole PF resin is quite short (around 3 min) and the extension of phenolic resin with urea more than doubles the B-Stage time.

Emissions of VOC: The emissions ofVOCs such as monomethylol phenols, trimethyl amine, ammonia, phenol, and formaldehyde, into the environment are mainly at the site of mineral wool production. Spraying and pre-drying operations, especially can lead to high emissions. It should also be noted that isocyanates (mainly methyl isocyanate) can be formed above 350°C (because of nitrogen content in the air), such as inside an incinerator used to treat VOC emissions. The main focus concerning the reduction of these VOCs is directed to ammonia, formaldehyde, and phenol. The phenol emissions occur from the free phenol in the resin, while the formaldehyde emissions come from both the free formaldehyde in the resin, and that released during the cure (Scheme 10.2).

The ammonia emissions have their origin in the utilization of the urea and ammonia in the binder composition. It has been shown that the main source of the ammonia emissions, apart from the ammonia added to form the binder, occurs from the free urea in the resin or binder [24].

Thermal decomposition of DMU at 200°C for 25 min releases around 14 mmol of ammonia per mole of DMU, whereas 1 mol of urea emits, under the same conditions, 1 mol of ammonia. The possible reactions accounting for the ammonia emissions are depicted in Scheme 10.3.

The main decomposition reactions releasing ammonia are the cyanuric acid formation and the biuret or triuret reactions [40]. Hence, the more free urea and ammonia that are present in the resin, the higher will be the ammonia emissions.

Tensile strength of mineral wool: The tensile and burst strengths of the articles bonded by the resins are important features of the adhesive. Concerning the insulation resins, various methods and their modifications for testing the strengths are described. Principally, the methods can be divided into two groups:

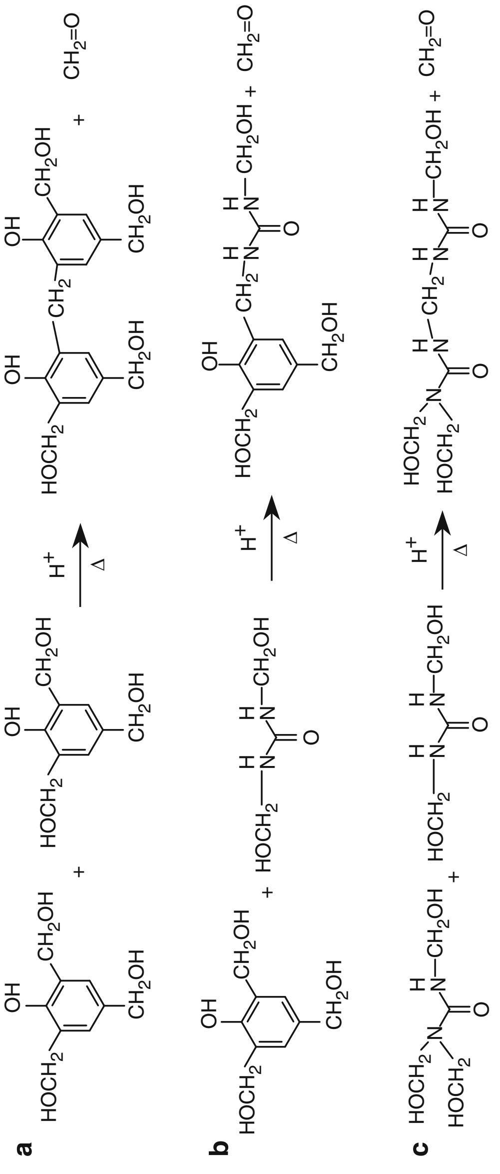
(a) Tensile strength determinations that are based on the soaking of the fiber wool, mat or paper in the resin with subsequent curing [7, 14, 35, 41]. The tensile strength is measured.

(b) *Burst strength*: The laboratory-scale manufacture of the mineral wool is troublesome, since not every laboratory is equipped with the expensive equipment necessary for laboratory-scale production of mineral wool; comprising, among other parts, a scaled down smelter. The direct spraying or soaking of the raw mineral wool has proved to be an unsuitable method for investigating the strength of the resulting mineral wool. An alternative method that is frequently used for obtaining the strength of the binder is as follows: The resin is mixed with sand, and with the use of a mould, bars are formed by pressing in the sand–resin mixture. The mould is then placed in an oven to cure the sand/resin, thus forming cured bars [31]. After cooling, the cured bars are measured for burst strength.

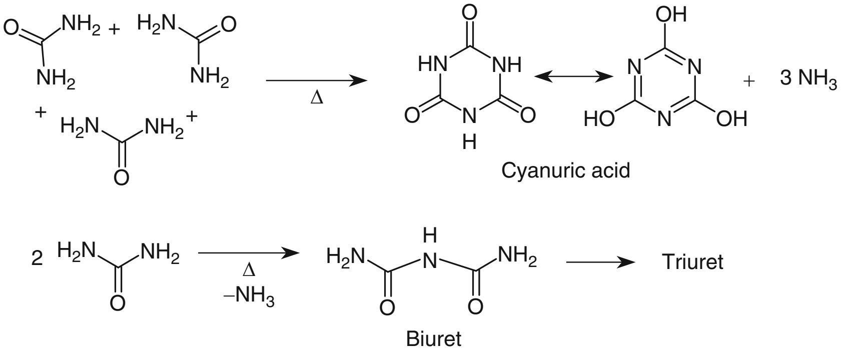
In both methods, the so-called "dry and wet strengths" of the articles are investigated. The wet strength determinations simulate the ageing of the bonded article in boiling water.

10.3.2.2 Ammonium Hydroxide

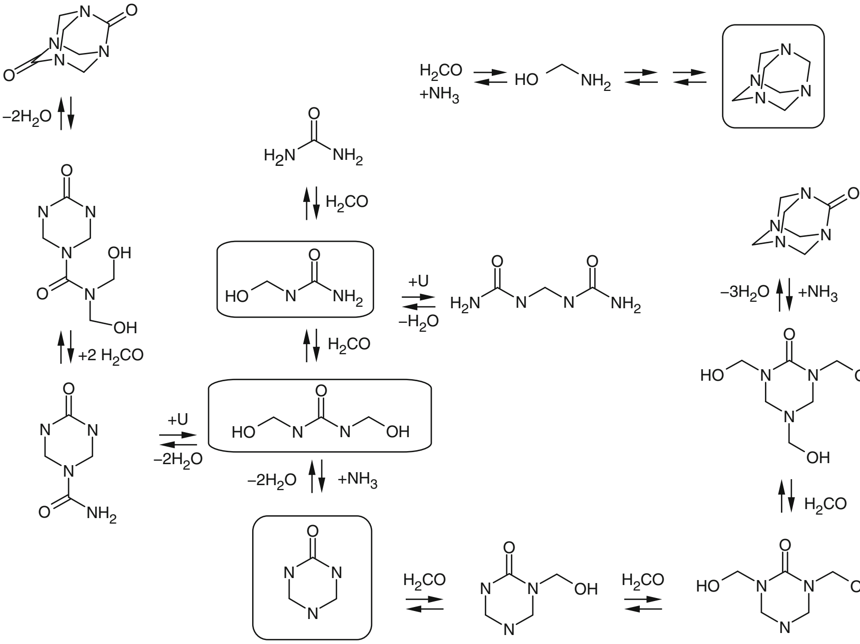
The addition of ammonia is usually added to the binder composition as a saturated aqueous solution of around 24% concentration. The ammonia brings the pH of the binder into the interval pH value of 9–10 and to "temporarily" stabilize the



Scheme 10.2 Examples of how formaldehyde is released during the curing process



Scheme 10.3 The main sources of ammonia emissions-reactions during the curing process



Scheme 10.4 Ammonia added to the binder formulation enters a complex reaction series with formaldehyde and urea

oligomeric species such as dimers and trimers from precipitation by remaining in solution. Note the word "temporarily" – the storage stability of the ammonia-extended PFU premix over a longer time is, in fact, often diminished! Ammonia also functions as a formaldehyde scavenger. In the overall composition, ammonia reacts via a complex series of reactions (Scheme 10.4).

Preferably, the ammonia reacts with formaldehyde yielding hexamethylenetetramine. The methylolated ureas with ammonia may lead to the formation of cyclic triazones. Triazones may undergo further methylolation with formaldehyde and thereafter, the methylolated product can be covalently bound into the cross-linked phenolic resin upon curing.

10.3.3 De-dusting Oil

As it may be inferred from the title, the de-dusting oil is used to reduce the dust produced during manufacture, especially with respect to cutting operations with the trimmers. Due to the presence of the oil, the sliding of the aqueous resin to the junction points of the fibers is also facilitated. The oil-treated mineral wool is hydrophobic, so the water-repelling properties are also enhanced.

High flash point mineral oils are used and typical suppliers to the industry are Sasol, Esso, Shell, Mulrex, Sips, and others.

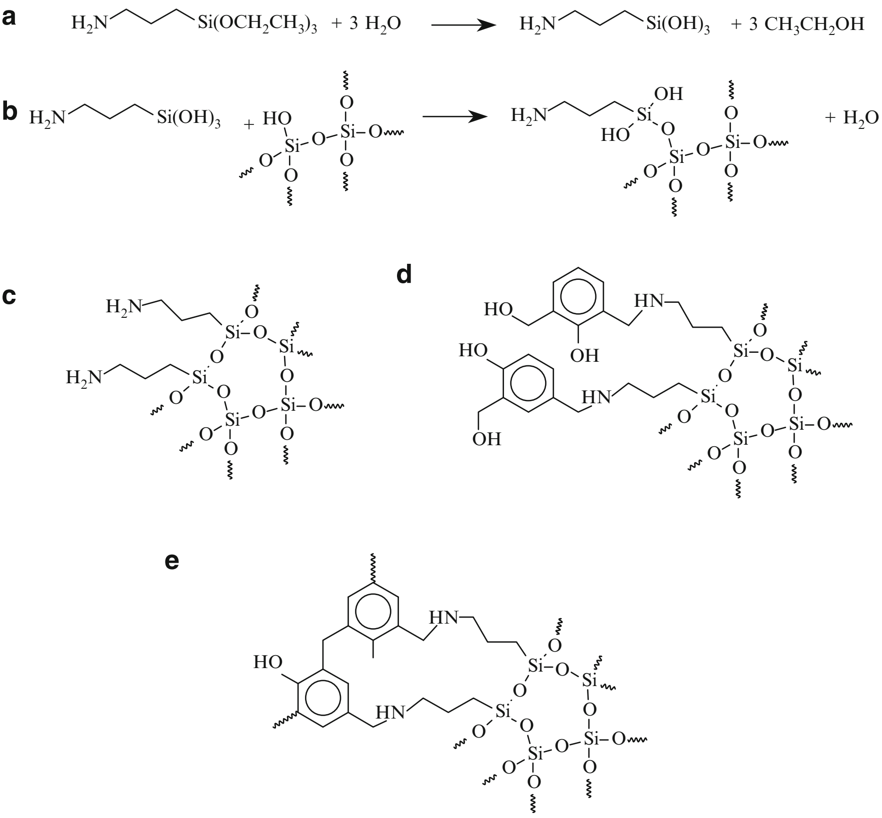
10.3.4 Emulsifier

Emulsifiers keep the aqueous binder combined with the mineral oil (de-dusting oil) in a stable emulsion, at least until the binder is used for the manufacture of the mineral wool. Non-ionic emulsifiers are preferred.

10.3.5 Silanes

The addition of small amounts of silanes significantly increases the tensile strength of the mineral wool. Most frequently, γ-aminopropyltriethoxysilane (AMEO-T) is added to the binder. This silane is stable in aqueous solution at pH 7 and hydrolyses only under acidic or alkaline conditions forming γ-aminopropylsilanol (Scheme 10.5, a).

The alkaline hydrolysis takes place upon the addition of the silane to the water-diluted binder composition. In the next step, the free silanol undergoes a condensation reaction with the hydroxyl groups attached to the silicate glass surface, making a covalent bond; thus, the amino moiety is linked via a propyl-spacer to the surface of the glass (Scheme 10.5, b). The already anchored silanols can mutually condense further affording the siloxane matrix (Scheme 10.5, c). In the final step, the methylolated species of the resole resin can condense with the amino group-linker of the silanol and results in covalent bonding of the resin species to the glass surface (Scheme 10.5, d). Upon complete hardening, the cross-linked phenolic resin is,



Scheme 10.5 γ-Aminopropyltriethoxysilane is used as coupling agent

in this way, chemically bound (at least partially) to the surface of the glass fibers (Scheme 10.5, e).

Optimization experiments were conducted to determine the relationship between the percentage of AMEO-T and the burst strength of the sand moulds (Chart 10.2).

In the absence of AMEO-T, there is no resistance against wet ageing. The application of 0.2% of AMEO-T (based on the SC of the resin) was found to be optimal.

10.3.6 Ammonium Sulfate

The PF resoles are self-hardening, due to the presence of methylol groups capable of forming methylene or methylene ether bridges in the C-Stage of the resin. The polycondensation reaction shown in Scheme 10.2, may proceed under acidic or basic conditions. However, in the manufacturing process of mineral wool, only

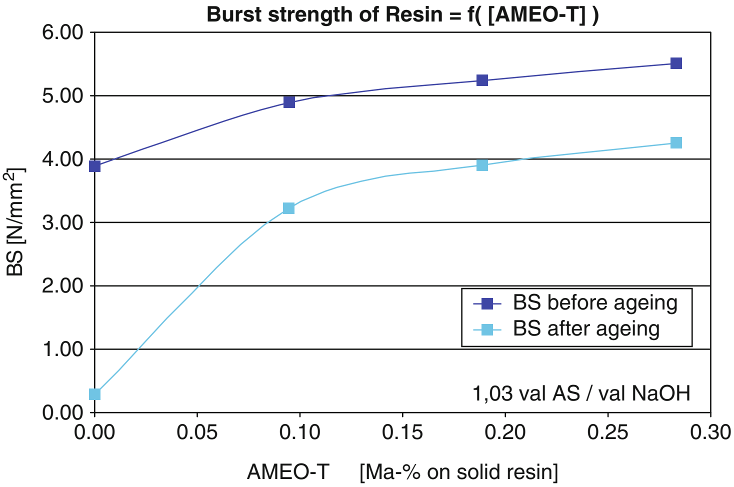


Chart 10.2 The dependence of the burst strength of the sand bars on the amount of γ-aminopropyltriethoxysilane (AMEAO-T)

urea-extended PFU premixes are used. These PFU premixes comprise methylolated ureas which undergo effective polycondensation reactions (Scheme 10.2, a and b) only under acidic conditions. This means that the mineral wool will develop a satisfactory tensile strength only if it is cured under acidic conditions [24]. Thus, it is desirable to use acidic conditions during the curing of the mineral wool. With organic base-catalyzed resole resins, the catalyst evaporates in the hot end of the mineral wool production line. The remaining phenolic components shift the pH into acidic range, thus facilitating the curing process. In contrast, the resins catalyzed by nonvolatile inorganic bases require the utilization of an acidic catalyst for curing. The resole PFU resins for insulation are, in most cases, not stable under acidic conditions and condense further, leading to limited water dilutability, or in a worst case, to instant precipitation of polycondensated species. So, the direct addition of an acid to the resin binder in order to adjust the proper acidic pH level is not possible. Therefore, the so-called latent acidic catalyst is added to the binder to achieve the optimal pH during the curing process. The latent catalyst is added to the binder at the mineral wool manufacturer's site, just prior to use of the binder. Upon the addition of the latent catalyst, the pH of the formulation is not changed considerably. The working principle of the latent catalysis is based on the release of the acid only at elevated temperatures and so reaches the necessary acidic conditions required for curing on time in the oven. The latent catalysts are usually salts of a strong acid with weak bases, the most common being AS and ammonium phosphate, especially the former due to its low cost.

Another function of AS is to regulate the B-Stage time (Chart 10.3).

Most commonly, the B-Stage time is longest during the application of 1 mol of AS. In general, phenolic resins have the slowest gel time under neutral conditions [42].

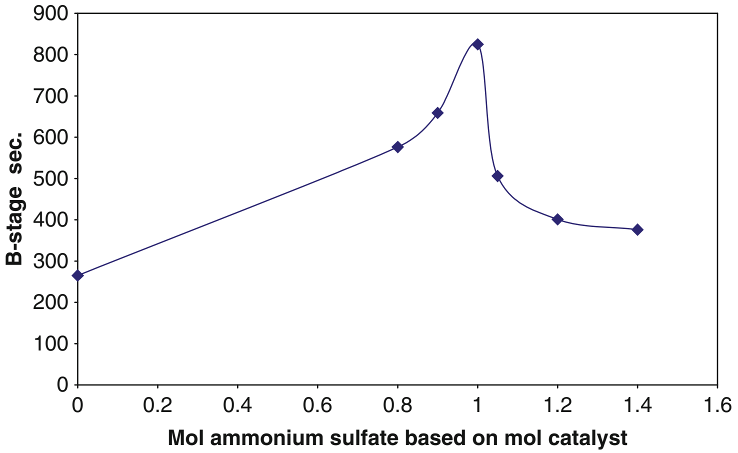


Chart 10.3 The effect of the addition of ammonium sulfate on the B-Stage time of the PFU premix at 130°C

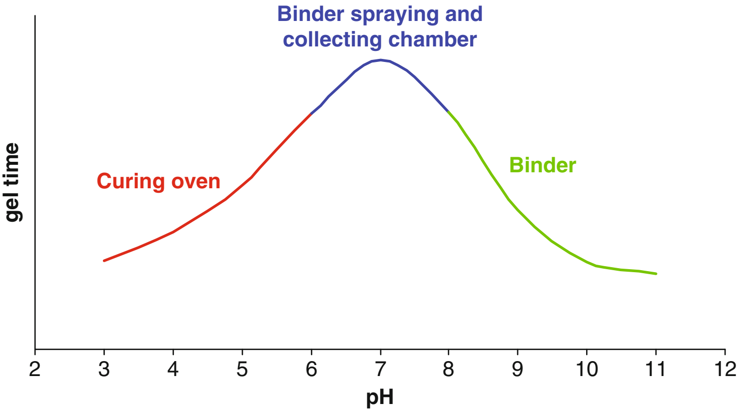


Chart 10.4 The effect of pH on the rate of thermal hardening of phenolic resole resin. The gel time is plotted against the pH (Dynea)

Thus, the proper amount of ammonium sulfate is used to avoid pre-drying of the mineral wool on the receiving conveyor belt entrance and to achieve a complete hardening in the curing oven on exiting. Pre-drying allows the viscosity to increase and provides a good binder flow on the fiber surface onto the fiber junction points. Too much pre-drying results in poor binder efficiency.

It is believed that during the manufacturing process of mineral wool, the pH is varied in the different production steps due to the addition of a proper amount of AS. Hence, the latent catalyst sequences the proper production steps of mineral wool by pH change. The initial addition of AS to form the binder results in a pH value in the alkaline region (Chart 10.4).

Upon spraying the binder onto the hot fibers, the crude mineral wool is transferred to the collecting chamber. Here, at around 80°C, the pH starts to shift toward a neutral area of around 7, where the gel time is longest. In the collection chamber while moving along the conveyor belt, the binder slides along the fibers toward their intersection points. This long gel time assures a complete covering of the fiber intersection locations with the binder. If the pH of the binder at the collection chamber stage is acidic or alkaline, a pre-curing of the mineral wool would take place before the mineral wool enters the curing oven. This pre-cured mineral wool cannot be compressed to a desired shape/thickness in the curing oven and the final mineral wool product would not have its shape recovery property.

From the collecting chamber, the wool moves on to the curing oven, where the pH becomes acidic and a complete curing takes place. It should be noted that this is only a hypothesis and that the real pH is not measured during the different steps in the mineral wool manufacturing process.

Lastly, AS provides the mineral wool its characteristic color. When the raw mineral wool leaves the spraying chamber and moves along the receiving conveyor belt, it is white. Only after the curing, the color of the glass wool turns to yellow (Fig. 10.10).

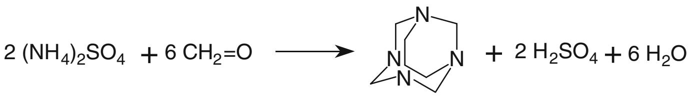
The brightness of the yellow color increases with the amount of AS. The red color of the PFU premix with a prevalent PF component may be attributed to the presence of the quinones in the resin and undergoes a blue shift during curing with AS.

It is possible to consider other side reactions that occur as they relate to chemistry, emissions, and product quality. Upon the addition of AS to the resin (resin prepared with sodium hydroxide catalyst), an acid–base neutralization reaction takes (Scheme 10.6) place.

Fig. 10.10 The effect of the extension level of the PFU premix and the amount of ammonium sulfate on the color of the glass wool (Dynea)

$$2\ \mathrm{NaOH} + (\mathrm{NH_4})_2\mathrm{SO_4} \rightleftharpoons \mathrm{Na_2SO_4} + 2\ \mathrm{NH_4OH}$$

Scheme 10.6 Primary reaction of ammonium sulfate with the catalyst of the resin



Scheme 10.7 Reaction of ammonium sulfate with formaldehyde leads to the lowering of the pH by the formation of hexamethylenetetramine sulfate

The released ammonium hydroxide contributes to ammonia emissions. Since the AS is applied in more than 2:1 stoichiometric amount, the excess AS enters into a possible condensation reaction with free formaldehyde, leading to hexamethylenetetramine sulfate (Scheme 10.7).

Formaldehyde is not only present in free form in the binder but is also liberated during the curing process (Scheme 10.2). As ammonia is a stronger base ($\mathrm{p}K_\mathrm{b} = 9$) than hexamethylenetetramine ($\mathrm{p}K_\mathrm{b} = 5$), the reaction of AS and formaldehyde results in a reaction mixture that is more acidic. This reaction is the “keystone” of the latent catalyst principle. It should be noted that a latent catalyst such as AS is actually not a catalyst, because it is chemically modified during cure. A more accurate designation would be a “hardener”.

As mentioned at the beginning of this section, only an acidic cure is effective for PFU resins. This can be demonstrated by the dependence of sand bar burst strengths with the amount of AS (Chart 10.5) [24].

In the absence of AS (alkaline curing), the sand bars did not possess any resistance to wet ageing. The application of 1.03 mol of AS to 1 mol of catalyst optimizes dry and wet strengths. It should be noted that each resin requires different amounts of AS to achieve the maximum burst strengths. The amounts of AS are usually in the range of 1.03–1.3 mol.

10.3.7 Extenders

Extenders are used to extend the resin or binder. For example, carbohydrates [18, 43], polyacrylic acid [21], melamine [44, 45], dicyandiamide [46, 47], animal bone glue [46], polyvinyl alcohol [43], and lignins [43, 45–51] have been reported. In most cases, the addition of extenders reduces the tensile strength of the mineral wool and so only a limited amount can be tolerated. On the other hand, the application of extenders reduces the emissions of VOCs. Moreover, it may reduce the cost of the resin or binder.

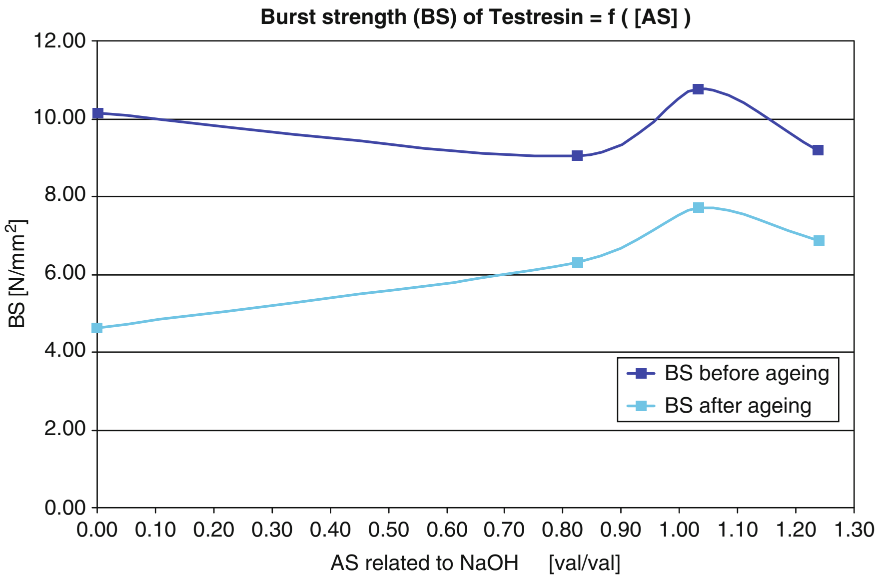


Chart 10.5 The effect of the amount of ammonium sulfate on the burst strengths of the sand moulds. Arbitrary PFU insulation resin was used (Dynea)

10.3.8 Water

Water plays a critical role in the binder formulation. Primarily, it works as a diluent, that is, the concentrated resin is diluted to 5–20% SC. During the spraying, the water cools the hot mineral wool and thereby prevents pre-curing of the resin. The temperature of the water used for dilution has to be considered, since it influences the oil emulsion stability; if it is too cold, the emulsion will get destabilized. It should also be noted that the water dilution is necessary to facilitate the distribution and flow of the resin solids over the glass fibers.

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Chapter 11
Laminates

Karin Lepedat, Robert Wagner, and Jürgen Lang

Abstract The use of phenolic resin for the impregnation of a carrier material such as paper or fabric based on either organic or inorganic fibers was and still is one of the most important application areas for liquid phenolic resins. Substrates like paper, cotton, or glass fabric impregnated with phenolic resins are used as core layers for decorative and technical laminates and for many other different industrial applications. Nowadays, phenolic resins for decorative laminates used for furniture, flooring, or in the construction and transportation industry have gained significant market share. The Laminates chapter mainly describes the manufacture of decorative laminates especially the impregnation and pressing process with special emphasis to new technological developments and recent trends. Moreover, the different types of laminates are introduced, combined with some brief comments as they relate to the market for decorative surfaces.

11.1 Introduction

Impregnation of a carrier material such as paper or fabric based on either organic or inorganic fibers generally requires saturating them with excellent resin penetration. Many of the fabric impregnating operations consist of fiber impregnation for fiber reinforced plastics (FRP) and molded laminates for industrial uses. The FRP area will be discussed in Chap. 12. The latter area was extensively discussed in the previous book. Further, those involving impregnation of paper for electrical

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laminates are trending downward with much of these phenolic paper laminates being manufactured in China and the Far East. In spite of the fact that majority production of paper electrical laminates is centered in the Far East, it is estimated the market value of paper laminates for 2008 is slightly over $1 billion with most production in Asia, especially China.

The major portion of the this chapter considers decorative laminates and the various products that are available. The role of phenolic resin as the core material will be discussed, as also the preparation of these laminates.

Plastic laminates were introduced in the early 1900s using phenolic resin and paper as insulating material at Westinghouse, Pittsburgh, PA for the use in radio sets and radio exterior. Later in 1927, it was discovered that by adding decorative paper through a lithographic printing process, laminates could be manufactured with patterns that simulated wood grains and marble.

11.2 Surfacing Materials

A variety of surfacing materials and the types of products that emerge from these materials can be considered.

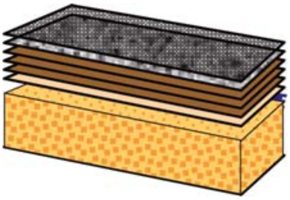
In the field of surfacing materials, a multitude of solutions exists in the market place. In principle, these technologies can be divided in two groups, resin/paper based and paperless surfacing materials.

For the paper/resin based surfacing solutions, HPL (high pressure laminates, Scheme 11.1), CPL (continuously pressed laminates Scheme 11.2), CL (compact laminates, thick and self supporting HPL), LPL (low pressure laminates), paper based finished foils, and paper based edge banding material are mentioned. All of them consist of one or more layers of resin saturated papers.

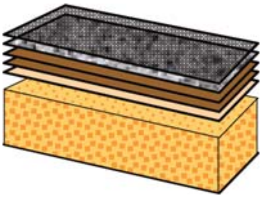
Paperless surfacing solutions contain among others pigments, varnishes, veneers, and thermoplastic foils.

11.2.1 Paper/Resin-Based Surface Materials

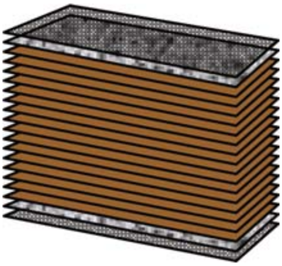
A typical thin HPL (generally 0.2–3 mm) is a material composed of several layers of PF saturated kraft paper which are pressed together with a sheet of MF



Scheme 11.1 HPL



Scheme 11.2 CPL



Scheme 11.3 Compact board

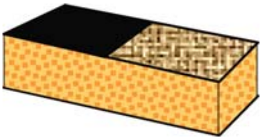
(melamine formaldehyde resin) saturated décor paper in a discontinuous high pressure (55–90 bar) and hot (up to 160°C) process during which the resins are fully cured. For some applications, such as laminate flooring, an MF impregnated corundum overlay paper is used on top of the décor layer to ensure desired abrasion resistance. Usually, a thin HPL is glued on top of a substrate like particle board or HDF (high density fiberboard). Typical applications such as thin HPL are kitchen countertops, worktops, and furniture elements.

Compact Board (Scheme 11.3) is basically manufactured in the same manner as thin HPL but the final laminate is sufficiently thick to maintain its own structural integrity.

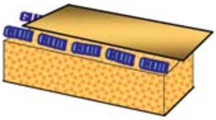
A typical CPL consists of several layers of PF impregnated Kraft paper, superimposed by a layer of MF impregnated décor paper and in some cases by MF impregnated overlay paper. Generally, the thickness of CPL is in the range of 0.2–2 mm. The laminate is manufactured in a continuous, double belt press at high temperatures (180–190°C), at pressures of 20–70 bar, and at line speeds of 10–20 m/min during which the resins are fully cured. CPL can be rolled or cut in sheets, the product performance is similar to HPL, but the lower pressure applied during manufacture prevents it from being called "high pressure laminate." As HPL, CPL is glued on top of a substrate like particle board.

Typical applications are similar to HPL.

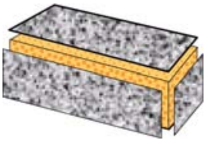
LPL ((Scheme 11.4), also LPM for low pressure melamine, TFM for thermally fused melamine, MFC for melamine faced chipboard, DPL for direct pressed laminate) consist of amino resin (UF, MF, or blends of both) impregnated sheets of different papers directly pressed on top of a substrate like particle board, MDF (medium density fiberboard) or HDF (high density fiberboard) (Scheme 11.4). The resin saturated papers are self bonding which means that the resin flows into the surface of the substrate as they are finally cured in a discontinuous short cycle press



Scheme 11.4 LPL



Scheme 11.5 Foils



Scheme 11.6 Edgebanding

at typical temperatures of 160–220°C, pressures of 20–40 bar within 10–40 s. Main applications are furniture elements and laminate flooring.

Paper based finished or decorative foils (Scheme 11.5) are manufactured by an impregnation process using cellulose paper of 30–80 g/m^2 paper weight and blends of resins (e.g., UF and acrylic emulsion), depending on the final application. These impregnated papers do not require a topcoat, but depending on the application, a finished topcoat is normally added. A few technologies to cure the topcoat are heat set, electron beam cure, and UV radiation. Finished foils are supplied fully cured and require a glue system to bond them to a substrate. Typical applications are in the furniture industry.

Typical edge banding material is CPL, HPL, or highly flexibilized melamine resin impregnated paper used to decorate the edges of any kind of substrate like particle board (Scheme 11.6).

11.2.2 Decorative Surface Markets

As one examines the total European market of surface finishing materials, the importance of laminates (mainly melamine films for LPL, but also CPL and HPL) is apparent (Fig. 11.1).

As impressive as the above graph illustrates, the predominance of melamine films is expected to be even greater in the future. Some growth is also expected for HPL, CPL, and paper foils whereas varnishes, lacquers, and thermoplastic foils are expected to be static or sluggish.

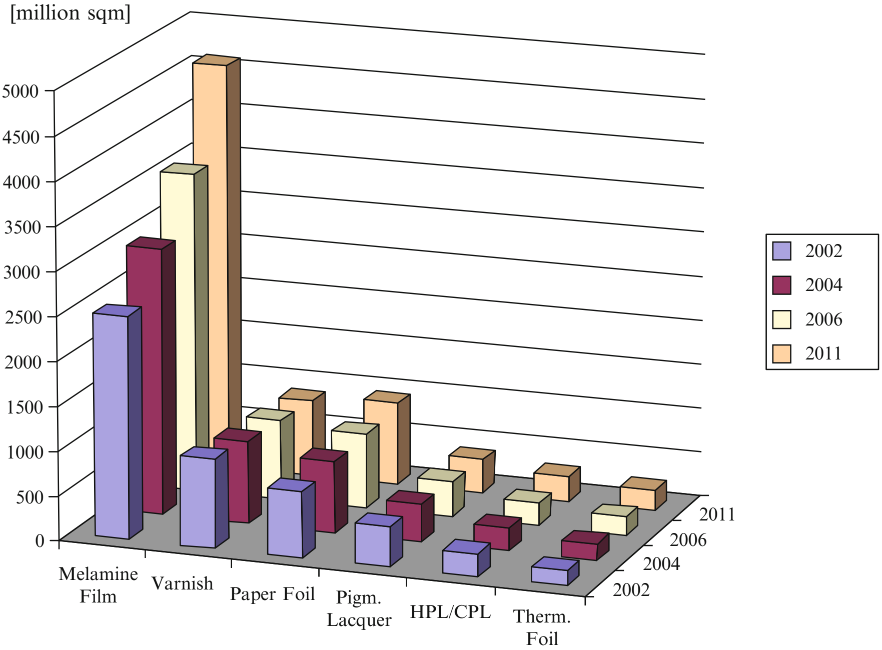


Fig. 11.1 Consumption of surface finishing in Europe (2011 forecasted)

The world decorative laminates market is expected to reach $23.6 billion by 2012. It is estimated that global sales in 2009 will be greater than $21.2 billion with United States sales exceeding $7 billion in 2009, Europe sales of over $6 billion, and Asia–Pacific about $3.1 billion [1]. According to the market study, continuous innovation is expected to result in more novel applications in consumer audio–visual electronics and interior fitting of automobiles, boats, and caravans. The study emphasizes the impact of fashion and cultural trends in interior design. These trends are captivating the interest of consumers as digitally produced images and patterns in vivid, bold colors are entering the marketplace.

Besides HPL (thin and compact laminates) and CPL, LPM (low pressure melamine) products are considered as "laminates." A careful examination of these markets indicates that "real laminates" like CPL and HPL are experiencing a continuous decrease in market share whereas LPM are gaining market share during these past few years. This trend is mainly due to the fact that LPM not only continues to replace HPL and CPL in laminate flooring but also in furniture and worktop applications (Fig. 11.2).

For the production of estimated 290 million m of laminates, consisting of 180 million m HPL, 95 million m CPL, and 15 million m compact boards, approximately 180 kt of PF resin and 30 kt MF resin have been used in 2007 [2]. During the

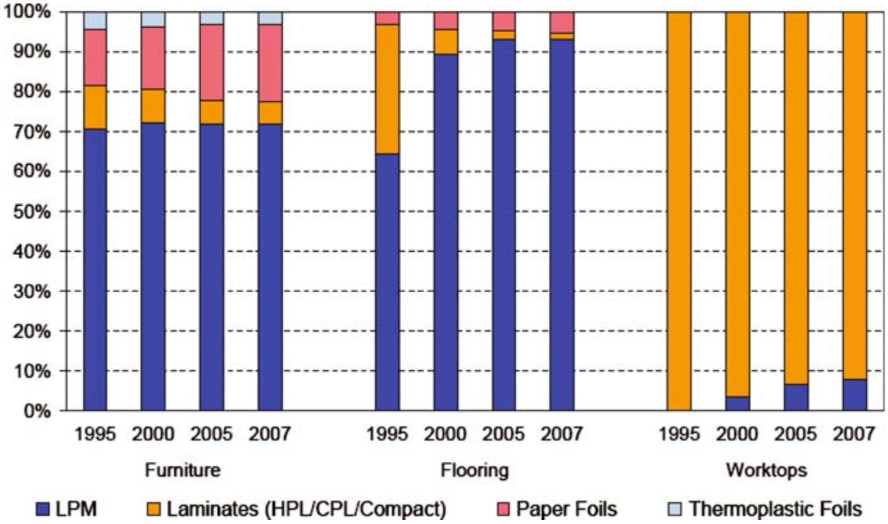


Fig. 11.2 Consumption of different surface finishing in Europe (with permission of Dr. Cormac O'Carroll and Dr. George Goroyias of Pöyry Forest Industry Consulting, London, UK)

same time the total European market for MF has been 550 kt and for UF 200 kt. This reflects the dominance of LPM and paper based foils as panel surfacing materials.

Overall, the share of real PF resin containing laminates is expected to remain static or decrease to a level of 6% showing significant growth only in the segment of compact boards. If there is growth in thin laminates, then the growth originates from CPL.The growth in compact boards is mainly originating from its growing exterior applications.

In Europe, the most important countries producing PF resin based laminates are Germany, Italy, Spain, Poland, The Netherlands, The United Kingdom, Finland, and Austria. Although Western Europe will remain the main location for laminates production, a shift toward the current net importing countries in Eastern Europe and Turkey is expected.

11.3 Decorative Laminates

In general, decorative laminates consist of a core impregnated with phenolic resins and a decorative surface impregnated with melamine resins.

For the production of the core layers, kraft paper with a raw paper weight of 80–260 g/m^2 is impregnated in a continuous process and then dried under defined conditions at temperatures of 100–160°C.These prepregs are pressed under heat and pressure together with melamine resin saturated decor-paper impregnated in a similar process.

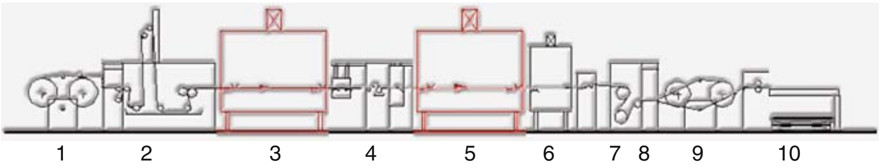
A good and detailed introduction to the different manufacturing steps from producing resins to the final laminate by several authors of leading suppliers to the laminates industry can be found in [3].

11.3.1 Impregnation Process

11.3.1.1 Core Layers

Kraft paper from an unwinding device is transferred to an impregnation bath filled with phenolic resin. With squeezer rolls the resin content of the paper is adjusted before the paper enters the drying sections. Here the paper web is transported on a cushion of hot air. With an appropriate temperature/line speed profile the impregnated paper finally reaches the desired parameters regarding remaining volatile content, flow, and condensation degree of the resin. After a cooling section the paper is cut to sheets for multi daylight presses or rewinded for CPL presses.

Modern impregnation devices (Fig. 11.3) are highly automated with automatic roll changer devices, online measurement of volatiles, and paper weight. To reach high line speed (>200 m/min) raw paper can be preheated and sky rolls are used to improve penetration. To increase the output modern devices run with double width (about 2.70 m). Pilot impregnation devices are used for the development of suitable paper/resin systems (Fig. 11.4).



1. Unwinder
2. Impregnation device
3. Dryer
4. Intermediate coating (Amino Resins)
5. Dryer
6. Cooling device
7. Web aligner
8. Cooling device
9. Rewinder
10. Sheeter

Fig. 11.3 Principle scheme of a horizontal impregnating system for decorative laminates

Fig. 11.4 Pilot impregnation line from company VITS at Dynea Austria GmbH, Krems, Austria

11.3.1.2 Decorative Surface

The principle process is quite similar. Paper printed with different decors is impregnated with melamine resin. In some cases urea resins are used in a first bath and at an additional coating station the paper is coated with a melamine resin. A corundum containing MF-coat can be applied on the surface (liquid overlay) to achieve high abrasive resistance. The penetration is normally worse compared with PF resins, so sky rolls are in use. Generally, and in contrast to PF, a (latent) catalyst is required additional to heat for curing MF and UF resins. Current trends involve better penetrating resins, wetting agents, and modern lines to increase line speed. Other additives are used to improve gloss, scratch resistance, chemical resistance, conductivity… and to decrease dust formation.

11.3.2 Pressing Process

Thermosetting resins like PF-, MF-, and UF-resins are cured under heat and pressure.

Different press processes are possible (Fig. 11.5).

From the above listed press types the following types are established for decorative laminate production:

- Multi opening press
- Isobaric double band press

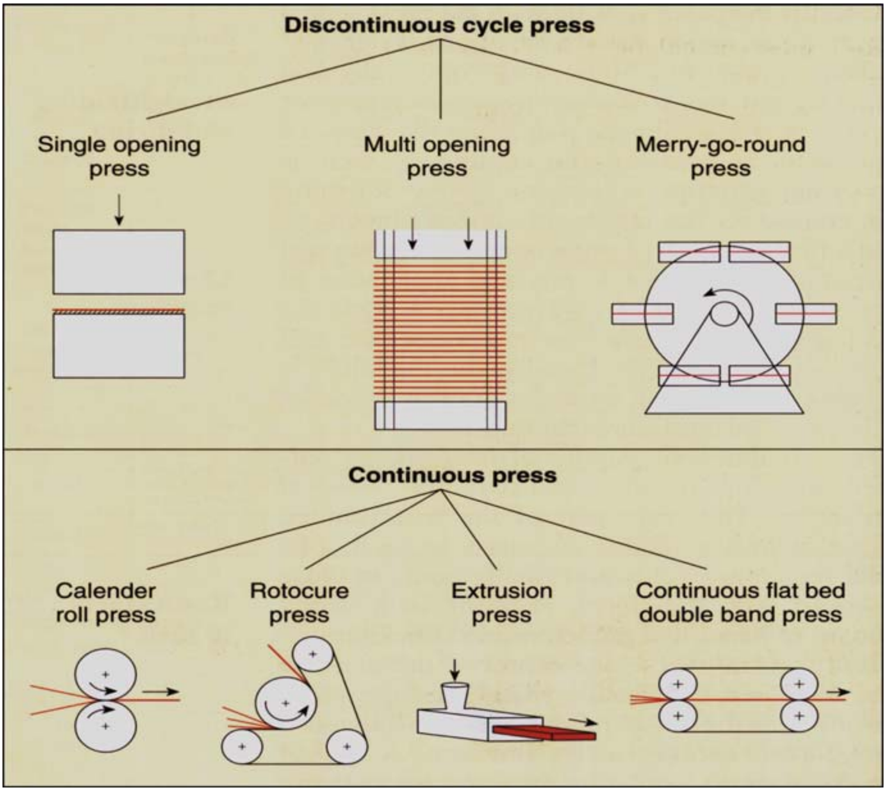


Fig. 11.5 Overview pressing systems

As every general overview has its exemptions, a few short-cycle presses can be found for the decorative laminate production as well as a few multi opening presses for the production of melamine boards.

11.3.2.1 HPL Production with Multi Opening Presses

This is a discontinuous pressing process (loading, pressing, unloading). Pressure is applied by hydraulic cylinders and the heat is transferred through the press plates. The number of laminates pressed in one cycle is dependent upon the number of openings and the thickness of the laminates. In a normal press cycle the press is heated to the pressing temperature (130–160°C), stays at this temperature for 10–25 min and is finally cooled down to 40–60°C-all under high pressure of 7–10 MPa.

Press lines (Fig. 11.6) for HPL normally consist of the following elements:

1. lay-up station for the core layers and decorative layers together with the steel plates

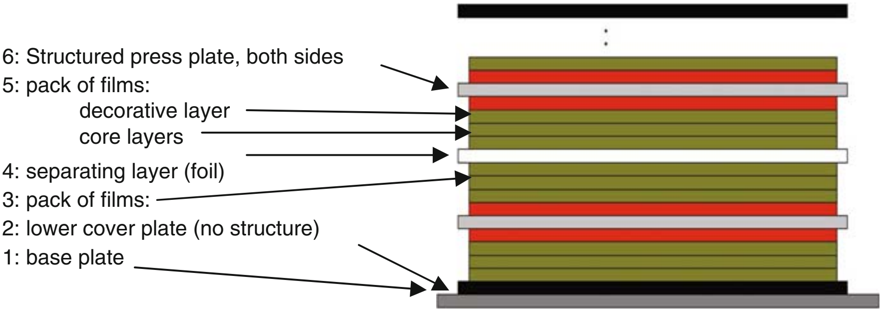


Fig. 11.6 Build up of a press stack

Fig. 11.7 Multi opening press

2. loading basket in front of the press
3. multi opening press
4. unloading basket behind the press
5. dismantling station to separate the finished laminates from the steel plates
6. conveyor system for steel plate circulation

The films are delivered in sheets to the press line (Fig. 11.7). Core layers can be prepared to sets (number of core layers) already in a separate core preparation department. The films have to be composed to sets (book-building) of decorative layers and core layers. After preparation of the required number of sets and removing them from the loading basket in front of the press, the whole batch is fed at once into the open press. After closing the press and achieving the required pressure, heating commences. The heat is transferred from the heated press plates throughout the sets of films, until the resins have reached the required temperature for curing.

Cooling the laminates before unloading the press will prevent vapor from protruding through the surface. After finishing the pressing cycle, the press is unloaded at once into the unloading basket. From there, the single packs of finished laminates are fed forward to a dismantling station, where the laminates are separated from the steel plates and the separation foil.

This technology is most effective for thick laminates (2–15 mm).

Different surfaces are possible (even metal foils); especially high gloss surfaces.

Nowadays, the production of compact boards (4–15 mm) with multi opening presses is increasing. New trends are moving toward compact boards for outdoor use with UV resistant surfaces and fire retardant compact boards fulfilling different national standards.

This continues to be the traditional way to produce laminates.

11.3.2.2 HPL Production with Short Cycle Presses

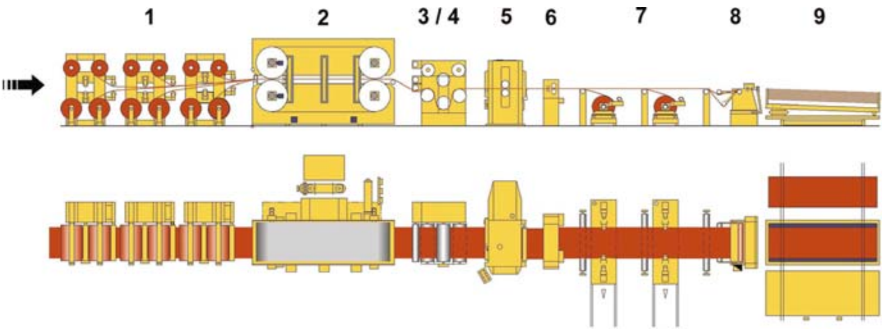
Short cycle presses (Fig. 11.8) are widely used for the direct lamination process where a MF decor-paper is directly pressed on a wooden substrate like particle board or MDF/HDF. In some cases, a PF impregnated underlay is used to improve properties. For HPL laminates, this technology is rather seldom used. The advantage is the size of the finished laminates having dimensions up to 5.70 m × 2.70 m. By this process, two thin or one thick laminate can be produced. The press is opened without a cooling cycle, so the production of high gloss laminates is limited to lower gloss levels.

Fig. 11.8 Short cycle HPL press

With short cycle presses, HPL with 0.2–15 mm can be produced. With specially developed resins from Dynea, fire-retardant laminates and flexible compact boards for bowling lanes can be produced.

11.3.2.3 CPL Production with Isobaric Continuous Double Band Press

In the last decade, the continuous production of decorative laminates with Double Band Presses (Figs. 11.9 and 11.10) has gained greater prominence, particularly in Europe. With newly developed pressing – and resin systems, the quality of CPL has



1 – film unwinding
2 – double band press
3 – cooling station
4 – release paper rewind
5 – rear side sanding
6 – edge cutting
7 – laminate rewind (for thin laminates)
8 – clipper, cutting laminates to sheets
9 – sheet stacking

Fig. 11.9 Principle scheme of a double band press

Fig. 11.10 CPL double band press

improved remarkably. CPL with new properties has entered the traditional markets for HPL produced with multi daylight presses. The development of new melamine resin systems for decorative layers and overlays, and phenolic resin systems for the core, has had a major impact on increasing the variety of possible applications. It is now possible to produce almost any type of thin laminates with CPL technology.

11.3.2.4 Special Features of CPL Process

It is a continuous pressing process which is suitable for thin laminates (0.2–2 mm) mainly 0.2–0.8 mm. Most of the laminates are post-formable with bending radius (0.6 mm laminate) up to 3 mm.

The laminate build up is similar to HPL:

- Overlay/decor – MF impregnated
- Core layer – PF impregnated
- Backing – raw paper; parchment; PF-impregnated paper

The pressing temperature is about 180°C–190°C.

Depending on the press parameters and the thickness of the laminates the line speed is 10–15 m/min. With an efficient press, it is possible to operate at about 40 m^2/min.

Older presses operate with 2–2.5 MPa pressure whereby modern presses can reach up to 7 MPa which means they can produce HPL in a continuous manner.

Due to the short pressing time, fast curing core resins are necessary. Dynea provides co-condensed MF/PF resins with special flexibilizer combinations and latent hardeners.

11.3.2.5 New Developments

Products manufactured via CPL technology have now penetrated the following application areas which were once the domain of laminates produced exclusively by static presses:

- Standard and post-formable laminates as HPL ($p > 5$ MPa)
- Flame retardant laminates fulfilling all relevant fire tests in building and transportation industries
- Decorative laminates with different surfaces:
  - Melamine surfaces with different pore structures
  - Wear resistant surfaces
  - Metal foil surfaces with aluminum, stainless steel, and copper
  - Digitally printed decors
  - High gloss melamine surfaces

11.3.3 Laminate Properties

Due to different final applications, the decorative laminates must meet different market requirements.

Basic properties are described in different industrial standards, for example, DIN EN 438.

11.3.3.1 Surfaces

The classical surface layers still consist of a monochromatic or printed MF impregnated décor-paper.

For outdoor use, UV protection can be applied in different ways (protection foils, lacquering, additives...).

For laminate flooring, wear resistant surfaces with paper overlays or liquid overlays are used.

Other special properties which can be achieved at the surface are chemical resistance, high gloss, antibacterial surface for flooring and kitchen work tops and antistatic properties for computer desks.

For special optical effects, metal foils or even true wood veneer can be pressed on the core layers.

11.3.3.2 Core Layers

The type of phenolic resins used in the core layers defines the laminate properties.

Regarding the basic properties in principle we could differentiate in

Standard HPL laminates	0.2–4 mm
Post forming laminates	0.2–1 mm
Compact boards	4.0–15 mm
Fire-retardant laminates	0.4–15 mm

All thin basic types can be produced in static presses or continuous press-lines.

11.3.3.3 Standard HPL Laminates

For environmental reasons, methanol based resins are being replaced by waterborne resins as well as an accompanying reduction of free monomers like Phenol and Formaldehyde.

To achieve higher line speed at the impregnation line, resins with improved penetration properties have been developed.

Due to the price explosion of synthetic raw materials, there is a trend to use – at least partly – renewable materials like sugar derivatives.

11.3.3.4 Post Formable Laminates

Especially for the production of kitchen tops, the laminates are curved around the edges of a wooden substrate in a post forming line .For this purpose the laminate is exposed to heat for a short period of time provided by hot air or infrared radiation and then bent around the edges. The bending radius has become much smaller, and nowadays, there is a demand for bending radius' of 2 mm (0.6 mm laminate). In earlier times, PF resins with high amounts of free Phenol were used. Modern resins include combinations of flexibilizers. CPL resins with MF-modification and flexibilizer provide very good post formable properties.

11.3.3.5 Compact Boards

Compact boards are self-supporting, which means they are not glued on a wooden substrate. They consist of many layers of core paper, normally covered with an MF-impregnated decor-paper on both sides. These continue to be a growth market in the construction industry including outdoor applications (Fig. 11.11). Special resins are used especially under humid environment conditions to guarantee low water absorption, high dimensional stability, and good flexibility to avoid micro cracks.

Fig. 11.11 Chelsea Arts Tower New York City with Compact Board Facade from the Company Trespa

11.3.3.6 Fire-Retardant Laminates

With higher standards in fire protection, fire retardant laminates are becoming more and more important.

Laminates used in the construction industry especially in public buildings must fulfill different standards. This is also true with respect to laminates used in the vehicle industry.

In principle, there are two ways to achieve flame retardancy:

- the use of special paper types containing ATH (alumina-tri-hydrate) with a standard resin or
- the use of resins with flame retardant additives and standard paper

Today, there is a tendency to use resins with flame retardant additives using phosphorous and nitrogen compounds as synergists instead of halogen containing compounds.

Trends

The major trends in the laminates we see currently are issues like high gloss for LPM to better compete with HPL, improved transparency of overlay films to fit to the trend of dark decors in LPM, improved scratch resistance of LPM, CPL, and HPL, chemical resistance, and the ability of narrow postforming radii of less than 2 mm of 0.5 mm thick laminates. Additionally and driven by the increasing demand for exterior grade HPL, improved UV and weather resistance are issues.

For flooring manufacture, new technologies like indirect printing (Fig. 11.12) or digital direct printing are gaining increasing importance. In these, the décor is

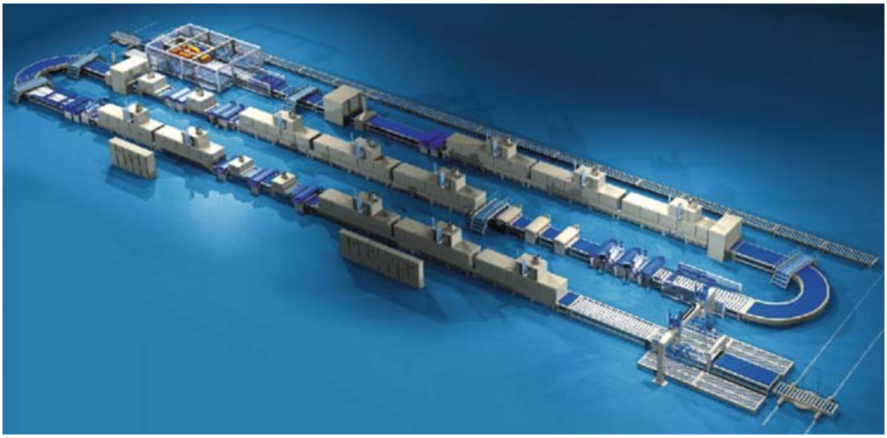


Fig. 11.12 Schematic production line for indirect printing, with permission from Hymmen GmbH, Bielefeld, Germany

printed on top of the raw panel which of course requires a perfect raw panel surface; the print pattern is then protected by several layers of lacquers.

11.4 Miscellaneous Impregnation Applications

11.4.1 Industrial Filter Inserts

Filter elements of fibrous materials and unfilled papers or paper-type materials such as webs or accordion folded tubes are used to separate solids from liquids or gases and to remove water from fuels or mineral oils. Adequate strength is achieved by impregnation with alcoholic solutions of phenolic resins, followed by partial curing. The advantages of phenolic resins are primarily superior heat and aging resistance.

The impregnated filters (Fig. 11.13) are used as air, oil, and fuel filters in the automotive industry as well as general purpose filters for liquids in various industrial fields like the chemical industry, and even dust filters or filters for air conditioners. The usual dip impregnation conditions are used for the desired resin level. Drying is staged to prevent full cure of the resin. The pre-dried, resin impregnated papers become easily flexibilized when heated to 100°C and shaped (pleated or napped). After pleating, the papers may be cured as a continuous web or finished paper elements.

A new trend is the production of pre-cured filter papers where the resin is already pre-cured at the impregnation line, so that the filter manufacturer only uses an IR

Fig. 11.13 Different car filters and battery separators

curing device for the final curing of the corrugated paper. For this purpose high flexiblilized resins are necessary.

11.4.2 Battery Separators

The impregnation of paper for storage battery separators is another special paper impregnation application. Separators are used in lead acid storage batteries to prevent direct contact of the oppositely charged lead plates. These electrically insulating paper separators exhibit high resistance to acids as well as oxidation with adequate mechanical strength.

Nowadays, battery separators based on polyester substrates impregnated with modified phenolic resins are used for high quality batteries in submarines, fork lifts, or as back up batteries for mobile phone antennas.

11.4.3 PF-Impregnated Paper for Cooling Pads

Evaporative cooling systems are easy and cost efficient solutions to create a suitable indoor climate for people, animals, food, and plants. The principle behind is that warm and dry air passes over a moist surface shaped like a pad (Fig. 11.14). This pad consists of corrugated cellulose paper sheets with different flute angles impregnated with special phenolic resins. The special structure of the phenolic resin ensures a strong self supporting product, with high absorbance, which is protected against decomposition and decay and therefore guarantees favorable longevity.

This method employs the “Munters’ Evaporative Cooling System” in which warm and dry air passes over a moist surface shaped like a pad. This pad, which is the key component in CELdek® and GLASdek® units, is composed of special

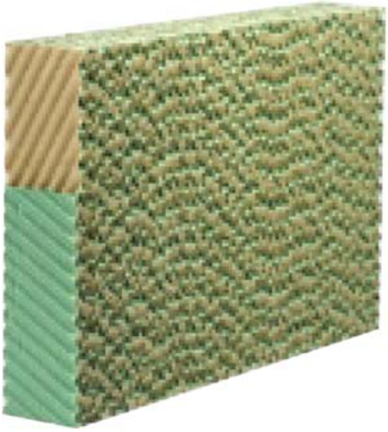


Fig. 11.14 Cooling pad for evaporative cooling systems

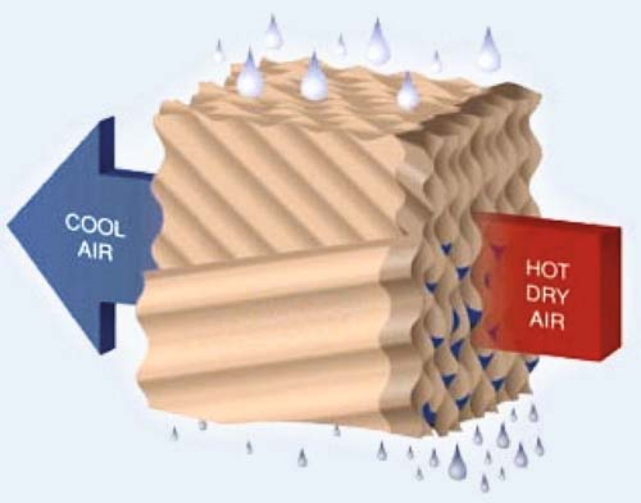


Fig. 11.15 Operation of cooling pad

materials in the form of cellulose or glass fibers with a geometry that maximizes the surface area over which the air passes (Fig. 11.15).

Together with fans, these products comprise the foundation for Munters' evaporative cooling systems. Munters' system for climate control is primarily used to create a favorable indoor climate for people, animals, food, and plants.

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Chapter 12
Composites

John G. Taylor

Abstract The Composites market is arguably the most challenging and profitable market for phenolic resins aside from electronics. The variety of products and processes encountered creates the challenges, and the demand for high performance in critical operations brings value. Phenolic composite materials are rendered into a wide range of components to supply a diverse and fragmented commercial base that includes customers in aerospace (Space Shuttle), aircraft (interiors and brakes), mass transit (interiors), defense (blast protection), marine, mine ducting, off-shore (ducts and grating) and infrastructure (architectural) to name a few. For example, phenolic resin is a critical adhesive in the manufacture of honeycomb sandwich panels. Various solvent and water based resins are described along with resin characteristics and the role of metal ions for enhanced thermal stability of the resin used to coat the honeycomb. Featured new developments include pultrusion of phenolic grating, success in RTM/VARTM fabricated parts, new ballistic developments for military vehicles and high char yield carbon–carbon composites along with many others. Additionally, global regional market resin volumes and sales are presented and compared with other thermosetting resin systems.

The quality that all phenolic composites offer is the capability to provide a fire safe, light weight composition at a relatively low material cost. Phenolic composites are commonly used in high temperature environments and wherever they can be applied to protect human life from fire. These crucial applications generally require extensive development and testing, allowing suppliers to demand a premium for many of their products. There are a variety of innovative methods to make a myriad of products for a number of industries, and each of the processes and applications are discussed in detail. Specifically, new processes such as the Quickstep™ Rapid Curing Process and the Double Vacuum Bag process have

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been developed and are expected to expand the use of phenolic resins in composites by reducing cost through improved efficiency and increased structural component size.

The Composites chapter examines both the advantages and disadvantages associated with the use of phenolics, along with the technologies that have been developed to enhance their attributes and mitigate their drawbacks.

12.1 Introduction

Composite materials are engineered systems made up of two or more distinct components that are combined in a design that imparts complimentary properties to the compounded product. The first composites could arguably be identified as the sun-dried bricks composed of clay and straw that were used to construct the adobe brick buildings of early civilizations. For reference going forward, composites will be discussed as fiber reinforced materials. These materials are to be distinguished from other short fiber-reinforced phenolic materials known as Molding Materials and discussed in Chap. 16.

The development of composite materials in the United States began over 60 years ago with the military's wartime need for lighter and faster aircraft and missiles that would give better performance while maintaining the strength of construction. The innovations required to meet those new requirements resulted in long lead times and high development costs that could only be tolerated by resourced military and civilian aerospace programs. Private sector cost constraints may not have allowed for that kind of development in those early days, but the advancements that were made in composite materials have subsequently been applied to a variety of industries and markets [1, 2].

Today, the composites market includes products for aerospace, aircraft, mass transit, defense, marine, mine ducting, off-shore, corrosion resistance, infrastructure, electrical apparatus, and sports products. The industrial production of fiber-reinforced plastics (FRP) composite materials is estimated at about 3 billion pounds in the United States (U.S.) [1], accounting for around 40% of the global market value [3]. Europe represents 35% of the value, while Asia-Pacific contributes 22% to the total. Polyester resins dominate the FRP thermoset resin market, controlling over 80% of the share. Epoxies and vinyl esters supply about 10% of the market, while phenolics provide less than 2% of the total FRP resin volume. Regarding cost, polyesters and phenolics are the least expensive and comparably priced, followed by vinyl esters and then epoxies [1].

The global market for thermosetting composites resins is approximated to be about $8–10 billion, with fire-resistant resins making up about 10% of the total. Phenolic resins comprise about 4–5% of the fire-resistant resin market, with polyesters and vinyl esters consisting of about 30–40% of the market and epoxies garnering most of the sales dollars at about 55–65% of the total [4].

Regarding fire-resistant materials, phenolic resins have demonstrated superior Fire, Smoke and Toxicity (FST) properties relative to other organic binder systems. They also provide excellent resistance to moisture and various other chemicals in combination with high temperature stability in the range of 200°C. The FST properties of phenolic resins are the primary factors that drive the selection of these products in many applications. There is no other matrix material available, which provides the same FST performance at a comparable price level. Formulations with other resin systems may be considered fire resistant as well, but that depends upon the additives used, the requirements of the application, and the definition of “fire resistant.”

The global phenolic composites market is dominated by the aircraft (interiors) and mass transit (buses, railways) industries with an increasing interest in marine applications. The success of phenolics in these areas is a reflection of the perspective to use fire-safe materials in “confined-space human occupancies” [5]. Even so, it is the preference of U.S. specifiers (e.g., for mass transit) to engineer for low cost and safe escape versus the broader global inclination to put fire-resistant materials into place. It is believed by some experts that it will take a high-profile accident (or incident) to bring FST issues into serious consideration [5]. Despite a growing need for flame-retardant materials and improved FST performance, the consumption of phenolic resins for composite applications has been relatively flat in recent years.

The use of phenolics outside the existing opportunities has been limited by process challenges associated with the emission of volatiles and by the lower mechanical properties of phenolic composites relative to those made with polyester, vinyl ester, and epoxy. The reluctance of fabricators to consider phenolics is exacerbated by the toxicity of volatile organic compounds (VOCs) such as phenol and formaldehyde, often requiring additional investment in exhaust devices. In spite of these obstacles, advancements in materials, processes, and in phenolic resin technology have resulted in a wide range of products for markets beyond the original aerospace and aircraft applications. Although the use of phenolics is still primarily driven by the need for good FST properties, these advancements have created the potential to continue to expand the use of phenolics into nontraditional applications.

12.2 Composites Market Segments

Relative to the broad labels given to the individual market segments previously identified, phenolic resins generally occupy niche sub-markets that are typically driven by the need for good FST properties. The sub-markets and the associated composite processes and resin technologies are described in detail in the chapter sections that follow. As a prelude, a general overview of the specific applications and traditional processes of phenolics within those markets is provided in the accompanying Table 12.1.

Table 12.1 Markets and market segments utilizing phenolic composites

Market	Segment	Process
Aerospace and aircraft	Ablatives	Pre-preg
	Aircraft friction	Pre-preg
	Aircraft interiors	Pre-preg Honeycomb Compression molding
	Cargo liners	Pre-preg
Automotive	Molding	Compression molding
Construction	Architectural	Hand lay-up
	Structural	Infusion molding
Defense	Ablatives	Pre-preg
	Ballistics	Pre-preg
	Shelters	Pre-preg Honeycomb
Electronics	Clean rooms	Filament winding
	Corrosion resistance	Hand lay-up
Infrastructure	Electrical conduit	Filament winding
	Mines	Filament winding
	Sewage abatement	Filament winding
Marine	Off-shore	Filament winding
	Off-shore	Pultrusion
	Military	Infusion molding
Mass transit	Bus and train interiors	Infusion molding
	Electrical conduit	Filament winding
	Underground	Pultrusion Hand lay-up

12.3 Resin Developments

Phenolics not only offer superior FST properties with respect to resins such as polyesters, vinyl esters, and epoxies, they also provide a very favorable cost – performance ratio. A primary constraint prohibiting their more widespread use lies in the processing difficulties that are encountered, as compared to alternative systems [6]. The vast majority of composites fabricators are reluctant to select a phenolic resin as the resin of choice unless mandated by the end-use requirements or specifications [5]. Consequently, a significant amount of development has been dedicated toward improving the processing characteristics of phenolic systems so as to enhance their attractiveness as a viable option.

Some of the principal challenges that are presented in the processing of phenolics are related to volatiles, shrinkage, and cross-link density. In addition to processing considerations, each of these issues can potentially compromise the mechanical performance of the finished composite as well.

Standard phenolic resins cross-link through a condensation mechanism. The by-products of this reaction are primarily water and some formaldehyde (trace amounts that do not react further into the cross-link structure), which manifest as volatile components that must be effectively managed in order to avoid vapor-related defects such as delamination and/or high void content in the composite matrix.

Because composite processes typically employ resole resins, the problem is compounded by the presence of solvents that can include additional water. The phenolic condensation mechanism results in shrinkage during cure, producing a dense, three-dimensional, hard but brittle cross-link structure.

Several approaches have been considered to address these issues. Acid catalysts or patented delayed action catalysts allow for resin cross-linking (or resin "cure") to occur at much lower temperatures (including ambient) than those required for standard thermosetting products. The result is a composite that is produced without "volatilizing" the solvents during cure, reducing or eliminating blisters and delamination. This technology has found utility in fast cure pre-preg, filament winding, infusion molding, and hand lay-up. Novel, patented, proprietary "impact modifiers" help reduce void content as well as cross-link density (fast-cure pre-preg, filament winding, and resin transfer molding (RTM)).

Progress has occurred with respect to the technology of impact modifiers as well. The company Nanoresins AG, Geesthacht, Germany, has developed a product in which a silicone elastomeric component is reacted with a phenolic resin, eliminating the presence of free silicone. The Albiflex H 1083 S1 is normally used at levels of 5–15% to provide elasticity to molding compounds containing phenolic resins [7]. Traditional additives such as polyvinylbutyral (PVB), nylon, and rubber can provide strength enhancements as well, but could be difficult to process and may compromise FST performance.

Void reduction enhances mechanical strength, and lower cross-link density promotes impact resistance by reducing the brittleness of the matrix. Modifications to the phenolic backbone architecture are another approach taken to reduce shrinkage and cross-link density. This technology has been combined with chemistry that provides a unique curing profile that gives a broader processing window to allow volatiles more time to escape during cure, further reducing void content (pultrusion). Oxazolidine chemistry may be used in combination with phenolic novolaks to offer potential benefits with regard to the management of formaldehyde emissions. The oxazolidine technology is employed by Shea Technology in combination with a novolak made with formaldehyde and phenol and/or resorcinol [8] to provide a room temperature or low temperature curing system for most of the composites processes, and by Dow Chemical for a novolak-based pultrusion system [6]. Finally, the development of benzoxazine technology presents an alternative to traditional phenolic condensation chemistry, eliminating the problems associated with the volatiles that are generated during the condensation reaction (aircraft interiors and composites general) [6].

The systems described are referenced in the following sections that discuss the various composite fabrication processes and applications.

12.4 Fiber Developments

FRP consume a significant quantity of fiber-based reinforcing material. The global production of glass fibers for FRP tops 3.5 billion pounds annually, compared to 30 million pounds of carbon fiber, and 10 million pounds of aramid [1]. Given the relative volumes, the following review of fiber developments for phenolic composites will center on fiberglass. There are four major North American fiberglass manufacturers, led by OCV (a division of Owens Corning and formed by the merger of Owens Corning's and Vetrotex's glass composite business) with over 45% of the market, and followed by PPG (Pittsburgh Plate Glass) (about 20% of the market), AGY (Advanced Glassfiber Yarns), and Johns Manville.

The key to all phenolic resin-based composites is the surface chemistry of the substrate (such as glass) and the subsequent adhesion at the resin–substrate interface. For most applications, a strong adhesive bond is desired, as this will increase the mechanical properties of the phenolic-glass composite. Generally speaking, amino silane-type sizings are best. However, ballistic phenolic composites benefit from a less than optimum adhesive bond. Ballistic performance is enhanced by failure at the resin–fiberglass interface, permitting the glass plies to behave as discreet entities that can more effectively dissipate energy. In this instance, a semi-compatible sizing is preferred, one that will provide sufficient handling strength for the composite while still allowing for delamination upon projectile impact.

OCV offers single-end rovings specifically designed for use with phenolic resins targeting applications requiring good FST performance. Their SE 8380 type 30 with silane-based sizing was developed with regard to phenolic resin pultrusion applications. Made from Advantex® glass fiber, this single-end roving combines the electrical and mechanical properties of E glass with the corrosion resistance of E-CR glass [9]. The 158B type 30 is another phenolic compatible roving. Other available phenolic compatible materials include the chopped strand products 183F (11C, 13C, 14C, and 14P), 497A (14C), 405D (17C), and DS5102 (13C). Milled fibers recommended for phenolic applications are 371, 737, and 739. Owens Corning has also developed a family of high-performance fibers for specific applications. WindStrand™ (wind blades), FliteStrand™ (aerospace), and XStrand™ (industrial) are typically used with epoxies and vinyl esters, but can be used with phenolics as well. A new ballistic grade glass fiber known as ShieldStrand™ is designed to be compatible with US military-approved phenolic resins to produce light weight composite armor that meets US military specifications for ballistic performance. The ShieldStrand™ composite armor provides a light weight, high performance and cost-effective alternative armor solution to S2 glass, K29 aramid composite armor, and Aluminum and Steel armor systems [10].

PPG also offers a number of phenolic compatible products. Type 1383 is used with different resins (including phenolic) and targets pre-preg applications for the aerospace market. Type 4588 has been used successfully for both filament winding and pultrusion processes that utilize phenolic resins. Finally, Type 3156 chop strand product has been specified for friction applications. PPG also distributes high-strength fibers designated as HS2/HS4, produced at the Sinoma Science & Technology facility in Nanjing, China. The products are used in aerospace and ballistic applications where phenolic resins are employed [11].

Likewise, Saint-Gobain Vetrotex provides materials that are suitable for use with phenolic resins. Their ZeroTwist products can enhance efficiency during impregnation, and the TD22 and TD37 (next generation) starch-free plastic sizings that are used contain silane bonding agents that promote compatibility with phenolics [12].

Although AGY produces a variety of glass products, their S-2 glass for ballistic applications is the recognized product for use with phenolics (see section on ballistics).

12.5 Composite Fabrication Processes

12.5.1 Introduction

The form and function of finished composites are determined by the fabrication process, the materials chosen, and the interaction between the two. Similarly, the selection of a process is limited by the materials required and vice-versa. These relationships are complicated by the availability of appropriate reinforcements and resin systems that must be compatible with each other and with the process itself.

Within these constraints, the various composite fabrication methods may be broadly divided into three general categories that are defined by the cost and performance criteria for a particular application. Commodity grade products are primarily price driven by definition, and have historically included those that are made by hand lay-up. However, a commodity is classified by availability, and phenolic systems that are proven to perform well in some hand lay-up applications are not commonplace. High-performance composites are found in applications that might require specific properties and shapes that can only be attained through unique processes such as pultrusion or filament winding [13]. Finally, advanced composites are generally defined as high-strength materials that are reinforced with continuous fibers of specific orientation [14]. Aerospace, aircraft, and military structures incorporate advanced composites that are typically manufactured using a pre-preg molding process. In these applications, performance of the advanced composite is more critical than cost.

Each of the fabrication processes that will be described is constrained by the design requirements of the end-use application. The benefits and limitations of each must be understood and considered within the context of the reinforcement and resin materials that are needed. For those applications in which fire performance is important, there are phenolic resin systems that have been suitably designed for the variety of process and reinforcement options.

12.5.2 Pre-preg

The term “pre-preg” is an abbreviation that refers to “pre-impregnated” fibers and fabrics that are used to make composites. Fiberglass and carbon fibers are the most common reinforcements, but other fibers made from aramid, quartz, boron,

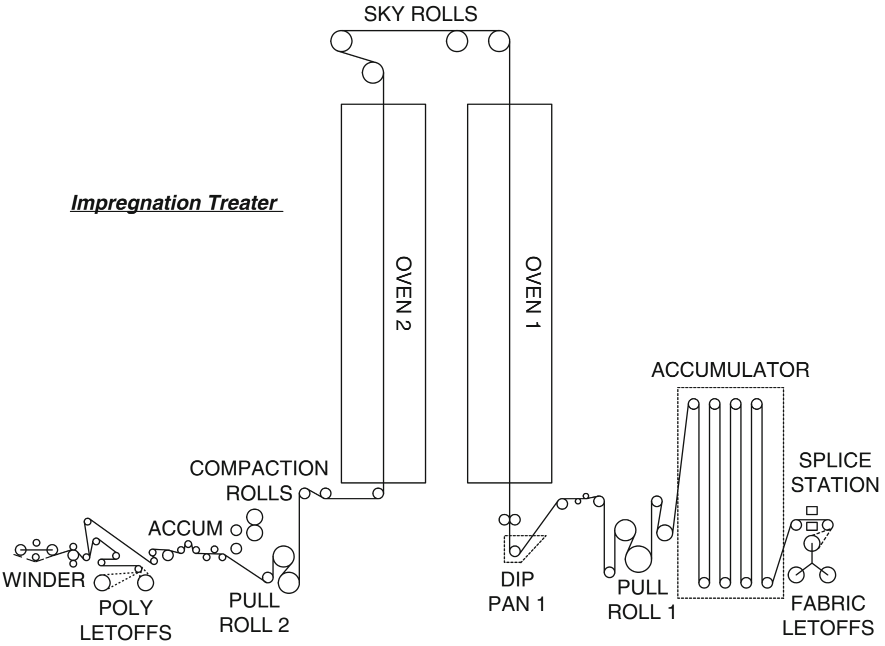

Fig. 12.1 Process for making pre-preg (figure: Cytec Engineered Materials)

polyester, nylon, and rayon are also used. Fibers are typically provided as woven biaxial fabrics, single filament rovings, or unidirectional tapes made up of multiple single filament yarns [15]. These materials come in a variety of lengths and widths according to customer desires and inputs.

The process for making pre-impregnated fiber and fabrics begins (Fig. 12.1) with the unwinding of continuous fibers and fabrics under controlled tension. The fibers/fabrics are guided through a series of rollers and tensioning devices that enable the fibers/fabrics to be spread to the desired level while maintaining uniform tension across the web.

The fibers and fabrics are then brought into contact with pre-wetting rollers and taken through a resin bath. Metering devices (i.e., head rolls, nip rolls, bars, etc.) control the amount of resin placed on the fibers/fabrics. The resin content can also be controlled by controlling the specific gravity (density) of the resin solution.

The saturated fibers continue through a vertical or horizontal oven (Treater), where the resin is partially advanced (or “B”-staged) and dried to a specific volatile content and resin flow (volatiles are made up of residual process solvent and reaction by-products). The pre-preg may be “boardy,” slightly tacky or tacky, depending upon the heat history and the customers’ handling needs [16].

Finally, the finished pre-preg is layered with a release paper or polyethylene film and then wound into large rolls. The rolls of pre-preg must be kept refrigerated until they are ready to be used in order to prevent the phenolic resin from advancing beyond its useful shelf and tack life.

The primary molding processes for pre-preg are compression molding (using a large, high pressure single opening press or a large, high pressure multi-opening press), oven/vacuum bag molding, and autoclave/vacuum bag molding [16].

Although pre-preg is conventionally considered to be a product for molding processes to make aircraft interior panels, such is not always the case. Tow-pregs are made from single filament rovings and are used in filament winding processes (see filament winding section); ablative applications also typically use a winding process to fabricate parts, and pre-preg for aircraft friction (brakes, etc.) is generally supplied as a molding compound (chopped strands or squares of pre-preg).

12.5.2.1 Aircraft Interiors

The largest applications for the composite materials used in aircraft interiors lie with the manufacturers who create and combine thermoset pre-preg and honeycomb core to produce light weight sandwich structures for walls, floors, ceilings, stow bins, galleys, lavatories, and partitions. Because interior component parts do not require the same structural qualities as their counterparts in primary structure composites, their design is driven more by stringent flammability requirements and load-carrying capabilities. These are the main design drivers for selecting phenolic pre-preg's for the interior cabin components, while epoxy/glass or epoxy/carbon pre-pregs are used to provide the higher mechanical strengths needed for load-bearing floors, wings, and fuselage structures [16]. The panels made from phenolic pre-preg's and honeycomb core are constructed to provide a desirable blend of characteristics, combining light weight and high stiffness with good load-bearing capabilities and excellent FST properties (Fig. 12.2).

The service life for interior cabin components typically ranges from 3 to 7 years but can be as long as 10 years. Consequently, the market for aircraft interior composites includes both original equipment manufacture (OEM) for new aircraft and aftermarket refurbishment of older planes. Once the OEM and aftermarket demands are combined, the consumption rate for phenolic pre-preg materials can be estimated to be about 13 million pounds annually [17].

Aircraft interior panels are typically fabricated by "sandwiching" a phenolic Nomex® honeycomb core (see section on Honeycomb) between layers of pre-preg and co-curing the entire assembly in a heated press. Conventional flat panels are normally processed at temperatures of 140–160°C using pressures ranging from 50 to 100 psi. Press times can vary from 30 to 100 min and often include "bumps" in the cycle in which the press is partially opened to allow the volatiles generated from the phenolic condensation reaction to escape.

Boeing, Airbus, and their largest Tier 1 suppliers employ a "crush core" process that is designed to shorten cycle times, improve part consistency, and provide the process flexibility to make curved and tapered structures. This method uses higher temperatures and pressures in crushing the laminated core to a predetermined thickness. Although press cycles can be as low as 8–12 min, high throughput

Fig. 12.2 Aircraft interior component made from pre-preg and honeycomb sandwich panel (photo: Cytec Engineered Materials)

volumes are necessary to justify the capital cost of the large presses that are required [17].

There are a number of commercial pre-preg products for aircraft interior panels. Cytec Engineered Materials (CEM) (formerly, Fiberite and Culver City Composites companies), a US-based and global supplier, offers a wide variety of phenolic pre-pregs for use in both sandwich structure and in solid laminate structure. CEM offers modified phenolic resole systems for use in core crush and press curing, as well as for vacuum bag and autoclave curing. Gurit AG, Zullwil, Switzerland (formerly, Stesalit), a European supplier, also offers a series of resins which are also based on modified phenolic resoles [16].

The requirements with regard to flammability for such materials are defined in and regulated by CFR 14, Part 25.853. This document regulates a multiplicity of test criteria such as flammability via Bunsen burner, NBS smoke density, OSU heat release, and toxicity of the smoke generated during pyrolysis. This FAA regulation defines the test methods and the acceptance criteria for all aircraft interiors [16].

Limitations of phenolic resins include brittleness and relatively low adhesive properties. Additional benefit could be derived from faster curing systems to shorten cycle times. Consequently, there have been significant efforts to develop tougher, faster curing phenolic systems. Several products from Hexion have resulted from those efforts. Hexion's EPONOL Resin 2493 is a rubber-modified phenolic resin for the production of pre-pregs with increased adhesion toward metals, wood, or honeycomb. This material provides peel strengths of 250N on Nomex honeycomb, nearly equivalent to that of unmodified epoxy systems [18].

The Cellobond® J2027L/Phencat 382 phenolic resin/delayed action catalyst system can provide low temperature or fast cure. The Durite® SL-575B/Phencat 382 combination also offers fast cure while imparting "toughness" (as measured by impact resistance, see sections on Filament Winding and Infusion Molding) to the composite matrix. The outlife of the pre-pregs formulated with these systems is expectedly more limited than that obtained with conventional technology. It is expected that these pre-pregs will be usable after a storage of 1 week at 20°C or 3–8 weeks at 5–7°C. Catalyzed systems of this type are also used in filament winding and infusion molding processes, and would most easily be adapted to pre-preg operations that are vertically integrated to make both pre-preg and the subsequent composite panels. CEM's Cycom 2400, Cycom 2280, Cycom 6825-1, Cycom 6826, and Cycom 2290 are all examples of formulated, toughened resole phenolic resins that are used extensively in aircraft interiors globally. They have excellent adhesion to honeycomb and foam core while maintaining their flame, smoke, and toxicity properties [16].

Pre-pregs made with phenolic resins can be used as skin layers for honeycomb sandwich panels or to cover flammable materials like wood, or even structural components which are not inherently flame retardant. For example, an Airbus flooring panel is constructed using both epoxy and phenolic resins in a "co-curing process." Normally, the chemistry of an epoxy pre-preg is not compatible with that of a phenolic resin. However, this process utilizes a novolac pre-preg containing hexamethylene tetramine as the curing agent and is in direct contact with a rubber-modified, "dicy" cured epoxy pre-preg. Some commingling of the uncured resins occurs at the pre-preg interface, and under the typical curing temperature of 120°C, the novolac serves as a curing agent for the epoxy resin, leading to covalent bonding between both matrices. The resulting panel combines superior adhesion and mechanical strength of the epoxy component as well as outstanding flame resistance and low smoke liberation of the phenolic component [18].

Future developments include the consideration of alternative flame-retardant thermosets such as cyanate esters and benzoxazines to improve surface quality, lighten the color of the cured composite, and to reduce or eliminate the release of volatiles and water during processing and cure. Despite the significantly higher price of cyanate esters in comparison with phenolic resins, the advantages could justify their use in future special applications.

There are a number of phenolic resin producers who have developed benzoxazine resin technology. Suppliers of these materials include Huntsman (XU3560), Henkel (Epsilon products), Georgia-Pacific, and Shikoku [6]. Benzoxazine pre-preg is available from Gurit (PB 1000), CEM (Cycom 2300 and Cycom 2310), and Toray [16]. A variety of backbone modifications are possible using different bisphenols or diamines. Most current commercialized benzoxazines are based on either Bisphenol-A or Bisphenol-F, which can react and polymerize with other resins (such as epoxies and cyanate esters). Benefits include the absence of volatiles during cure, high Tg, good moisture resistance, excellent mechanical properties, and minimal shrinkage of the resin during cure. Some of the drawbacks include the high temperatures needed for curing (180°C plus), lack of “toughness”, and select availability in liquid form. Work is ongoing to remedy these product limitations.

12.5.2.2 Cargo Liners

Protection of the fuselage in the baggage and freight compartments has been a concern since the beginning of commercial aircraft transportation. Early airplane designs gave little consideration to weight or flammability, primarily because airplanes were smaller and material options were limited. As airplanes became larger and the demands for weight control became more important, the search for lighter weight materials began.

Historical statistics have shown that accidents generally occur during or immediately following take-off or landing, with fatalities mostly resulting from the ensuing smoke and fire. Consequently, a need was identified for materials with better flammability resistance and lower smoke toxicity properties to allow for passenger egress to safety.

Building on the inherent FST properties of phenolic resins, new products were developed, which met the growing demands for puncture resistance, weight reduction, and fire protection. Phenolic resins, in the hands of formulation chemists, can be modified with a wide range of additives to further enhance their intrinsic properties.

Product development activities continue to focus on stronger, lighter, and more durable laminates and sandwich panels to meet the stringent demands of airplane designers for new aircraft. Advances in phenolic resin chemistry have helped meet these new engineering demands while maintaining excellent flame, smoke, and toxicity properties. This has become increasingly important as larger aircraft are designed to carry more payload farther distances [19].

A next generation bulk cargo compartment floor liner developed by M.C. Gill has been qualified for Airbus aircraft. The Gillfab 4523 exhibits a 71% increase in impact strength over its predecessor, Gillfab 4223. Gillfab 4523 is suited for the rough treatment encountered in the bulk cargo hold area, allowing for more flights between repairs.

This panel has high impact resistance and is qualified to Airbus Technical Specification No. 5360 MIM 000500, Issue 6, FAR 25.853 and ABD 0031, and Type BCC3 and exceeds Airbus specification impact requirements by 33% with minimal increase in weight [20].

12.5.2.3 Railway

The railway market in Europe realized a significant increase in the consumption of phenolic resin during the 1990s because of the high standards regarding fire smoke and toxicity requirements in many European countries, which resulted from several severe accidents in previous years. Relevant test standards are the BS 6853 in the

United Kingdom, the French AFNOR NF F 16101, or the RENFE Spec. DT/PCI-5A in Spain as well as the future European railway standard EN 45545 [18, 21].

Activities have focused on improving the FST performance of typical low cost resins in order to meet future requirements. Typically, such resins contain substantial amounts of inorganic fillers such as ATH or polyphosphates, usually up to three times the weight amount of the resin used. These resins have the advantage of being processed by inexpensive and highly automated processes such as those used to make sheet molding compound (SMC) and bulk molding compound (BMC). Consequently, phenolics have primarily been used in the very demanding underground and high-speed train applications that require both FST performance and light weight [18].

12.5.2.4 Ballistics

Although the term "ballistics" describes the behavior of projectiles, the expression is used in the context of composites to discuss anti-ballistic protection. Fear of terrorism and wartime needs have produced a growing demand for physical security products, spurring technology development and productivity increases that have resulted in a market growth rate forecast at 14% per year [22]. The "hard composites" required for troop transport comprise about 10% of the ballistic market, and a significant portion of the growth is stimulated by the requirements for phenolic-based composite armor for military vehicles. The military theater of operations requires vehicles that are light, fast, maneuverable, and well protected. The steel plates used in early ballistic technology required a compromise between protection and weight. However, advancements in composite armor have allowed for lighter vehicles that are not only fast but also more fuel efficient and maintenance free.

A number of fibers have been developed for the composite armor market, each with their benefits and limitations. High strength, elongation, and delamination are primary mechanisms by which high-performance fibers help dissipate impact energy. Para-aramid fiber (Kevlar etc.) has high tensile and "elongation to break" properties, but has relatively low compressive strength and is susceptible to water absorption. Polyethylene fibers (Spectra, Dyneema) have high modulus, high strength, and are resistant to moisture, but have low service temperatures (less than 120°C) and relatively poor adhesion to resins. A high-performance glass known as S-2 glass (from AGY) is a current industry standard that has excellent tensile, compressive, and elongation properties, but it is also the heaviest of all ballistic fibers at 2.5 g/cc. The inorganic nature of the S-2 glass gives it excellent FST properties, and the surface chemistry can be modified to benefit the specific ballistic application needs [22]. A next generation fiberglass, ShieldStrand™ from OC, has been developed to provide a balance between cost and performance relative to S-2 glass.

The most widely recognized application for phenolic composite armor is the HJ1 armor system patented and licensed by AGY. The system was originally developed in the late 1980s, but war efforts have resulted in a surge in demand, specifically for the "up-armored" US Army M1114 HMMWV (Humvee) (Fig. 12.3). The build rate

Fig. 12.3 Uparmored Humvee (photo: Militaryspot.com)

for this military workhorse has increased by over 800% in recent years. The Humvee was not designed to be an armored combat vehicle, but is being used in that role. Consequently, the next generation Joint Light Tactical Vehicle (JLTV) is under development and is designed to be more survivable while accommodating a greater payload [23]. The demand for the Mine Resistant Ambush Protected (MRAP) has also significantly increased, with more than 6,400 vehicles deployed in 2007 [24]. AGY has approved a number of licensees to provide the woven roving, pre-preg, and armor respectively.

The HJ1 armor system incorporates the use of S-2 glass along with a phenolic resin that meets MIL-R-9299C Grade B. The phenolic resin is applied to the S-2 glass to make a pre-preg (see pre-preg), which is then layered in plies and formed into a ballistic panel using a heated compression molding process. Besides meeting MIL-R-9299C, the phenolic resin must also possess process and performance qualities that will allow for the fabrication of a consistent finished composite that meets the requirements of MIL-L-64I54. In addition to ballistic performance, a primary benefit realized with this system is the excellent FST properties expected from a fiberglass substrate bonded by phenolic resin.

Hexion’s Durite® SC-1008 is a MIL-R-9299C Grade B certified phenolic resin used for a wide range of composite applications and is named in the HJ1 patent [25]. Georgia Pacific and Ashland have qualified products as well. Typical properties are found in Table 12.2.

Helmets are another example of phenolic-based composite ballistic protection. Ballistic performance is primarily determined by the fabric (typically, Kevlar), and phenolic resin is the adhesive used to consolidate the fabric layers of a ballistic helmet. Conventional phenolics are rigid, but flexibility is needed to absorb the energy of a projectile and spread it over the largest possible area. Typically, the

Table 12.2 Phenolic resins systems for pre-preg applications

Resin system	Feature	Application	Solvent	Visc (cps)	Solids (%)
Durite® SC-1008	High temp resistance	Ablatives, ballistics, interiors	Isopropanol	180–300	60–64
GP445D05 [35]	PF resole	Various	Isopropanol	400–800	64–68
Durite® SL-433	PF resole	Ablatives	Water	1,500–2,500	75–79
Rutaphen 9405	PF resole	Ballistics	Ethanol	180–260	65–67
Rutaphen 9905	PF liquid novolac	Ballistics	Furfuryl alcohol, ethanol	225–325	67.5–71.5
Durite® SC-748A	PF resole	Aircraft interiors	Methanol	510–770	70–75
Hexion proprietary	High char	Aircraft friction	Methyl ethyl ketone	110–210	57–63
Durite® SL-575B/ part B	Toughened, low temp/fast cure	Aircraft interiors	Water	950–1,600	69–77

flexiblity is enhanced by adding another resin, such as PVB. The phenolic resin and PVB co-react during cure.

The viscosity of the phenolic-PVB resin must be controlled to prevent excess flow, which can adversely affect ballistic performance. Resin flow is controlled by minimizing or eliminating solvents during the coating of the fabric. One unique process for eliminating solvents is to first coat a film material with the phenolic-PVB resin, then dry the coated film to remove solvents, and finally transfer the solventless resin to the fabric. A secondary process can be used to further B-stage the resin on the fabric to increase the hot melt viscosity of the resin when the fabric layers are pressed or molded [26].

12.5.2.5 Carbon-Phenolic Composites

One of the most distinctive features of carbon-based composites is the capability to withstand extremely high temperatures for relatively long periods of time. Phenolics are selected as the resin of choice for these applications because of their high carbon yield relative to other organic resin systems. When combined with a substrate that can be suitably carbonized (such as rayon, polyacrylonitrile, or pitch fiber), pre-pregs that are made with these components can be thermally converted into a carbon–carbon or carbon-phenolic composite depending on the process.

12.5.2.6 Aircraft Friction

The development of an alternative aircraft braking technology began in the 1970s as an initiative to replace steel to reduce weight on the Concorde supersonic jet

[27, 28]. Furthermore, traditional materials that were used to make aircraft brakes could break down and melt under extreme braking conditions (such as aborted take-off), resulting in failure. Consequently, a braking system was developed, which consisted of a stack of carbon–carbon discs that were fixed to the wheel (rotors) and to the hub (stators) [27]. This new assembly resulted in a 60% weight reduction in the braking system [28] and the technology has since been applied to numerous commercial and military aircraft (Fig. 12.4).

Longer brake life is another desirable attribute realized through the application of carbon–carbon technology. Although the mechanism is not clearly understood, the carbon–carbon composite is known to form a self-lubricating "friction film" that protects the brakes in a certain operating temperature range [29]. However, it is also known that the carbon–carbon composite can oxidize at very high temperatures (500–1,000°C), resulting in rapid deterioration of the brakes [27, 29]. Efforts to address this issue are continuing.

Besides having the benefits of longer wear and lower weight, carbon–carbon brakes are capable of more effectively managing aborted take-offs, all of which provide value relative to the significantly higher cost of these friction products, as compared to steel.

A process for making the pre-preg/molding compound for carbon–carbon brakes begins with pitch fiber. The fibers are pulled through a trough of phenolic resin and then through a drying oven where the material is B-staged. The fibers are chopped to an appropriate length and then shipped by the pre-pregger to the brake manufacturer, who then charges the pre-preg/molding compound into a mold where it is subjected to appropriate conditions of heat and pressure to form the disc. The discs are placed in a furnace under nitrogen purge and carbonized, and then removed and densified by carbon vapor deposition (CVD). The CVD is the most time-consuming

Fig. 12.4 Carbon–carbon aircraft brake MD90 (photo: Cytec Engineered Materials)

step in the process. Densification can take from weeks to months and could become a production bottleneck. Consequently, phenolic resins with high carbon yield are desired to minimize weight loss during carbonization and reduce the time required during CVD so that throughput can be optimized. The properties of a proprietary high char yield phenolic resin provided by Hexion exclusively to CEM for friction applications are shown in Table 12.2.

An optional technology has been developed, which utilizes a polyacrylonitrile fabric. The fabric is molded to produce a disc-shaped pre-form that is then subjected to carbonization temperatures. This alternative approach reduces cost by eliminating the need for pre-preg. The primary disadvantage of this technology is the high weight loss that occurs during the carbonization step, resulting in the need for extensive densification, either through CVD exclusively or in combination with liquid phenolic impregnation (LPI) [30].

Carbon–carbon brakes are also used in the “high end automobile market” (i.e. race cars) and are being considered for high-speed trains [13]. Manufacturers of carbon–carbon brakes include SGL Carbon, Aircraft Landing Systems, B.F. Goodrich, Dunlop Aerospace, and Messier-Bugatti [13].

12.5.2.7 Ablatives

Some of the most demanding environments for any organic resin system are encountered in ablatives applications. The most severe of these result from the extremely high temperatures generated by the reusable solid rocket motors (RSRMs) for the Space Shuttle. These are the only solid rocket motors rated for human flight, providing 90% of the thrust required to lift the 4.5 million pound vehicle into space [31]. The carbon-cloth phenolic ablative materials used to make the rocket nozzles for these motors are located at the flame surface and subjected to high velocity flame-fronts that reach temperatures in excess of 3,300°C (6,000°F) during launch, roughly two-thirds the temperature of the surface of the sun. Steel will boil at these temperatures, so it is imperative that the selected ablative provides optimum protection for the structural metal housing forming the nozzle, so that the housings may be re-used for subsequent flights. Otherwise, new metal components would be required for each launch, significantly escalating costs. A favored ablative material is one that can maintain its integrity for the maximum amount of time before it begins to vaporize following exposure to these conditions. Carbon-phenolic composites perform admirably in severe high temperature environments of this kind (Fig. 12.5).

The construction of certain ablative composites starts with a rayon fabric that is woven and then carbonized. The carbonized rayon cloth is made into a phenolic pre-preg that is cut on a bias-ply and then stitched together so that it can be wound, with the edge contacting the surface of the (typically) conical shaped mandrel. The assembly is then placed in an autoclave under conditions of vacuum, pressure and heat so that volatiles are removed to minimize voids as the binder undergoes cure to produce the carbon-phenolic composite.

Fig. 12.5 Re-usable solid rocket motor for Space Shuttle (photo: ATK Launch Systems)

The resin used to make the pre-preg for the RSRMs is Hexion's Durite® SC-1008 (see Table 12.2). A unique combination of specific raw materials and proprietary manufacturing techniques imparts distinctive processing and performance characteristics to this resin system, which significantly contribute to the reliability of the rocket nozzles. Certification to MIL-R-9299C Grade B is further evidence of the excellent mechanical properties and high temperature performance that can be provided by this product.

In addition to the Shuttle RSRMs, nozzles for other launch vehicles are similarly constructed by ATK Launch Systems using pre-preg provided by CEM. The Ares Program is in the design and test phase and is being pursued as the follow-on program to replace the Space Shuttle Program, which is scheduled to be decommissioned by the end of 2010. The Ares solid rocket motors are derived from Shuttle technology and will also utilize the ATK RSRM design to help launch both the Crew Exploration Vehicle (CEV) and the Heavy Lift Vehicle (HLV).

The requirements for some other ablative materials are less demanding and do not require the level of performance associated with space applications. Therefore, a phenolic product that is made with typical raw materials by a more standard process was selected and qualified by CEM for a proprietary application.

12.5.2.8 Process Developments

Besides the compression molding process previously described (heated matched metal dies), a method alluded to in the discussion of ablatives involves the use of an autoclave. Many parts made with the hand lay-up or pre-preg processes must be cured under the proper conditions of heat, vacuum, and pressure in order to remove volatiles during cure without creating vapor-related defects. This is done by first placing the part in a vacuum bag and then into the autoclave. Vacuum is applied to the bag as heat and pressure are generated within the autoclave (generally, under an inert atmosphere), essentially squeezing the volatiles out of the composite as it cures [15]. Large and complex structures can be made, but capital costs are extremely high for tooling that is large enough and strong enough to withstand the rigors of the process [32].

Creative alternatives have developed from the need to reduce cost, improve efficiency, and increase the size of the composites that can be manufactured. Two of those alternatives are known as the Quickstep rapid curing process and the Double Vacuum Bag (DVB) process.

The DVB process evolved from the more traditional Single Vacuum Bag (SVB) process as a solution to problems encountered by the Naval Air Warfare Center in repairing aircraft composites. The SVB process has typically been employed with epoxy binders, primarily because volatiles are not an issue. But excessive “flash” can result, as the resin in the composite is “B”-staged (partially cured and dried) during the first part of the process before cure is completed in the latter stage. Phenolic pre-pregs pose an additional challenge associated with the generation of volatile materials that could become entrapped within the composite as it cures if the SVB cure cycle is not effectively managed.

The issue of excessive flash generated during the SVB process is the consequence of the substantial compaction of the pre-preg which results from the elevated vacuums employed. The DVB design reduces the pressure on the composite while the volatiles are removed during “B”-stage, mitigating the compression effect. This is accomplished by augmenting the SVB model. The DVB assembly begins with the pre-preg that is placed on the tool, covered by a “caul” plate, which is then covered by a vacuum bag that is sealed around the edges onto the tool, just as it is with SVB. The problems in SVB occur when vacuum is applied and all the materials are compressed. The DVB assembly adds a perforated steel tool of appropriate stiffness, followed by an additional vacuum bag (the outer bag) that is likewise sealed around the edges onto the tool plate. Higher vacuum is applied to the outer bag relative to the inner bag, allowing the inner bag to balloon against the perforated steel tool while maintaining sufficient vacuum to remove the volatiles while the resin undergoes “B”-stage, minimizing flash and volatile entrapment in the cured matrix [33]. The DVB process was successfully applied by CEM to their Cycom® 6070 phenolic novolac pre-preg. The composite that was fabricated contained fewer voids than the one made by SVB and demonstrated a significant increase in all mechanical properties (8.5% tensile, 35% flex, 45% SBS).

The Quickstep process also uses low compression techniques to remove the volatiles during cure. Circulating heat-transfer liquids (generally, water or oil) allow a flexible membrane to maintain constant heat and pressure on the mold, while deliberate vibration of the liquid promotes the release of volatiles as the matrix consolidates. Two separate pressure chambers are employed, allowing compression of the laminate without distorting the mold as it floats in the heat-transfer liquids [32].

The Quickstep invention was conceived out of the desire to economically produce aerospace grade composites. The pressures required are an order of magnitude less than those needed for an autoclave process, and cure cycles are reported to be a fraction of the time. Coupled with relatively low capital investment, these enhancements lend themselves well to mass production and could create potential opportunities in the automotive and marine composites markets [32]. This process is applicable to thermosets in general, including phenolics. An optimization program for Quickstep is expected to result in a process that will produce a composite with a superior performance relative to autoclave, vacuum, or atmospheric curing methods [34].

12.5.3 Honeycomb

There are a number of composite constructions that contain core materials designed to reduce weight while maintaining mechanical strength and FST properties. Balsa, for example, has been utilized in resin infusion processes. In the case of sandwich panels for aircraft and defense structures, a honeycomb core is used. Although honeycomb core can be made from a variety of materials that includes glass, carbon fibers, and aluminum [13], the primary substrates that are used with phenolic resins are made from aramid-based products (such as Nomex® supplied by DuPont Advanced Fiber Systems, Richmond, VA) for aircraft interior panels and paper based for portable build-in-place defense assemblies that require compliance with ASTM-1091 [36]. The incorporation of a honeycomb core into sandwich panels for these applications imparts strength and stiffness to the composite while maximizing weight savings to provide optimal efficiency for aircraft performance and for effective deployment of defense shelters. The process to construct sandwich panels from laminate and honeycomb is discussed in the section on pre-preg.

There are high-performance niche applications that require phenolic-based honeycombcore as well. Aramid core sandwich panels are used for America’s Cup sailing yachts and for SpaceShipOne, the first private, manned sub-orbital spacecraft. A specialized energy-absorbing paper honeycomb has been developed for proprietary strategic reusable shipping containers as well [36]. Products for these specialized applications are provided by Advanced Honeycomb (San Marcos, CA).

The preferred method for constructing the honeycomb core begins with a stack of sheets that has been individually printed with a node adhesive. These nodes tie the sheets together and are off-set so that the hexagonal shape of the individual cells is formed as the plies are pulled away from each other as part of an expansion process.

The honeycomb core is then coated with a phenolic resin to obtain the target densities for a given function. Typically, the core is immersed in a dip tank, removed to allow the resin to drain from the cells, placed in an oven to B-stage the polymer, inverted, and the process repeated until the desired density is attained. Inversion of the honeycomb addresses uneven distribution that results from the draining of the excess resin after the core is removed from the dip tank.

Traditional phenolic resins used for the densification of honeycomb core typically employ solvent-based systems such as those provided by Durez and GP.

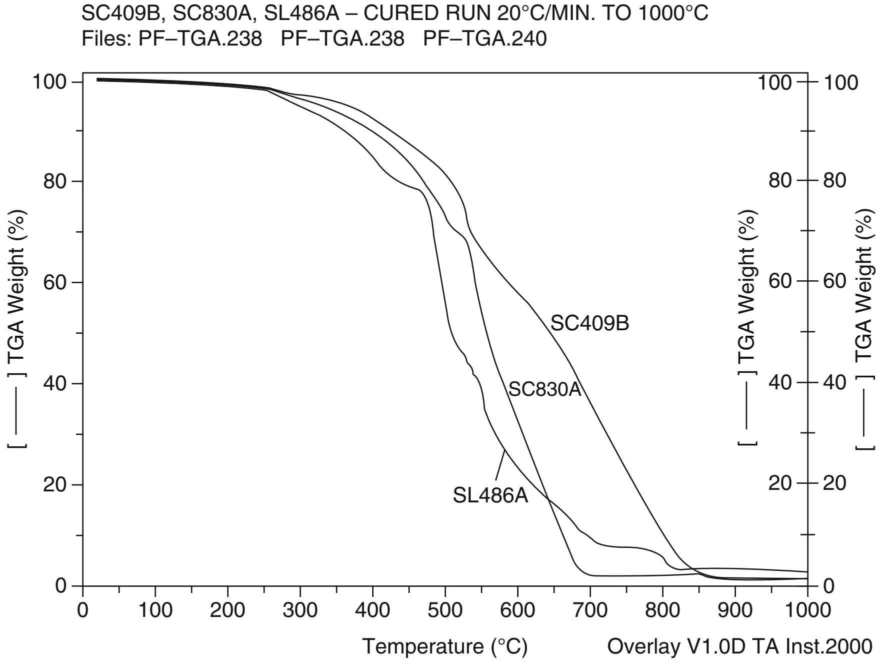

Fig. 12.6 TGA in air comparing alkali metal catalyzed (SC-830A, SL-486A) vs. ion-free phenolic resin (SC-409B) for relative weight loss as a function of temperature [37]

Water-based systems can provide a low VOC alternative. A phenolic that is water dilutable is typically derived from conventional alkali metal catalysts. However, it is generally understood that the presence of sodium on the phenolic ring can make the methylene bridge more susceptible to oxidative thermal degradation. Consequently, Hexion's novel ion-free, water dilutable phenolic resin Durite® SC-409B has been designed to provide greater thermal stability (as evidenced by the results obtained from TGA (thermo-gravimetric analysis), (Fig. 12.6). Products (Table 12.3) using both these kinds of catalysts have been developed and meet the requirements for MIL-R-9299C Grade B and for BMS-8-124N Table 12.4) [37].

Manufacturers of phenolic-based honeycomb products include Hexcel, MC Gill, Advanced Honeycomb, Plascore, Aerocell, and Eurocomposites [13].

12.5.4 Filament Winding

Filament winding may very well be the oldest automated method for manufacturing composite materials [38]. The process originated in the late 1950s as an advanced technique for making lightweight rocket motor cases and pressure vessels [39]. It is unique in that the products made by this method are not constructed in a series of plies. Rather, continuous roving is pulled from creels through a resin bath and

Table 12.3 Properties of resins for honeycomb [37]

Resin	Viscosity (cps)	% Water dilutability	Solids (%)	121°C Sunshine gel (min)	Free phenol (%)	Free formaldehyde (%)	Metal ions	Color of cured resin
Durite® SL-486A	500–800	400–1,000	67–72	10–14	1–3	1–2.5	Yes	Purple
Durite® SC-830A	200–300	200–500	67–72	9–12	5.5–8.5	<1	Yes	Brown
Durite® SC-409B	200–300	500–1,000	67–73	15–21	5–8	<1	None	Yellow
EtOH based	150–200	–	~60	15–25	5–8	<2	None	Yellow
IPA based	400–800	0	64–68	15–25	15–20	<1	–	–

Table 12.4 Mechanical properties of 3 PCF aramid honeycomb core made with water-based resins [37]

Test	Psi	BMS-8-124N specification minimum	SC-409B	SC-830A	SL-486A
Bare compressive	Ultimate	220	365	287	321
"W" shear	Ultimate	84	103	92	94
	Modulus	2,800	3,316	3,344	3,294
"L" shear	Ultimate	155	205	178	166
	Modulus	5,200	7,570	6,414	6,496

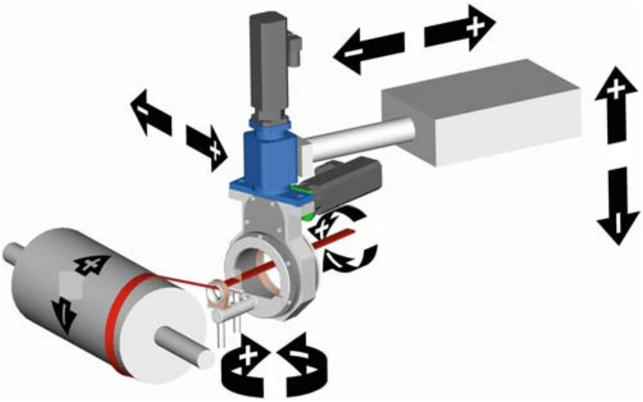

Fig. 12.7 Filament winding process (figure: EHA/BSD)

guided onto a rotating mandrel by a "head" that travels up and down the length of the mandrel. The rotation of the mandrel pulls the fiber from the creels and creates tension in the fiber as it is applied (Fig. 12.7). This tension allows for high compaction, high fiber volume, and a reduction in void content, all of which contribute to excellent mechanical properties. Many software packages are available for filament winding different circular or oval shapes. The strength of the composite is further enhanced by the ability to engineer wind angles to meet applied load requirements. The wind angle may be controlled by the speed with which the mandrel rotates relative to the rate at which the traveling head moves up and down the length of the mandrel. Although the process is very fast, economical, and capable of providing composites with high structural properties, it is mostly limited to the rendering of round or convex shapes. Innovative combinations with other composite processing techniques can allow for more complex structures [40].

Filament Winding has led to the development of Fiber Placement, a significant process development for the fabrication of large and complex aircraft components.

There are primarily two types of filament winding, traditional wet winding (as previously described), and pre-preg or tow winding. A separate section of the chapter provides details of how pre-preg is made. Essentially, for a given pre-preg substrate (generally, fiberglass), a controlled amount of thermosetting resin is applied, dried, and partially cured to a prescribed tack, drape, or flow. The pre-preg is then sold to the fabricator. Pre-preg (or tow) winding provides convenience and better control of resin content, but costs can be higher, engineering options are limited, and compaction is more critical to obtain the desired properties [40].

Besides rocket motors and pressure vessels, filament wound products are also found in a wide range of markets that include corrosion-resistant tanks and ducts, infrastructure applications for column wrapping and utility poles, oilfield shafts and piping systems, marine masts and booms, and a variety of sports and recreation applications [40].

The primary markets for filament wound phenolic products are corrosion-resistant ducts and piping systems. These materials are used in Clean Rooms for the semiconductor industry, which require fume and exhaust ducting approval per Factory Mutual Research protocol Class 4922 and 4910. Phenolic pipes are also used in oilfields and in off-shore oil well platforms to carry deluge water because of their resistance to sea water and their capacity to maintain their integrity in the event of a fire. The Jet Fuel Fire Test is the standard for pressure pipe for deluge systems as per UKOOA (UK Offshore Operators Association) guidelines [41]. This test requires that the filament wound pipe carry water at 10 bar pressure following exposure to a 1,000°C propane jet flame (Fig. 12.8) [13].

Developing markets that are utilizing phenolic filament wound composites include new opportunities for electrical conduit in the hydro-electric and underground transportation industries. Power utility providers such as Consolidated Edison of New York (sub-stations) and Hydro-Quebec (Beauharnois Power Dam) have installed these conduits for the fire safety benefits that they deliver in high voltage applications [42]. A number of transit authorities have implemented phenolic filament wound conduit because of the fire protection and corrosion resistance that they offer. Numerous examples in mass transit include materials in service for the Massachusetts Bay Transportation Authority (MBTA), the Société des

Fig. 12.8 IMO Level 3 pipe (photo: Mektech composites)

Table 12.5 Phenolic resin systems for filament winding

Property	Durite® SL-575B	Cellobond® J2027L
Viscosity at 25°C (cps)	950–1,600	220–320
Solids (%)	71–75	–
Water content (%)	6.5–7.7	10–13
Modified	Yes	No
Part B	Delayed action catalyst	Delayed action catalyst
Mix life (h)	~4	~3–4

Transports de la Communauté Urbaine de Montréal (STCUM), the Toronto Transit Council (TTC), the Chicago Transit Authority (CTA), the New York City Transit Authority (NYCTA), Amtrak, and a host of other European transit companies [42].

These new market developments are being driven by FRE Composites (Quebec, Canada) using their new BreathSaver™ Fiberglass Conduit System. The properties of the high-performance filament wound conduit used are given in Table 12.6.

Liquid resole resins are the phenolic products of choice for the wet-winding process (Table 12.5). The high temperatures required to cure conventional resoles result in bubbling, foaming, delamination, and other vapor-related defects that compromise the integrity of the composite. Consequently, low temperature (below 100°C) curing systems have been developed to mitigate the generation of gases during the curing process. These systems can be pH catalyzed, curing under either very acidic or very alkaline conditions using a part B catalyst or co-reactant. Novel delayed action catalyst systems designed to maintain a balance between pot life and reactivity are being used commercially. Alkaline catalysis is less energetic and is augmented by the use of more reactive phenolic species. The use of catalysts or co-reactants allows for the filament wound composite to cure at temperatures below the boiling point of water (to minimize bubbling) and in an acceptable amount of time to maintain the desired productivity rates. Nevertheless, care must be taken during the curing process to ensure that bubbling does not occur. Optimally, the mandrel is internally heated to allow the phenolic resin to cure from the inside out, allowing the volatiles to escape to the surface. The application of external heat is more likely to trap volatiles as the resin cures.

Innovations in phenolic resin chemistry have resulted in filament wound composites with improved impact and flexural properties that approach those made with epoxies. These novel phenolic systems are formulated with patented modifiers that are designed to give low shrinkage and low volatile generation that can translate into enhanced mechanical performance without compromising FST properties. Another advantage that is unique to the system is the capability to bend the composite to a desired angle when it is processed under proper conditions prior to the final cure. For example, FRE Composites manufactures elbows as part of its Breathsaver™ product line that range from 1″ to 6″ trade sizes to various radii to accommodate horizontal or vertical transition of an electrical and telecommunication raceway [42].

Additionally, manufacturers of filament wound pipe have invented novel ways to improve the flexibility and impact resistance of their product. Ameron offers its new Bondstrand® PSX™ fire-resistant piping that combines the fire-resistant

Table 12.6 Physical properties and FST performance of phenolic filament wound conduit vs. epoxy [42, 45]

Test	Method	Specification	Conventional phenolic	SL-575B	Epoxy
Compressive load failure (lbs)	ASTM D 2412	400	450	525	700
Flexural strength (psi)	ASTM D 4923	4,000	3,000	10,000	12,000
Impact strength (in.)	ASTM D 2444	60	6	48	60
Modulus of elasticity (Msi)	ASTM D 2105	1.0	0.7	1.2	1.3
Flame test	UL 651	3 applications of 60 s	Self extinguishing	Self extinguishing	Not meeting specifications
Surface flammability	ASTM E 162	<35 (index value)	–	1	–
Vertical flame test	FT4	<1.5 m	–	0.15	–
Specific optical density at 1.5 min	ASTM E 662	100	–	Flaming 1 Non-flaming 1	–
Specific optical density at 4.0 min	ASTM E 662	200	–	Flaming 4 Non-flaming 1	–
Maximum specific optical density	ASTM E 662	–	–	Flaming 12 Non-flaming 1	–
Maximum corrected optical density	ASTM E 662	–	–	Flaming 11 Non-flaming 1	–

properties of a phenolic with the flexibility and impact resistance of patented polysiloxane chemistry [43]. This technology includes the capability to form phenolic polymers that contain siloxane groups [44].

Table 12.5 describes typical properties of commercially available resins systems for filament winding and Table 12.6 demonstrates the improvement in mechanical strengths that were benefited by the implementation of innovative chemistry.

The providers of phenolic filament wound products include FRE Composites (Quebec, Canada), Ameron (Houston, TX), and Composites USA (North East, MD).

12.5.5 Pultrusion

Pultrusion is a process developed in the 1950s in which fiberglass roving is pulled through a resin bath and then through a heated die to produce a cured composite [46]. The pultrusion process is continuous and mostly automated, providing cost advantages over more labor-intensive fabrication methods (Fig. 12.9). The market for pultruded composites in the US is over 300 million pounds, generating over $700 million dollars in sales, with a projected yearly growth rate of 5–10% [47].

Pultruded composites are used in a wide array of commercial applications because they are lighter than comparable steel or aluminum structures (70% and 20–25%, respectively) and stronger than steel on a weight-for-weight basis [48]. The continuous fiber used in pultrusion provides for higher strength (particularly flexural) relative to composites that use chopped or discontinuous fibers. A variety of panels, rails, tubes, shafts, and beams are made for markets that include aerospace, military, building and construction, consumer products, infrastructure, marine, and transportation [49]. See also Chap. 9, discussion of Foam that describes the pultruding of phenolic foam between phenolic/glass fiber pre-pregs.

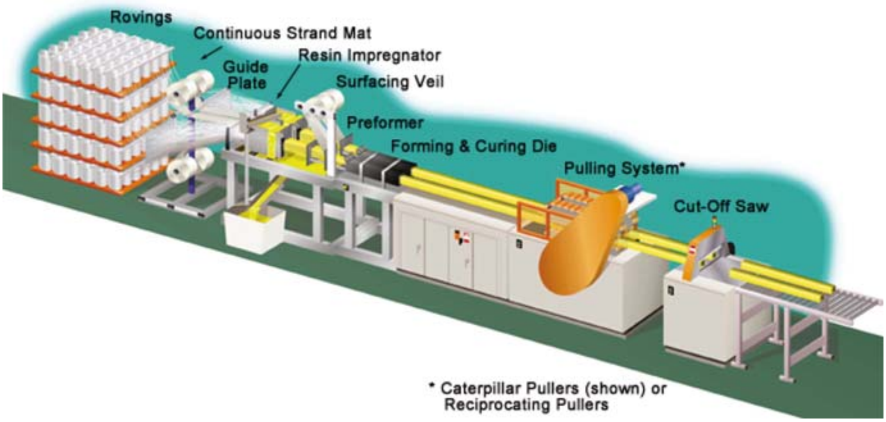

Fig. 12.9 Pultrusion process (Figure: Pultrusion Industry Council website)

The largest volumes for pultruded phenolics are for off-shore grating. The development of this market was pioneered by Strongwell using resin from Georgia Pacific. The FST properties of phenolic composites and their resistance to sea water make them ideal for this application [50]. Pultruded phenolic grating provides many advantages over traditional steel grating, with particular regard for weight savings and fire resistance. The weight of steel gratings limits the engineering options for oil-well platforms. In addition, steel conducts heat and will contort and twist when exposed to the high temperatures that can occur in an off-shore oil-well platform fire. Conversely, phenolics will form an insulating char layer that allows workers to travel across the grating to escape safely (Fig. 12.10).

Phenolic pultrusions were first introduced to oil-well platforms around 1990. The US Coast Guard became involved shortly thereafter and began to regulate and set performance standards to ensure the safety of the composite gratings that were being introduced. The USCG test method (Policy File Memorandum 2-98) cites the ASTM E-119 time-temperature curve for comparing composite to steel grating (Fig. 12.11). The composite grating must be within 100°C of the steel

Fig. 12.10 Pultruded phenolic grating (photo: Strongwell)

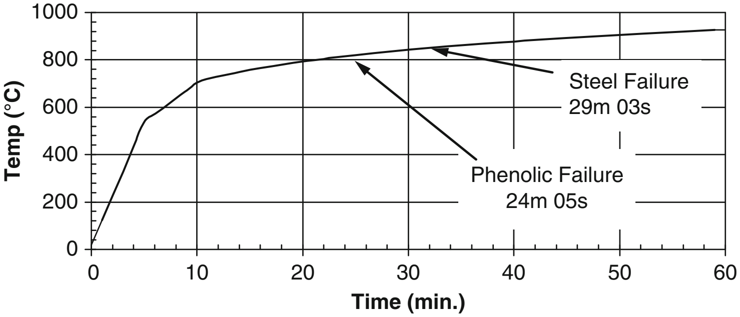

Fig. 12.11 ASTM E-119 time-temperature curve comparing phenolic grating to steel grating [51]

Table 12.7 E-84 properties of composite gratings [51]

	Molded grating			Pultruded grating		
	XFR	Corvex	ELS	Phenolic	Iso-FR	VE-FR
Flame spread	10	25	15	5	25	15
Smoke index	680	390	70	45	700	650

grating at a defined deflection limit. ASTM E-84 and E-662 for flame and smoke toxicity also help determine the approval criteria for composite grating. Composite grating made with phenolic resins have been able to meet the standards set forth, whereas fire-retardant polyester and vinyl ester resins have not [51]. Table 12.7 compares fire properties of conventional molded and pultruded grating to phenolic pultruded grating. The molded gratings listed for comparison are XFR®, a highly brominated vinyl ester system; Corvex®, a general purpose polyester, and ELS®, a Modar®-based molded system. The pultruded systems shown are phenolic, Iso-FR, an Isophthalic polyester system, and VE-FR, a vinyl-ester system. The E-84 results that were generated are considered typical for these gratings [51].

Many markets using phenolic resins are very mature and the development of pultruded grating provided a new application opportunity. Initially, the market supply was very exclusive and US-based. Over time, however, the relatively low overhead costs and attractive margins encouraged many pultruders to enter the market. Subsequent margin erosion and high US labor costs eventually resulted in a significant amount of the volume to move off-shore, particularly to China, Brazil, Malaysia, India, and some to Mexico. Time-tested quality products and branding have allowed some US companies to maintain volumes, but USCG-mandated re-certification periods are motivating some to enhance the value (durability and strength) of their products so as to preserve their position in the market.

Pultruded FRPs are also used to reinforce glue-laminated timber beams to enhance strength and stiffness. These glulam beams are sometimes preferred over conventional materials (such as steel) for the benefits that they provide with respect to weight, energy absorption, and corrosion and fire resistance. Applications include arches, domes, bridges, and other large open structures [13].

Creative approaches in the construction of glass fiber matrices have opened new potential applications for pultruded phenolic composites. Advancements include the development of engineered roving architecture that provides strength enhancements and improvements in cross-sectional integrity. Fiber innovations, combined with novel resin technology, have allowed for the pultrusion of phenolic composites up to one-inch thick, which is a significant accomplishment for phenolic pultrusions. This new capability is providing value to customers that are developing next generation materials for proprietary new markets.

Pultruding an acceptable phenolic composite, especially a thick profile, has been difficult to accomplish before the implementation of recent advancements. There are several challenges. Conventional phenolic pultrusion requires a liquid resin that can maintain a balance between acceptable pot life (the amount of time a resin-catalyst system remains usable) and reactivity. Phenolic liquids are typically resole resin solutions containing some amount of solvent (alcohols, ketones, water, etc.). Further, phenolic resole resins undergo a condensation reaction that creates water and formaldehyde. The solvents and condensation products volatilize in the heated die during the pultrusion process. The emission of volatiles results in a loss of die pressure, and the subsequent hydrodynamic behavior of the resin causes it to pool and stagnate within the die as the fibers pass through. The result is a build-up of cured resin within the die, a narrowing of the die profile, and eventual breakout of the fibers. Furthermore, the entrapment of volatiles can result in delamination of the composite and/or create voids in the cured resin matrix, compromising mechanical properties.

A variety of commercially proven phenolic resin modifications have successfully been applied to the pultrusion process. Alternative technologies have been developed as well to address the shortcomings of some systems. The range of products includes traditional thermosetting products, catalyzed resins (typically, acidic), and two component systems employing a co-reactant. Modifications to the cure behavior and the backbone structure of some offerings have resulted in process-friendly materials that provide excellent surface finish and mechanical properties and allow for the pultruding of thick composite profiles. Georgia-Pacific has commercial phenolic technology that is used to make Coast Guard-approved grating. A novel phenolic resin system (SC-644C/2026B) has been developed by Hexion (and incorporated into Coast Guard-approved grating [51]), which combines long pot life, acceptable reactivity, reduced shrinkage of the phenolic system during cure, and improved toughness of the composite matrix. Angus Chemical (a subsidiary of Dow Chemical) offers a novolac-based system that utilizes a proprietary part B co-reactant. The touted benefits of the Accelacure™ PT 1.0 system relative to traditional resole products include faster line speeds, no formaldehyde emissions, ease of processing, and excellent shelf life without refrigeration. Recommended processing temperatures in excess of 200°C [52] are higher than those of many resole offerings, however. A summary of some representative resin systems of varying chemistries is shown in Table 12.8.

Strongwell (Chatfield, MN) is a major manufacturer of pultruded phenolic composites, primarily for off-shore applications. Other US suppliers such as Creative Pultrusions and Fibergrate have either licensed their products or entered into a possible joint venture with companies, such as Cogumelo in Brazil and Kemrock in India, respectively. Additional growth is anticipated in the future due to continuing off-shore oil discoveries that will require oil platforms, grating, pipes, etc.

12.5.6 Compression Molding

Some markets for composite materials require high production volumes to meet demand. This is particularly true for the automotive, mass transit, and construction

Table 12.8 Phenolic resin systems for pultrusion

Property	Hexion Durite® SC-644C	Hexion Cellobond® J20/1256L	Hexion Cellobond® J2027L	Georgia-Pacific Resi-Set® GP-652D79 [53]	Accelacure™ PT 2000R
Viscosity at 25°C (cps)	2,700–3,300	500–700	220–320	1,600–2,400	1,000–2,000
Solids (%)	69.5–75.5	–	–	64–68	~80
Water content (%)	5 max	9–13	10–13	Not available	Not available
Ethanol content (%)	10	None	None	Not avaialble	~15
Part B	2026B novolac co-reactant	None	Delayed action acid	GP-012G23 base catalyst	Accelacure™ PT 1000H
Mix life (h)	~24	Not applicable	3	>8	~24

industries. Processes that utilize compression molding are best suited to meet the demand for many of these applications [54].

Compression molding utilizes molding materials that are placed in pre-heated matched metal dies that close with sufficient force to generate the conditions of pressure and temperature necessary to consolidate the material and cure the composite. Molding materials (see also Chap. 16) based on novolaks [13] as well as other resins are combinations of partially cured resin on reinforcement and include products such as SMC, BMC, and pre-pregs. Pre-pregs are generally associated with aerospace, aircraft, and military applications and are discussed separately.

12.5.6.1 SMC

As a first step in making SMC, the resin, fillers, thickeners, and other required ingredients are all combined to form a very viscous paste. The SMC machine then sandwiches the paste around chopped glass fibers of specific length. This is accomplished by applying the paste to a carrier film (generally, polyethylene), depositing a metered quantity of fiberglass, and then applying a top layer of the paste to complete the "sheet." The sandwich is compressed, rolled, and placed in a controlled environment where it is allowed to thicken to the desired viscosity by the virtue of additives such as magnesium oxide or magnesium hydroxide. The glass fibers may be continuous or chopped and oriented in a unidirectional or random pattern (or combinations thereof) depending on the application needs (Fig. 12.12) [54].

A phenolic-based SMC known as QC-2130 was developed by Quantum Composites (Table 12.9). Although the material has not been commercially produced for years, it is believed that such a product could have utility in aircraft interiors

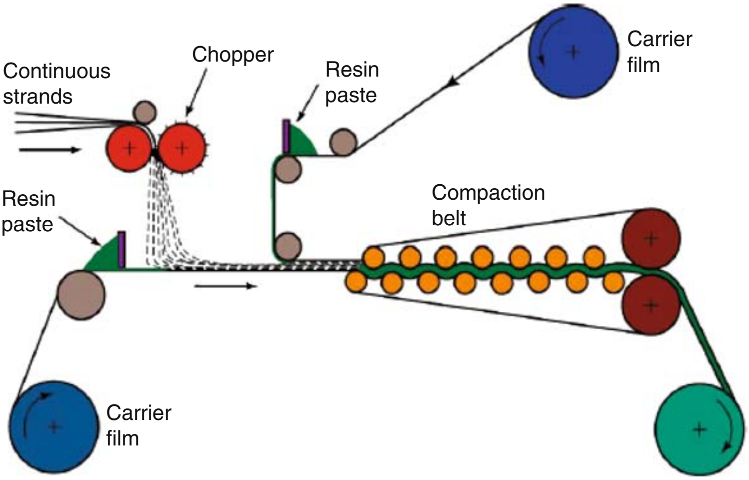

Fig. 12.12 SMC process (figure: Elettroplast srl website)

Table 12.9 Phenolic SMC properties of uncured product [55]

Property	Characteristic
Form	Sheet
Colors	Natural, black
Glass content	25–30%
Glass length	1 in.
Shelf life at −18°C (0°F)	6 months
Shelf life at 4°C (40°F)	2 months

and public transportation facilities. Excellent mechanical properties are realized while maintaining the FST properties that are characteristic of phenolics (Table 12.10) [55].

12.5.6.2 BMC

The primary difference between SMC and BMC is the way in which the glass fibers are incorporated into the molding compound. All of the components of the BMC are "bulk added" to a mixer, including the glass fibers. The blend is subjected to very high energy and high shear mixing, resulting in the breakdown of glass fiber length, consistency, and integrity. Consequently, mechanical strengths are similarly compromised, restricting end-use options to smaller parts. However, BMC does allow for the fabrication of complex components and has the flexibility to be used for injection molding processes as well [54].

Table 12.10 Phenolic SMC mechanical and thermal properties of cured product [55]

Property	Value
Specific gravity	1.8
Shrinkage (in./in.)	0.0001
Flexural strength (psi)	23,000
Flexural modulus (psi)	1.2×10^6
Tensile strength (psi)	14,000
Izod impact, notched (ft-lb/in.)	16
Compression strength (psi)	22,000
Compression modulus (psi)	1.1×10^6
Heat release: first 2 min (kW/m^2)	−8.1
Heat release Rate: at 5 min (kW/m^2)	26.6
Smoke release rate: at 5 min (Smoke/m^2 min)	0.4
Toxic gases	Very low
Flame spread index	10
Smoke developed index	5
UL 94 flammability	Passes
UL 94-5V at 0.040 in.	
Oxygen index	46

Table 12.11 Cellobond® J2041L for SMC and BMC applications

Property	Specification
Viscosity at 25°C (cps)	4,500–5,500
Specific gravity at 25°C	1.257–1.267
Solids content (%)	71.5–75.5
Water tolerance at 25°C	1:2.5–1:3.5
Heat hardening time at 130°C (min)	4.5–6.0

BMCs were first introduced as a thermoset molding compound used primarily in electrical applications. They provided an alternative to engineered phenolic molding compounds, offering higher quality appearance of molded parts, and faster cycle times. General purpose phenolic BMCs were later developed for higher temperature applications, but commercialization has been hindered by the difficulties associated with the managing of volatiles during the manufacture of the BMC. Even so, phenolic BMCs have recently been formulated to make bipolar plates for the fuel cell industry. The preference for these materials is a result of their inherent corrosion resistance and high temperature performance in the proton exchange membrane fuel cell operating ranges of 80°C–180°C. Additionally, the dimensional stability of the cured composite allows for stack assembly of the plates, providing another advantage over thermoplastics [56].

The phenolic resin used to make the SMC previously described has been engineered for compatibility with that manufacturing process. The reactivity, molecular weight, solids content, and associated viscosity are balanced to provide the process control necessary to obtain an optimum molding compound. The characteristics of a preferred phenolic resin are given in Table 12.11.

12.5.7 Infusion Molding

There are a number of liquid resin infusion processes for making composites. Depending on the process, pressure and/or vacuum may be used to introduce resin into a mold containing fiber reinforcement. Although similar in principle, these techniques may differ not only in the method for infusing the resin but also in the kind of mold, reinforcements, and supplementary materials that are used in product manufacture.

Resin infusion provides a number of benefits over other composite fabrication methods. Parts may be produced more quickly than those made by hand lay-up and with less labor. Relative to other fast, automated processes, such as pultrusion and filament winding, resin infusion offers a wider range of engineering and design options. Part size and complexity is not defined by the shape of a mandrel or the profile of a die. A greater variety of reinforcement types and geometries may be used to provide the desired structural properties. These include continuous strand, cloth, woven roving, long fiber, chopped strand, and 2-D and 3-D pre-forms, some of which can be made from fiberglass, carbon, or other materials. Additionally, core materials (such as balsa and foam) may be incorporated.

However, there are drawbacks as well. Tooling costs can be higher. Expertise is needed to understand cure kinetics and the dynamics of resin flow through fibers. Molds must be engineered to allow for air and volatiles to escape, avoiding entrapment. Despite similarities, each infusion process has unique benefits and limitations relative to each other and to other composite fabrication techniques.

The nature of the infusion process requires that a candidate phenolic system must cure at relatively low temperatures. Consequently, a catalyzed system is needed and the most common catalysts are acidic. Acid catalysts could be corrosive to machine parts and tools. Stainless steel or other materials which are inert to phenolic resins and organic acids should be used to protect equipment from corrosion. Likewise, the gelcoats selected should also offer the highest stability against acidic media. Therefore, it is not surprising that the best experiences have been with vinylester-based gelcoats.

Given that typical curing conditions are at relatively low temperatures, it is expected that the degree of cure is far from complete but sufficient to guarantee a Tg well above the desired level. It should be considered that such a "green" part contains a significant amount of water. Typically, the water content of an RTM phenolic resole ranges from 10 to 20% in addition to the water of condensation generated during the cure of the resin. Therefore, parts should be dried before painting in order to optimize adhesion.

12.5.7.1 Resin Transfer Molding

The RTM process uses pressurized injection to transfer resin into a two-sided matched mold. This is generally a cold molding process, but heated molds are being used for smaller parts. It is excellent for mass production, and has been used in the automotive (500–50,000 parts/year) and aerospace (50–5,000 parts/year) industries for decades, primarily with resins other than phenolics [57].

Mass transit has been the primary market for phenolic RTM composite products. The largest volumes within mass transit come from flooring for trains and buses. Although fire performance is the driving factor in selecting phenolic composites over traditional ply metal flooring, phenolic structures offer additional advantages such as little or no moisture absorbance (which affects part longevity), lower installation costs, lighter weight, and better thermal and acoustical insulation properties. Consequently, the use of phenolic composite flooring continues to expand globally and structures are in service today for the Baltimore subway, SEPTA trains in Canada, and for the Amtrak Super Liner [41, 58].

12.5.7.2 Vacuum Assist Resin Transfer Molding

As the name indicates, Vacuum Assist Resin Transfer Molding (VARTM) (aka “vacuum infusion process” or VIP) is distinguished from conventional RTM by the application of vacuum that draws resin into the mold. The mold assembly consists of a single-sided, open cavity tool on one side and a vacuum bag on the other. Consequently, there are a number of advantages relative to RTM. Tooling costs are lower and larger parts can be made. Additionally, the vacuum applied causes fibers to compress, allowing for higher fiber volume (Fig. 12.13).

The Helipad atop Cooper Hospital in Camden, NJ is an excellent example of phenolic VARTM using Hexion’s Cellobond® J2027L two-part system. Steel is normally the preferred material of construction, but a steel roof would have been too heavy without reinforcement of the supporting structure. Aluminum is light and strong, but would melt and burn in the event of a jet fuel fire. Hence, a fire safe composite rated to support an Apache Helicopter was developed and approved based upon performance history in offshore platforms and on results generated from the Jet Fuel Fire Test. The structure consists of sections as large as 16 × 26 ft. and 8 in. thick totaling over 3,000 sq ft of surface. The sections are 20 lbs/sq ft and composed of phenolic glass skins over an isocyanurate core. The final structure provided the light weight that was desired while passing all of the fire safety requirements, including the ASTM E1136 non-combustibility test (Fig. 12.14) [58, 59].

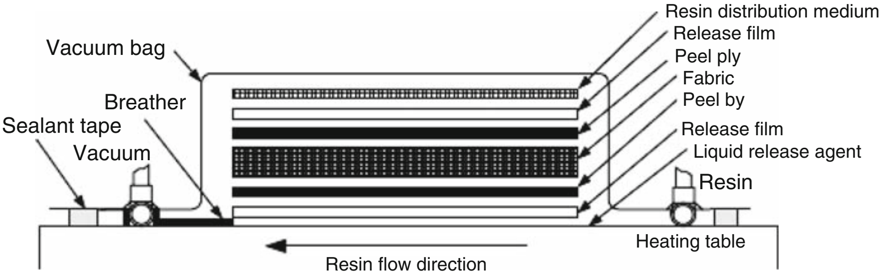

Fig. 12.13 VARTM process (figure: Archives of Materials Science and Engineering website)

Fig. 12.14 Cooper Hospital Helipad (photo: Mektech composites)

12.5.7.3 SCRIMP

A variation of VARTM is SCRIMP, or, Seeman Composites Resin Infusion Molding Process. Originally developed to make large and complex parts for US Navy applications, it has also been used with phenolics for the Tilt trains in the Norway Gardemoen Airport and for Adtranz Norway train fronts and ploughs. SCRIMP's patented technology utilizes exclusive resin feed and channel designs along with a unique flow medium and other ancillary materials that were all developed to optimize the vacuum infusion molding process [60, 61].

The licensors of SCRIMP originally approved Hexion's Cellobond® J2027L two-part phenolic resin system which consists of a part A resole and a patented acid catalyst that provides the required reactivity along with a long pot life of the resin-catalyst mixture. The same system has also been used successfully in all the other infusion molding processes previously described, and was designed with consideration given to those applications.

Next generation resin technology includes a patented system composed of Hexion's Durite® SL-575B modified phenolic and a delayed action catalyst designed to maintain desired reactivity and pot life while reducing the volatiles and improving mechanical properties. Although the system was developed with resin infusion processes in mind, it has found more immediate commercial application in filament winding (see filament winding section). The beneficial effect that the patented modifiers have on physical properties of an RTM composite can be seen in Table 12.12.

Marine applications have long been considered a potential growth market for phenolic composites. Some of the most demanding approval requirements are

Table 12.12 Physical properties of RTM composites [45]

Test	SL-575B	Post cure ramp to 125°C/2 h, hold 125°C/1 h	Post cure ramp to 150°C/3 h, hold 150°C/1 h	SL-575B No modifiers	Post cure ramp to 125°C/2 h, hold 125°C/1 h	Post cure ramp to 150°C/3 h, hold 150°C/1 h
Tensile Str. (psi)	34,000	43,700	36,470	30,630	24,680	20,930
Tensile Mod. (Msi)	2.3	2.6	2.4	2.3	2.6	2.5
Flex Stren (psi)	39,260	51,850	31,350	17,380	32,490	25,360
Flex Mod. (Msi)	2.4	3.1	2.1	2.0	2.3	1.5
Izod impact (ft-lbs/in.)	–	14.1	18.1	–	9.4	8.4
Resin content (%)	36.7			36.6		

Table 12.13 Phenolic composite cone calorimeter results [62]

Material	Heat flux kW/m^2	TTI sec		Peak HRR kW/m^2		HRR 300s Avg kW/m^2	
MIL STD 2031	25	300	–	50	–	50	–
	50	150	–	65	–	50	–
	75	90	–	100	–	100	–
	100	150	–	150	–	120	–
Phenolic material designation 1407	25	No ignition	PASS	5	PASS	0.15	PASS
	50	340	PASS	47	PASS	35	PASS
	75	163	PASS	72	PASS	49	PASS
	100	62	PASS	82	PASS	56	PASS

contained in MIL-STD-2031 for structural submarine members. This standard requires testing to a range of fire tests and specifications, including the quarter scale room corner test. Phenolic resin products have passed preliminary tests, and the results from cone calorimetry indicate that material approval to the MIL standard should be obtainable [62].

The properties and performance data of the described resin systems are given in Tables 12.12 and 12.13.

12.5.8 Hand Lay-Up

Hand lay-up might possibly be the most basic and versatile of all the composite manufacturing processes [54]. The process begins with the spraying of a pigmented gel coat or a surface paste onto an open mold face in order to provide the finished composite with a smooth, non-porous, and aesthetically pleasing surface. Once the gel coat or paste has reached a suitable degree of cure, the reinforcement is appropriately situated and the resin is manually applied and then distributed with rollers or other tools to remove the entrapped air. The number of layers and the type of reinforcement are determined by design requirements. Chopped strand glass fibers are typically used, but woven roving can increase the fiber weight from about 40 to 65%, resulting in higher strengths [54]. The resins used are catalyzed resin systems that allow for room temperature or low temperature cure (Fig. 12.15).

Low tooling and capital costs, coupled with the flexibility to design for the desired size, strength, and shape of a structure help make this the most commonly practiced composite fabrication method. In fact, the capacity to construct very large and complex shapes with high strengths at low cost are the primary advantages associated with hand lay-up. Other benefits include the capability to incorporate core materials, provide color options, fabricate on-site, and impart added strength to critical areas of the composite [54].

The most significant limitations are related to the human factor. This technique is the most labor intensive of the various processes and is the one that is

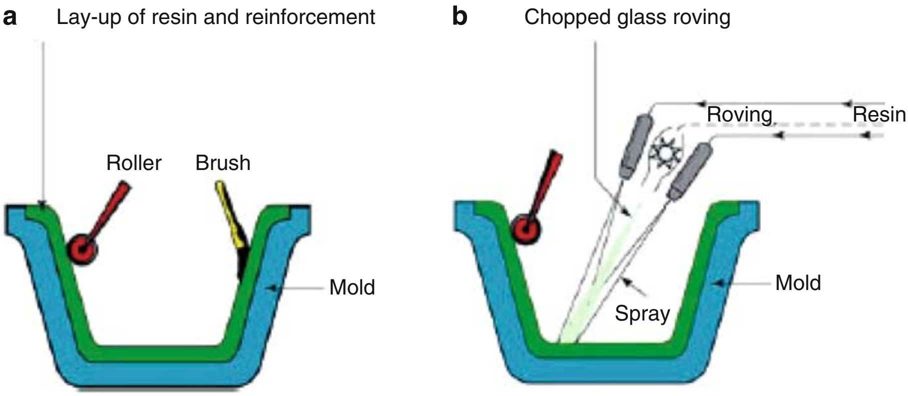

Fig. 12.15 Hand lay-up process (figure: Elettroplast srl website)

most dependent upon operator skill for part quality. Another limitation could be the management of the volatile emissions that are produced by organic resin systems.

Although hand lay-up has traditionally been used to make composite boat hulls, auto and truck parts, swimming pools, tanks, corrosion resistance structures, and ducts for air-handling systems [54], appropriately designed phenolic systems are now being used for applications that require fire safety.

Phenolic resin technologies developed for composite processes have been tailored to provide the requisite advantages in hand lay-up. Acid or latent acid catalysts allow for ambient or low temperature cure. These different catalysts are combined with optimally engineered resole resins to afford the process flexibility needed to balance the pot life of the resin-catalyst mix with a set time for the release of the composite from the mold surface. A phenolic surface paste provides a fire-resistant, non-porous surface that can replace traditional polyester gel coats. Mechanical properties of these phenolic composites are comparable to those associated with polyesters and epoxies and can be realized without compromising FST (Flame and Smoke Toxicity) performance. Next generation technology employed in other composite processes (i.e., filament winding) for improved toughness and flexibility may have application in hand lay-up as well.

The unique attributes of these phenolic systems have resulted in their selection for a variety of mass transit applications that include the following. The locomotive exterior for the Le Shuttle Chunnel train is a 530 pound one-piece hand lay-up molding, and interior panels are phenolic hand lay-up as well. Phenolic components were chosen to replace cracked and worn thermoplastic parts in Dallas/Ft. Worth People Movers, and the roofs for these vehicles were made using spray deposition around a phenolic foam core. BART (Bay Area Rapid Transport) interior panels and Amtrak Super Liner sleeper car heat shields, ceiling panels, and trash bins are other examples of materials that are currently in service (Fig. 12.16) [41, 58].

Fig. 12.16 Chunnel train (Mektech composites)

The potential to use phenolic hand lay-up in architectural applications is proven if not yet routine. Two exceptional examples are the City Hall clock tower in New York City and the dome covering the Quinnipiac College Law School. The clock tower had suffered fire damage on three different occasions, and the decision was made to use a phenolic-glass composite in the rebuild. The 12-foot tall tower was constructed in four sections. Each section required 10 h in order to laminate the phenolic and glass over a balsa core, and an additional 6 h to cure. The catalyst system allowed for the necessary pot life to carry out the lamination, while still providing the reactivity needed to cure at the relatively low temperature of 65°C. Similar methodology was employed in fabricating the 5-foot diameter turrets and the 20-foot diameter dome for the Quinnipiac Law School. Because the inside face of the dome would be open to the interior of the building, phenolic resin was specified to meet fire code requirements (Fig. 12.17) [63].

Electronic and sewage treatment plants often utilize ducting made with phenolic resins because of the excellent corrosion resistance and fire protection that they provide [64]. By extension, phenolics may also be used as a fire protective overwrap for epoxy pipes in larger corrosion-resistant applications. For instance, the carbon steel cooling water lines that were used to carry water from the Hudson River to the World Financial Center were replaced with corrosion-resistant epoxy pipes that were overwrapped with a phenolic glass laminate to meet the stringent requirements of the New York City building codes [65].

The J2027L described in previous sections is the resin that was used in many of the examples that were given. The phenolic surface paste J2042L is often used in tandem with the J2027L. This thixotropic paste is applied to the mold surface in

Fig. 12.17 New York City Hall clock tower (Mektech composites)

advance of the reinforcement to provide a void-free, ready-to-paint, fire-resistant surface.

12.6 Summary/Trends

Phenolic resins were the first synthetic polymers, and composite materials made with these resins have been commercially available for decades. Over time, other resin systems have grown to dominate the market as new applications were identified, while phenolics occupied a niche defined by the need for fire resistance and high temperature performance.

Despite a favorable price–performance ratio, phenolics have not been preferred by fabricators over alternative choices due to the processing difficulties and lower mechanical properties that result from volatile content and the condensation reaction associated with the chemistry. Consequently, efforts have focused on the development of products that are engineered to tailor backbone architecture and to manage and minimize emissions so as to enhance structural properties and improve processing characteristics. Technologies that provide low temperature cure, reduced shrinkage and void content, lower cross-link density, and a “toughened” matrix have been developed to address process and performance deficiencies. Silicone-based co-reactions reflect a more diversified approach to strength enhancement relative to traditional additives such as PVB and nylon. These advancements in phenolic-based technologies have resulted in an expanded assortment of viable options for the entire spectrum of composite construction techniques.

Process and fiber improvements combined with the evolution of phenolic resin technology have opened new opportunities for phenolics in aerospace, aircraft, defense, mass transit, off-shore, marine, construction, and anywhere else that public safety and fire protection are important. As fire safety standards for composite materials become more stringent, there will be phenolic resin systems available to meet those needs while providing manufacturers with products that process more easily to render a stronger, tougher composite.

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Chapter 13
Abrasives

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Abstract The historical development of the abrasives industry is noteworthy considering its evolution from a rudimentary beginning to a relatively mature industry. Presently, hardly a material exists that has not been exposed to a grinding operation. It can be stated without exaggeration that the abrasives industry represents a basic building block for all other branches of industry.

There are two basic types of abrasives: bonded abrasives or grinding wheels and coated abrasives. As one currently examines the abrasives market, the global market for abrasives is showing a downward trend for bonded abrasives while coated abrasives are increasing globally. In developing countries like China, India, and Thailand that are fostered by a robust economy, abrasives are increasing in use and are produced for industries such as construction, machinery, and automotive. Parallel to this activity, more abrasive production is moving from industrial nations such as US, Japan, and some European nations to these developing countries.

The performance of bonded abrasives and coated abrasives as they are used industrially is recognized by their physical behavior, stress, and heat generated during use. By examining the microstructure of both types of abrasives, abrasive performance characteristics are improved by a judicious evaluation of abrasive components. Bonded abrasive structure consists of two basic components such as grain and bond for most wheels, some voids or pores. The grain must be self-renewing during operation; bond created by phenolic resin provides strength and heat resistance as well as uniformity in bond strength to facilitate regeneration of grain during grinding, and finally the pores of the bonded abrasive draw out the grinding dust or debris. Too weak or too strong bond strength either facilitates rapid

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wheel wear or the pores are filled with debris and the grinding efficiency is reduced. “Trouble-shooting” suggestions are provided in the manufacture of bonded abrasives as they relate to plant environment (humidity/temperature) and adjustments of specific characteristics of liquid and powdered resins.

Coated abrasives are grain bonded on a backing material. The latter can be paper, vulcanized paper, cloth, or a non-woven. Coated abrasives are single layers of grain on backing material and quite different from bonded abrasives which are bonded aggregates of grains in a circular configuration. Grains of coated abrasives are not replaced; they just become eroded or possibly expelled. Coated abrasives lifetime ceases when the grain is nearly or completely eroded. The key phenolic resin bond requirement is to provide high bond strength between the grain and the backing material. Different resins both phenolic and non-phenolic are used in either the make coat or the size coat. Manufacturing conditions, various phenolic resins, and different backing materials are mentioned for the production of coated abrasives.

Attractive schematics within the chapter provide relationships of both liquid (viscosity, MW, water/solvents) and powdered resins (MW, hexa content, particle size) characteristics in guiding the manufacture of various grinding wheels with attractive wheel features such as good wear resistance, good self sharpening, good water dilutability, and good handling. Similar manufacturing features are mentioned for coated abrasives.

13.1 Introduction

Today, abrasive products are vital tools in the manufacture of industrial products. Abrasive products are able to cut as well as grind a variety of materials ranging from metals to organic materials and inorganic materials. The manufacture of industrial products depends on this ability to cut and remove excess material, rough and fine grinding, and polishing. Abrasives have existed since early times in the form of natural stone. In the twentieth century, abrasives technology advanced rapidly with the development of new production techniques and products.

To understand the working mechanism of abrasive products, it is necessary to explain the difference between abrasive tools and cutting tools. In industrial machine tools, there are abrasive tools and cutting tools for almost the same use. Abrasive and cutting tools seem alike. But, both tools differ a great deal in physical behavior, stress, and heat generated during use. Figure 13.1 shows the appearance during use. The cutting tool uses a bit made of super hard material for a cutting edge. Bits are held statically and the work material is rotated. The bit presses against the rotating material and shaves off a portion. With the abrasive tool, the abrasive is rotated and makes contact with a static material, grinding away the surface. The abrasive tool consists of many small grains acting as cutting edges that work the material. It is this property that gives efficiency to the abrasive product,

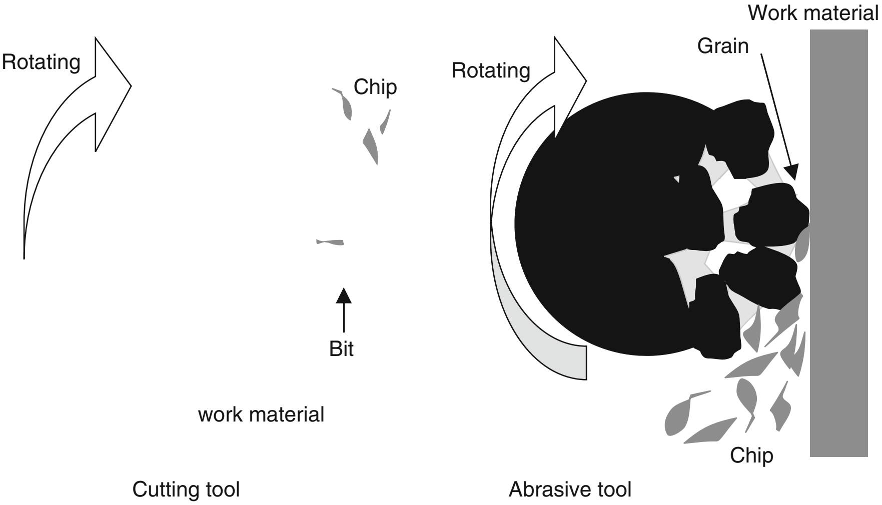


Fig. 13.1 Comparison of abrasive tools and cutting tools on working

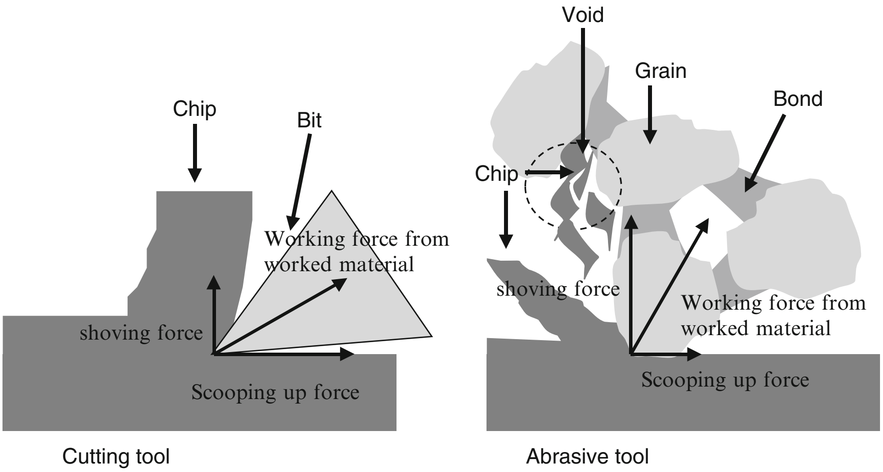


Fig. 13.2 Comparison of abrasive tools and cutting tools in operation on microscopic level

makes it suitable for rough or fine grinding and adaptable to various shapes of work material.

Abrasive products generate heat during heavy work. Abrasives must maintain their properties in the presence of this heat. Figure 13.2 shows the working force from work material and the broken force between a cutting tool and an abrasive product on a microscopic level. In the cutting tool, the force acts by scooping up and shaving. In contrast, in abrasive tool, the force acts by pushing strongly against the work material

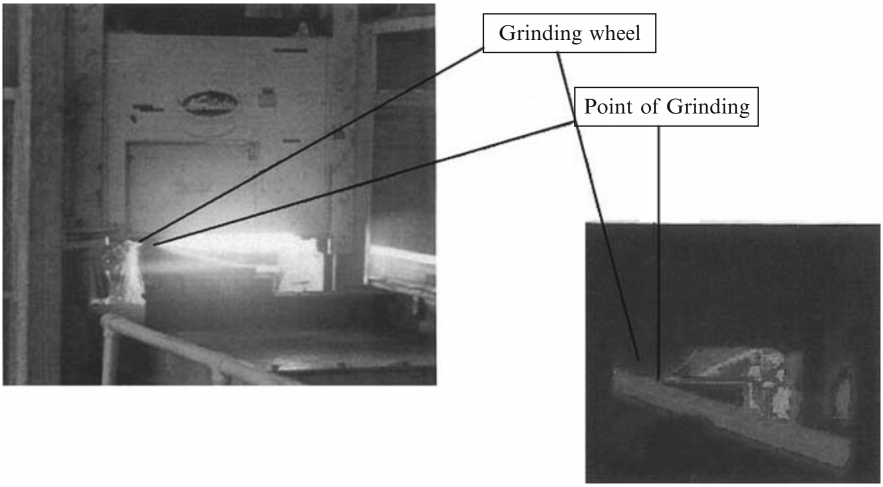


Fig. 13.3 Temperature of abrasive tools during grinding (photo: Noritake company limited co., Ltd, Japan)

and shaving chips are caught in voids in the abrasive. The pushing force is related to the frictional force and the deformation force of work material. These forces are greater in the abrasive tool than the cutting tool. So the amount of generated heat in abrasive product is greater than that of the cutting tool in the same work. In addition, the abrasive product usually rotates faster, and the heat during use is greater. At a microscopic level, it is estimated that the temperature at working point is over 1,000°C. Figure 13.3 shows the appearance of generated heat during use.

An abrasive product consists mainly of grain, for the grinding material, binder, for fixing the grain, and void or pores for removing shavings or dust (shown in Fig. 13.4). There are mainly three materials used as binders: a metal bond, a vitrified bond, or a resinoid bond. Metal bonds use metal as the binder. Vitrified bond uses ceramic material as the binder. Resinoid bond uses thermosetting resin as the binder. Of these, the resinoid bond has the greatest flexibility and safety during use.

Phenolic resin is the predominate polymer for the abrasive industry and is used widely in resinoid bonds. If a thermoplastic polymer is used for bond, the abrasive product will soften and melt during use. Other thermoset resins, like epoxies or urethanes, can be more flexible than phenolic resin, but these are only used in limited finishing applications. Their heat resistance is too low for use in dry grinding or high-efficiency applications. Phenolic resin has excellent properties and is used widely as the abrasive binder. Phenolic resin has high heat-resistance and provides strong adhesion to grain. When compared to the other heat-resistant resins, like polyimide, phenolic resin is less expensive in cost and easier to mold than other resins.

Abrasive products provide a vital step during production in many industries, that is, construction, machinery, automobile, wood, etc. So the market for abrasive

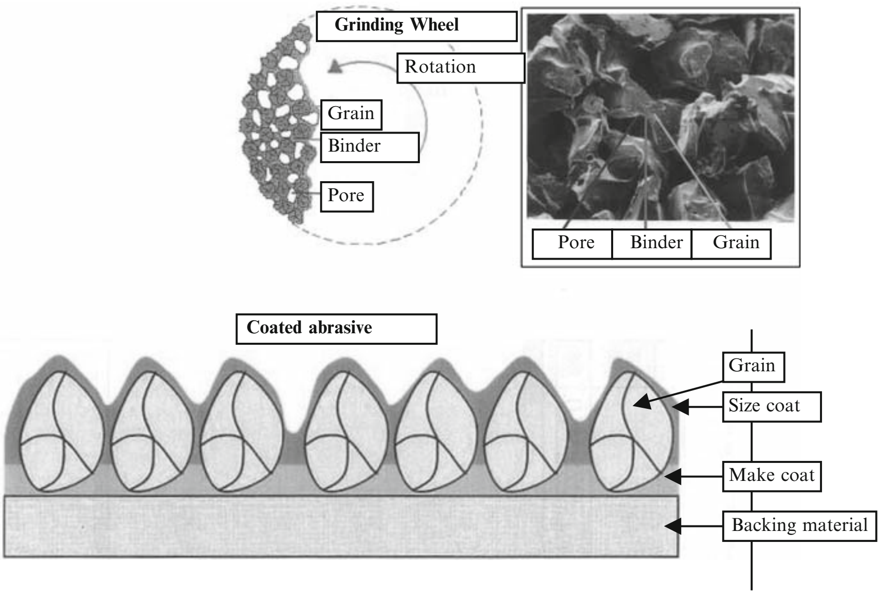


Fig. 13.4 The structure of abrasive tools during grinding (source & photo: Noritake company limited co., Ltd, Japan)

products is dependent on economic and efficient performance. Market trends of abrasive products, especially resinoid grinding wheels and coated abrasives that use phenolic resin are discussed in Sect. 13.2.

Abrasive products consist of grain and binder. The grain removes the work material and the binder, using phenolic resin, holds the grain. The grain is an inorganic material with exceptional hardness. Typical kinds of grain are alumina and silicon carbide. Industrial grain is generally produced synthetically and is rarely a natural product. Grain and the other raw materials are discussed in Sect. 13.3, raw materials.

Abrasive products are mainly divided into two types: bonded abrasive (grinding wheels), and coated abrasive (abrasive paper and cloth). The structural differences between bonded abrasives and coated abrasives are described in Sect. 13.4. In Sect. 13.5 bonded abrasives and the resins used are presented. In Sect. 13.6, coated abrasive and the resins used are discussed.

13.2 Market

Market trends of different global regions are shown in the following tables:

Table 13.1 shows production quantity and value of resinoid grinding wheels and coated abrasives in the USA. In the USA, the production quantity of resinoid grinding wheel and coated abrasive is decreasing [1].

Table 13.2 shows the production quantity and value of resinoid grinding in Japan where grinding wheels are decreasing and coated abrasive are increasing.

Table 13.3 shows the production quantity and value of resinoid grinding wheels and coated abrasives in Germany. In Germany, resinoid grinding wheels and coated abrasives are increasing slightly [2].

Today, India, China, and Thailand possess strong economies. In these countries, the production of resinoid grinding wheels and coated abrasives is increasing. In Table 13.4, the import and export values in China are shown [3].

Table 13.1 USA: production by categories

Year	1997	2001	2005
Bonded products (thousand of US$)	1,176	1,013	992
Coated products (thousand of US$)	2,026	1,579	1,764

Source: the abrasive industry in Europe and North America

Table 13.2 Japan: production by categories

Year	1998	2002	2005	2006
Resinoid grinding wheel (ton)	40,813	34,013	35,160	32,133
Resinoid grinding wheel (millions of yen)	30,962	27,600	27,907	27,042
Coated abrasive (ream)	1,405,751	1,377,581	1,583,358	1,697,115
Coated abrasive (millions of yen)	30,655	34,930	39,011	36,867

Source: Ministry of Economy, Trade and Industry

Table 13.3 Germany: production by categories

Year	1998	2001	2005
Bonded abrasive with resin bonding (ton)			
Reinforced resin-bonded	23,186	21,607	25,419
Resin-bonded without reinforcement	9,653	9,922	10,305
Total	32,839	31,529	35,724
Coated abrasive ($m^2 \times$ ′000)			
Woven fiber backing	27,017	29,212	23,066
Paper backing	36,660	35,032	34,876
Combination of textile and paper	670	689	230
Vulcanized fiber backing	2,120	2,436	3,245
Total	66,467	67,369	61,417
Bonded abrasive with resin bonding (Euro million)			
Reinforced resin-bonded	95	94	105
Resin-bonded without reinforcement	105	59	59
Total	200	153	164
Coated abrasive (Euro million)			
Woven fiber backing	213	237	237
Paper backing	100	95	105
Combination of textile and paper	6	7	2
Vulcanized fiber backing	27	28	43
Total	346	367	387

Source: Statistische Bundesamt BRD

Table 13.4 China trend amount by categories

China: export of bonded abrasive			China: export of coated abrasive		
Partner	Value (US$)	Net weight (kg)	Partner	Value (US$)	Net weight (kg)
World	115,673,278	97,035,074	World	52,587,956	24,558,801
USA	19,537,106	9,398,492	USA	4,396,828	1,518,921
Japan	15,361,697	4,625,942	Vietnam	3,176,589	1,634,172
India	8,466,412	10,395,634	Egypt	2,658,701	1,193,531
South Korea	5,657,392	7,828,423	Germany	2,545,126	1,447,867
United Arab Emirates	5,440,867	6,533,928	Indonesia	2,506,754	1,246,804
China: import of bonded abrasive			China: import of bonded abrasive		
Partner	Value (US$)	Net weight (kg)	Partner	Value (US$)	Net weight (kg)
Japan	57,161,585	1,260,425	South Korea	34,172,456	6,465,032
USA	22,089,275	915,249	Japan	27,982,639	2,503,654
Other Asia	12,841,820	1,801,093	Other Asia	13,562,338	2,043,220
Germany	11,771,987	632,547	USA	10,312,009	403,688
South Korea	8,209,822	1,039,655	Germany	8,677,112	1,392,030

Source: the abrasive industry in Europe and North America

The value of abrasive product is related to the growth of dominant industries like construction, machinery, automobile, wood, etc. So, the market for abrasive products in these developing countries is growing [4,5].

Overall, the global market for abrasive products is increasing due to the increase in economic activity. But the production of abrasives by industrial nations is moving to these developing countries [6].

13.3 Raw Materials

13.3.1 Grain

The main function of the grain is to grind the work material. The grain used is an inorganic material with high hardness. Typical kinds of grain are alumina and silicon carbide. Industrial grain is generally produced synthetically and is rarely a natural product. Alumina and silicon carbide are melted separately in electric furnaces to form crystallized ingot. It is crushed, and the particles are sieved and sized (see Fig. 13.5 and Table 13.5). WA, white alumina, A, bronzed alumina, GC, green general grain, and C, general grain, are the major kinds of grain. Other grains like PA, alumina including chrome, HA, including zirconium, and sintered grain are important. Microcrystalline aluminum oxide is also used and it is chemically synthesized by a sol–gel method [7]. The types of grain that are used are mainly determined by the nature and hardness of the work material. The typical reference index for characterizing the grain hardness and toughness is shown in Table 13.6. Generally, the grains with high hardness have a tendency to be brittle. So high

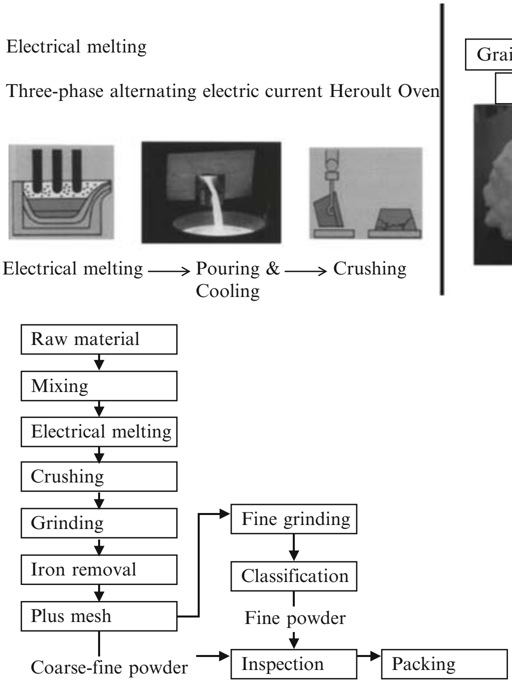


Fig. 13.5 Flow chart of the grain process (source & photo: Noritake company limited co., Ltd, Japan)

Table 13.5 Properties for grain quality

Property	Quality
Chemical property	Chemical composition
	Specific gravity
	Color
Mechanical property	Hardness
	Toughness
Thermal property	Specific heat
	Heat conduction
	Heat expansion
	Melting point
	Thermal shock resistance
Surface property	Hydrophilic property
	Cleanness
	pH
Electromagnetic property	Electrostatic characteristic
	Checking magnetic material
Particulate property	Grain size
	Bulk specific gravity
	Appearance

Source: Noritake company limited co., Ltd, Japan

Table 13.6 Properties depending on grain type

Grain type		Knoop hardness (kg/mm^2)	Friability index
Aluminum oxide	Pink/red (3% Cr)	2,260	65.0
	White	2,120	56.6
	Single crystal	2,280	47.7
	Regular	2,040	35.6
	Microcrystalline	1,950	10.9
	10% ZrO	1,960	10.9
	40% ZrO	1,460	7.9
	Sintered	1,370	6.5
Silicon carbide	Breen	2,840	62.5
	Black	2,680	57.2

Source: the abrasive industry in Europe and North America

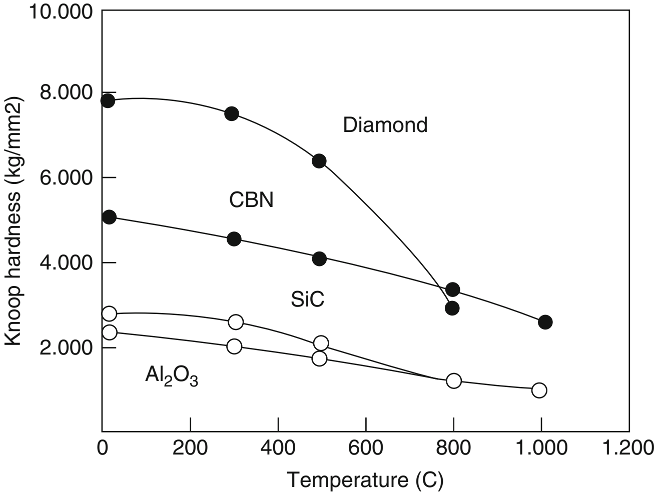


Fig. 13.6 Hardness relationship vs temperature for Diamond, CBN, SiC, and Al_2O_3
Source: S. Okada: Annals of CHIP, 25(1976)

hardness and brittle grains are mainly used for fine or mild grinding, and the type of phenolic resin used for the binder should possess flexibility rather than heat resistance. On the other hand, grains with low hardness and high toughness have fracture resistance and are mainly used in heavy-duty grinding. The phenolic resin used for binding heavy duty grinding has high heat-resistance and high strength [8].

An important property of the phenolic resin is that it furnishes adhesion to the grain. Prior treatment of the grain with a silane coupling agent is quite effective and is frequently used to improve adhesion beyond what the phenolic resin provides.

Super grains, like diamond and cubic boron nitride (CBN), are superior to general grains in hardness. Figure 13.6 shows hardness differences as a function of temperature for diamond and cubic boron nitride. Diamond has lower heat resistance, and the stable temperature of hardness for diamond is around 600°C. Because of this, diamond grain is generally used in wet grinding along with grinding fluids. Diamond and CBN are weakly bonded by phenolic resin. To remedy this, the super grain that is used with phenolic resin requires a high surface area such as a low-impact multi-crystal type or alternately metal coated (nickel) grain [8].

Finally, grain size is dependent on the grinding requirements. Figure 13.7 shows the relationship of grain size and surface roughness. Rough grinding and setting efficiency use large size grain. Fine grinding uses fine size grain. For reference, Tables 13.7 and 13.8 show grain size by F-code used in Europe, USA, and Japan [9].

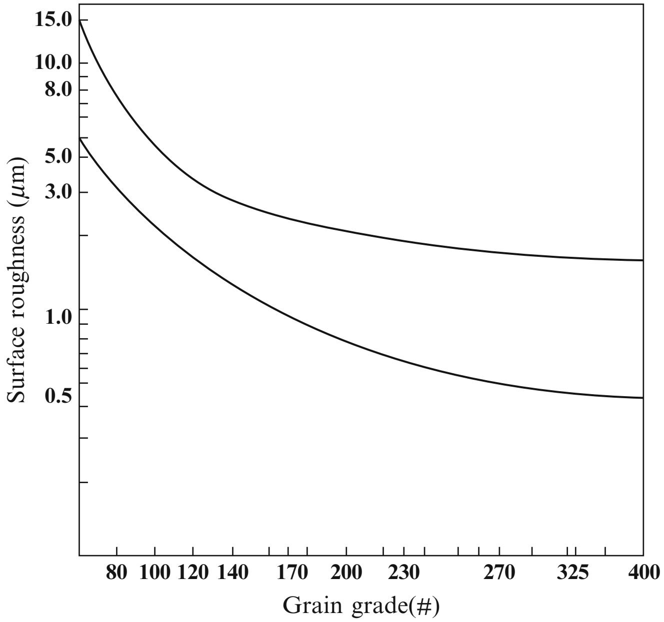


Fig. 13.7 Surface roughness as it relates to grain grade
Source: Manual for grinding wheel, Okawara (1990)

Table 13.7 Grain grade and grain particle size [1]

Designation	Average (50%) particle size in μm
F230	53.0 ± 3.0
F240	44.5 ± 2.0
F280	36.5 ± 1.5
F320	29.2 ± 1.5
F360	22.8 ± 1.5
F400	17.3 ± 1.0
F500	12.8 ± 1.0
F600	9.3 ± 1.0
F1000	6.5 ± 0.8
F1000	4.5 ± 0.8
F1200	3.0 ± 0.5
F1500	2.0 ± 0.6
F2000	1.2 ± 0.3

Source: the abrasive industry in Europe and North America

Table 13.8 Grain grade and grain particle size [2]

μm grade	Industrial US mesh	FEPA grade	Japanese JIS grade	Emery
1,000	#150	–	–	–
80	#180	–	–	–
60	#220	P240	#240	–
	#240	–	#280	–
40	#280	–	#320	–
	#320	P360	#360	–
	#360	P500	#400	1/0
30	#400	–	#500	2/0
	#500	P1000	#600	3/0
15	#600	–	#1,000	–
	#800	–	#1,200	–
12	–	P1200	#1,500	–
9	–	–	#2,000	4/0
5	–	–	#2,500	–
3	–	–	#4,000	–
2	–	–	#6,000	–
1	–	–	#8,000	–

Source: the abrasive industry in Europe and North America

13.3.2 Filler

In phenolic resin applications, fillers like calcium carbonate and wollastonite, are typically used to increase strength, heat resistance, and toughness. In abrasives, it is important for the filler to provide reinforcement and aid abrasion. Cryolite, iron sulfide, zinc sulfide, calcium sulfate, and calcium chloride are used as fillers. As the heat is generated during use, these materials react with the work surface to aid in grinding efficiency and help protect the grain [10].

Alkaline metal oxide products, like calcium oxide and magnesium oxide, are used for accelerating the phenolic resin cure and absorbing the water that is generated by the phenolic reaction. These materials are used in high density grinding wheels.

Glass chips are used for reinforcing around the wheel axis but not the grinding surface. Micro-balloons are added for porosity.

13.3.3 Glass Cloth

In cutting wheels and depressed center wheels, glass cloth is used to reinforce the wheel (see Fig. 13.8). These are referred to as reinforced grinding wheels. The glass cloth used for reinforcing the wheel is impregnated with phenolic resin. The procedure for coating this glass cloth is as follows:

The glass cloth is dipped in liquid phenolic resin, dried at 80–100°C for 3–10 min, and after drying, is cut to the size of the wheel. The amount of the wet impregnated resin on the glass cloth is controlled from 30 to 50%.

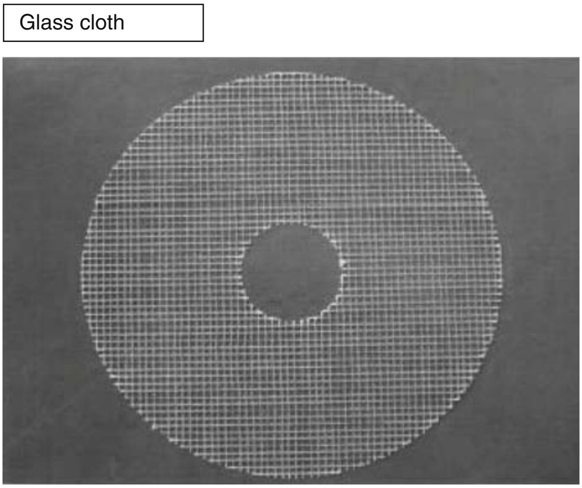


Fig. 13.8 Glass cloth (photo: Noritake company limited co., Ltd, Japan)

Table 13.9 Liquid resin product line for glass cloth

No.	Resin type	Solvent	Specific gravity	Resin content (%/135°C)	Gel time (s/150°C)
1	Novolac resole resin mixture	Methanol	~1.00	~60	~150

Source: Sumitomo Bakelite co., Ltd, Japan

The phenolic resin for this impregnation is mainly a resin consisting of a resole mixed with a novolac. Table 13.9 shows the properties. Phenolic resin is designed such that the glass cloth is not tacky when stored and the adhesion is increased between phenolic resin and the grain.

The strength of glass cloth determines rotational strength. Therefore, the fabric strength and the type of weave are important. This effect demonstrates the safe rotational speed of a glass reinforced wheel of 4,500 m/min verses 3,000 m/min for a wheel without glass cloth reinforcement [11].

13.3.4 Backing Material

In coated abrasive products which are discussed later, the grain is coated over a backing material with phenolic resin as the binder. The backing material is made of kraft paper, vulcanized fiber, polyester or cotton cloth, or nonwoven nylon. These materials generally need a treatment with liquid resin to promote the adhesion as well as prevent penetration by the coating binder resin. This treatment is more important for cloth or paper backing. It is essential that the treatment needs to adhere to both the binder resin and the backing material. For these materials, the treatment provides reinforcement, processability, and water resistance.

The treatment of waterproof sandpaper is with alkyd resin or latex emulsions with phenolic resin. This treatment makes the paper both waterproof and flexible. For a cloth abrasive product, polyvinyl alcohol or latex as an additive with a water soluble phenolic resin is used. The general treatment procedure is dipping or applying with water-soluble resin, and drying at about 100°C for 5–20 min. This procedure is repeated several times (see Fig. 13.9).

Table 13.10 shows resins for the treatment of backing material. These resins have high water solubility necessary for this application.

Treatment of backing material

Dip coating process
Backing material is dipped in treatment agent
to fill a space and to prevent extension

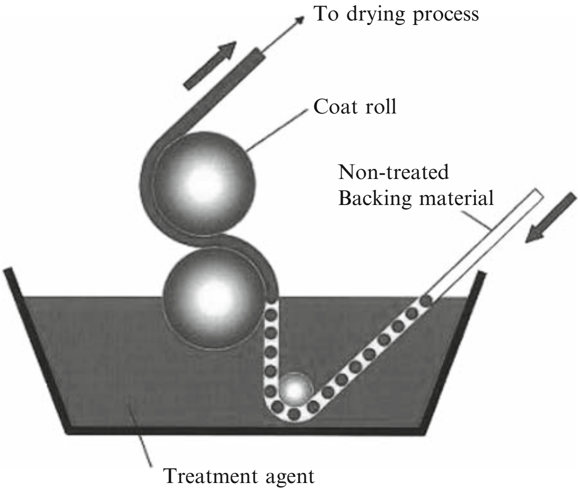


Fig. 13.9 Treatment process for backing material
Source: Noritake company limited co., Ltd, Japan

Table 13.10 Phenolic liquid resin product line for treatment of backing material

No.	Resin type	Solvent	Specific gravity	Resin content (%/135°C)	Gel time (s/150°C)	Water solubility (times)	Use
1	Low MW water soluble resin	Water	~1.21	~60	~250	>10	For PVA mixing
2	Medium MW water	Water	~1.24	~74	~135	~3	For PVA mixing For without adding other polymer
	High MW modified with high-polar-group	Water	~1.23	~57	~55	>10	For rubber latex mixing

Source: Sumitomo Bakelite co., Ltd, Japan

13.4 Structure of Abrasive Products

To understand the role of phenolic resins as they are used for abrasives, a discussion of the structural differences between bonded abrasives and coated abrasives is necessary. Bonded abrasive and coated abrasive both use phenolic resin as binder for the grain. But the structure and type of phenolic resin are quite different.

The structure of a bonded abrasive consists of three parts, grain, bond, and pores as shown in Fig. 13.4. Grain plays the role as the abrasive, the bond holds the grain, and the pores draw out the grinding dust. The abrasive grain is self-renewing, where the new grain is generated after the worn and dulled grain is ejected or removed during grinding. It is important for the bonded abrasive to constantly be renewed during grinding. If the grain bond is too strong and grain renewal is too slow, the pores become filled with grinding dust and abrasive efficiency is reduced. Conversely, if the grain bond is too weak and the grain is replaced too quickly the wheel will wear too quickly. The role of the grain during grinding under various conditions must be considered as one selects the phenolic resin from the powdered resin product line.

If a phenolic resin is selected with high strength and high heat resistance, and much higher than required for the application, the grain renewal is too slow and the abrasive efficiency is reduced. This phenomenon appears to occur in fine and light duty grinding wheels. On the other hand, heavy-duty grinding wheels must avoid ease of grain release during grinding and require a phenolic resin with high heat resistance and high adhesive strength.

The structure of a coated abrasive is shown in Fig. 13.4. It shows grain and bond on a backing. The grain is held on the backing by the resin bond. Coated abrasives are usually a single layer of grain. So, their structure is completely different from bonded abrasives. In coated abrasives, grains are never replaced, only worn out. The life of a coated abrasive is the time it takes for the grain to wear out, so the loss of grain is a defect. The critical requirement for the phenolic resin is high bond strength between the grain and backing.

Figure 13.10 shows a grinding wheel and sanding machine using coated abrasive at work. The rotating grinding wheel is pushed on to the work piece, and the grinding wheel is subjected to not only centrifugal force but also repelling and frictional force during use. The grinding wheel must function efficiently under these forces. The safety and wear of the grinding wheel are directly associated with resin strength. Additionally, key mechanical properties of the composite grinding wheel, which are modulus and hardness, etc., affect the grinding properties. Therefore the phenolic resin must be carefully selected while keeping these mechanical properties in mind.

In the sander unit using coated abrasives, the mechanical force or centrifugal force, repelling force, and frictional force are mainly absorbed by the contact wheel or backing material. Contact wheel is usually made of rubber with low modulus.

Figure 13.10 also shows the circumference distance for each rotation. This distance indicates the frequency of hitting and grinding the work piece at the same

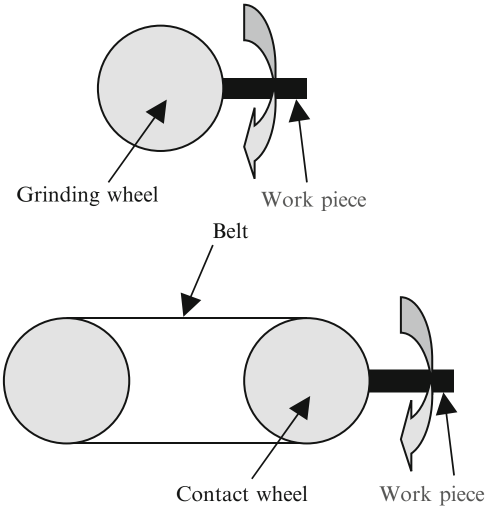


Fig. 13.10 Comparison of grinding wheel and coated abrasive during grinding

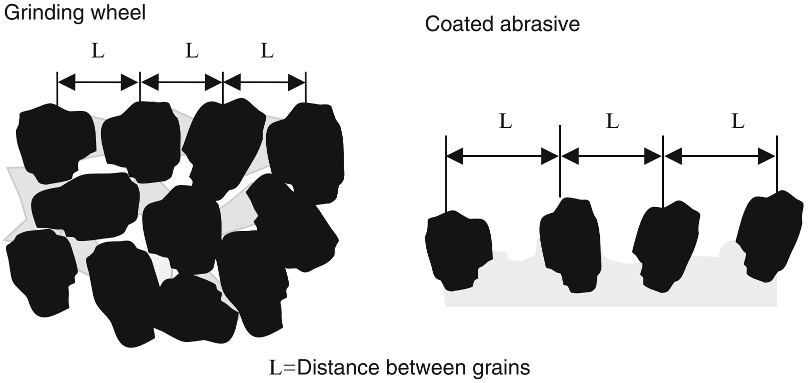


Fig. 13.11 Comparison of grinding wheel and coated abrasive with micro view

point. This frequency is closely related to heating and grinding efficiency. By reducing this distance with the same speed and diameter, the frequency of hitting and grinding is increased. Coated abrasive travel distance can vary and is related to the belt length. On the other hand the wheel diameter determines the distance for the grinding wheel. Thus, the grinding wheel encounters more heat and should be considered as the phenolic resin is selected or through the use of coolant water with the grinding wheel.

Figure 13.11 shows the different grinding characteristics of bonded abrasive and coated abrasive using a micro view. Generally speaking, the distance between grains in bonded abrasives is less than in coated abrasives. Examining the structure of a bonded abrasive, the grain is bonded by resin binder and its distance is fixed. So, it is difficult to control this distance. In a coated abrasive this distance can be varied or controlled when setting the grain. This distance is associated with heat generation and grinding efficiency. Using coolant water is an effective way to reduce heat in both abrasive products. Coolant water is generally used in fine grinding.

13.5 Bonded Abrasive

The type of binder classifies the specific bonded abrasive as vitrified, metal, rubber, and resinoid. Table 13.11 shows the tensile strength and Young's modulus of various binders. Tensile strength is related to the adhesion to the grain while Young's modulus is related to elastic deformation. The metal bond is high in adhesive strength while vitrified and resinoid bonds are low. Metal and vitrified bonds are low in elastic deformation but resinoid bond is high in this property. Rubber bond is even higher than resinoid, but the rubber bond has less heat resistance than resinoid. Because of this, rubber grinding wheels are typically used in finishing operations.

Bonded abrasives were developed in the 1890s without the use of resin. The resinoid grinding wheel was developed in the 1920s. In the beginning, furfural was used as a wetting agent, and then, powdered phenolic resin was mixed with it. This basic method of manufacturing has remained the same. Today, various types of bonded abrasive products are used (see Fig. 13.12).

13.5.1 Manufacturing Process

Figure 13.13 shows the manufacturing process for a resinoid grinding wheel. First, grain and phenolic resin are mixed. The mix which is known as "coated grain" is molded in a press. Molded parts are cured in an oven, finished, checked, and wrapped. Then the resinoid grinding wheel is shipped.

13.5.1.1 Mixing Process

The mixing process generally occurs in two stages. In the first stage, grain is mixed with liquid resin or solvent, like furfural. Grain is evenly coated with liquid resin or

Table 13.11 Physical and mechanical properties depending on binder type

Binder	Specific gravity	Hardness (Hv)	Tensile strength	Young's modulus	Rate of thermal expansion
Unit	g/cc	kgf/mm^2	kgf/mm^2	kgf/mm^2	10^3/°C
Resin	1.15	12	5	430	45
Metal	8.8	82	82	10,800	18.2
Vitrified	2.5	780	6	7,200	8

Source: Kensakukakou No Kiso. Nikkan Kogyo Shimbun, Japan

Fig. 13.12 Product line of grinding wheels (photo: Noritake company limited co., Ltd, Japan)

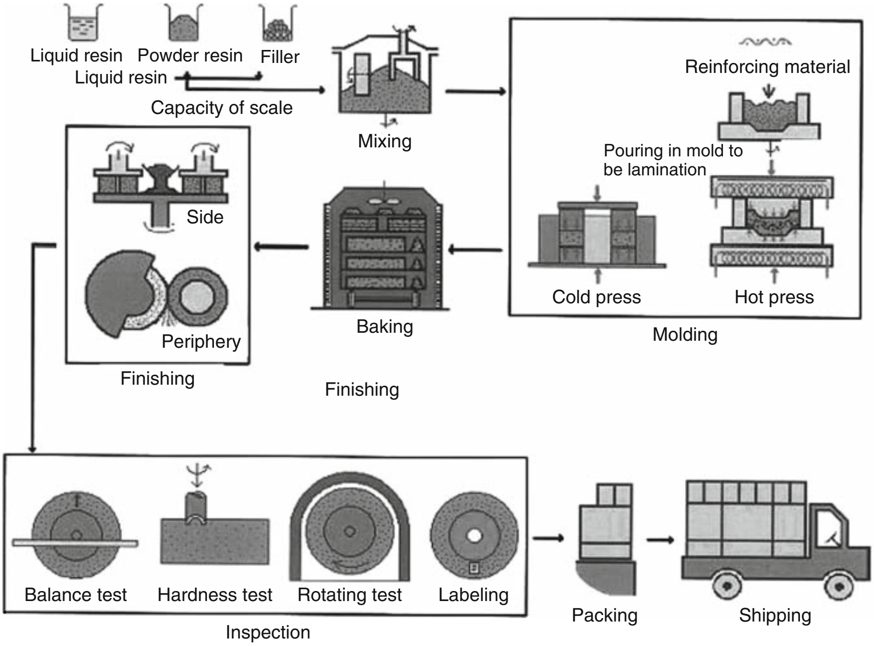


Fig. 13.13 Production flow process for grinding wheel
Source: Noritake company limited co., Ltd, Japan

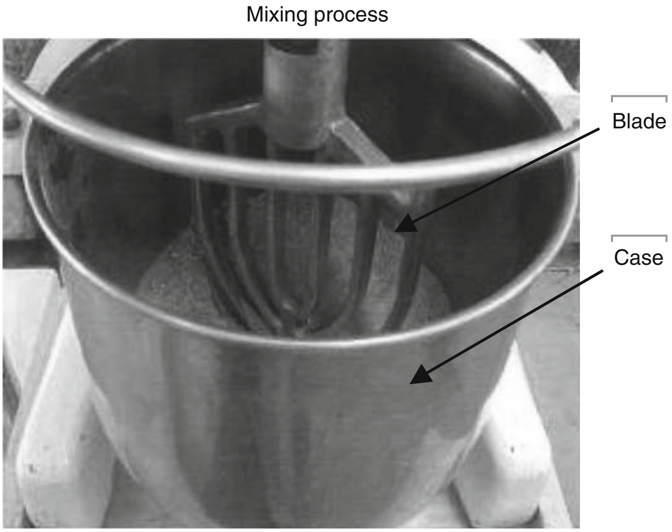


Fig. 13.14 Mixing process for grinding wheel (photo: Noritake company limited co., Ltd, Japan)

solvent. In the next stage, the wet grain is mixed with the powdered filler and resin. (Fig. 13.14 shows the mixer.) After mixing, any lumps that were formed are removed by screening. After screening, this mix is called "coated grain" and is an interim product. The condition of the coated grain is important for the uniformity of the grinding wheel for subsequent processing. If it has excess powder, the grinding wheel will not be uniform after molding, due to loss of some powder. If it is too wet, it will be tacky, difficult to process, be uneven in the mold, and yield a non-uniform wheel. The condition of the coated grain must be controlled, stable during storage, and uniform from lot to lot. Table 13.12 describes problems and steps to be taken for resolving these problems. Critical areas are the storage conditions of the raw materials and conditions in the work area. The ratio of liquid resin and powder resin is easily controlled to obtain satisfactory coated grain. But this method has the danger of resorting to a wide variation of grinding wheel properties due to varying ratios of liquid to powdered resins. So, it is important to keep same ratios of raw materials and control the work-place environment.

13.5.1.2 Molding

Coated grain is molded by compression molding. The molding procedure is conducted by two methods: (Fig. 13.15 shows a molding machine.)

1. Cold press and semi-hot press molding
2. Hot press molding

Cold press and semi-hot press are suitable for bonded abrasives with 10% or more void content. This molding method accounts for almost all the grinding wheels

Table 13.12 Action for adjusting coated grain by changing resin ratios (powder resin/liquid resin) for changing conditions

Factor	Condition factors	Variability conditions	Powder resin/liquid resin ratio of charged resin during abrasive production
Plant environment	Temperature	High	Part of powder resin is increased
		Low	Part of liquid resin is increased
	Humidity	High	Part of powder resin is increased
		Low	Part of liquid resin is increased
Liquid resin	Viscosity	High	Part of liquid resin is increased
		Low	Part of liquid resin is increased
	Molecular weight	High	Part of liquid resin is increased
		Low	Part of liquid resin is increased
Powder resin	Moisture	High	Part of powder resin is increased
		Low	Part of liquid resin is increased
	Particle size	High	Part of powder resin is increased
		Low	Part of liquid resin is increased
	Molecular weight	High	Part of liquid resin is increased
		Low	Part of liquid resin is increased

Source: Sumitomo Bakelite co., Ltd, Japan

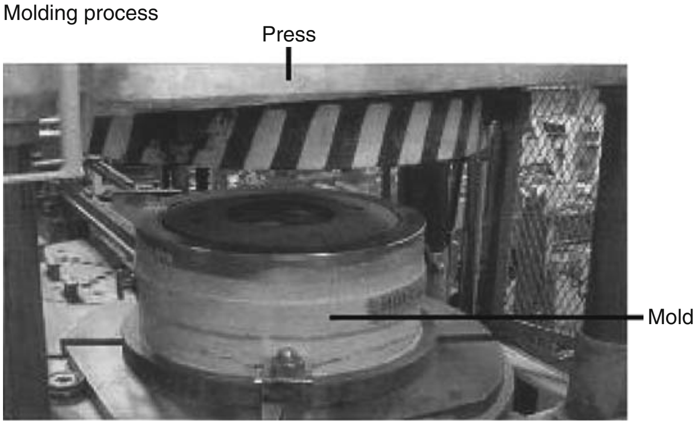


Fig. 13.15 Molding process for grinding wheel (photo: Noritake company limited co., Ltd, Japan)

requiring voids, cutting wheels, depressed center wheels, and grinding wheels for finishing. By adjusting the pressure, one can control the density of the grinding wheel. The molding time is short, from 10 s to 1 min. The mass production of grinding wheels, like cutting wheels and depressed center wheels is done by automatic molding machines using semi-hot press molding. The molded component, after cold pressing and semi-hot pressing, is an uncured composition. Curing takes place in an oven after the molding process. Curing ovens are programmed to provide optimum cure based on wheel size, shape, and the resin characteristics.

Hot press molding is suitable for high-density bonded abrasives without voids. Heavy-duty grinding wheels and diamond grinding wheels are almost always produced by this molding method. This molding method partially cures the resin during molding. After molding, the molded part is heated in an oven and is cured completely. The molding time is longer; from 20 min to 60 min. Temperature at the start is around 60°C, then it is heated in the mold with some degassing around 150°C, then held around 150°C for about 10 min. The pressure is about 100–1,000 kg/cm^2; it depends on the size of the wheel or void or resin ratio of the wheel. The pressure initially is lower than the set pressure. The point at which the resin has softened and starts curing during molding is identified as the set pressure. Degassing is important for eliminating defects. Longer mold time decreases void and internal defects, but increases manufacturing costs.

13.5.1.3 Cure

The curing process occurs in a programmed oven (Fig. 13.16 shows a typical oven). Cold or semi-hot molded wheels are without cure and somewhat fragile so more care must be taken during the curing process. Program patterns are shown in Fig. 13.17. If the bonded abrasive product is large and void ratio is low, it would need a long cure time in the oven. The curing program shown in Fig. 13.17 describes the importance of the holding time at a given temperature and the temperature increase rate. It is especially important for successful wheel formation that the holding time and temperature increase rate be controlled during the resin softening point and

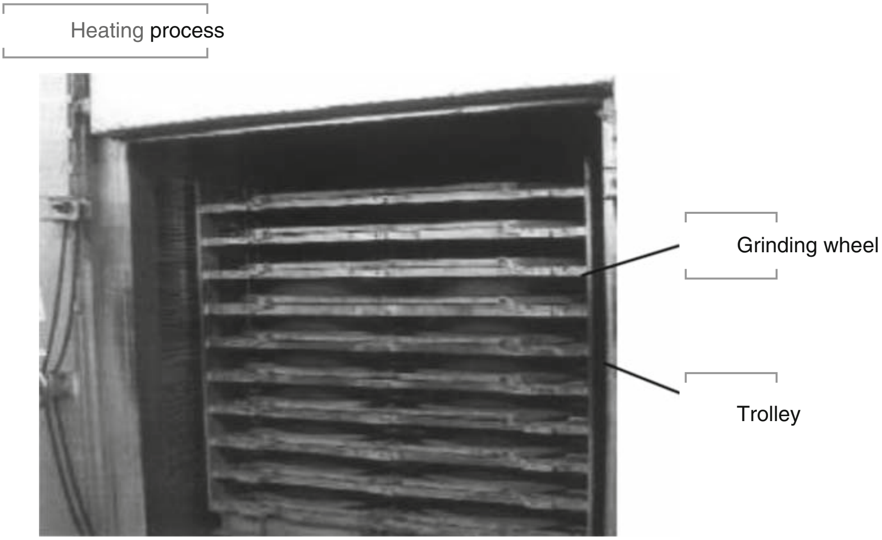
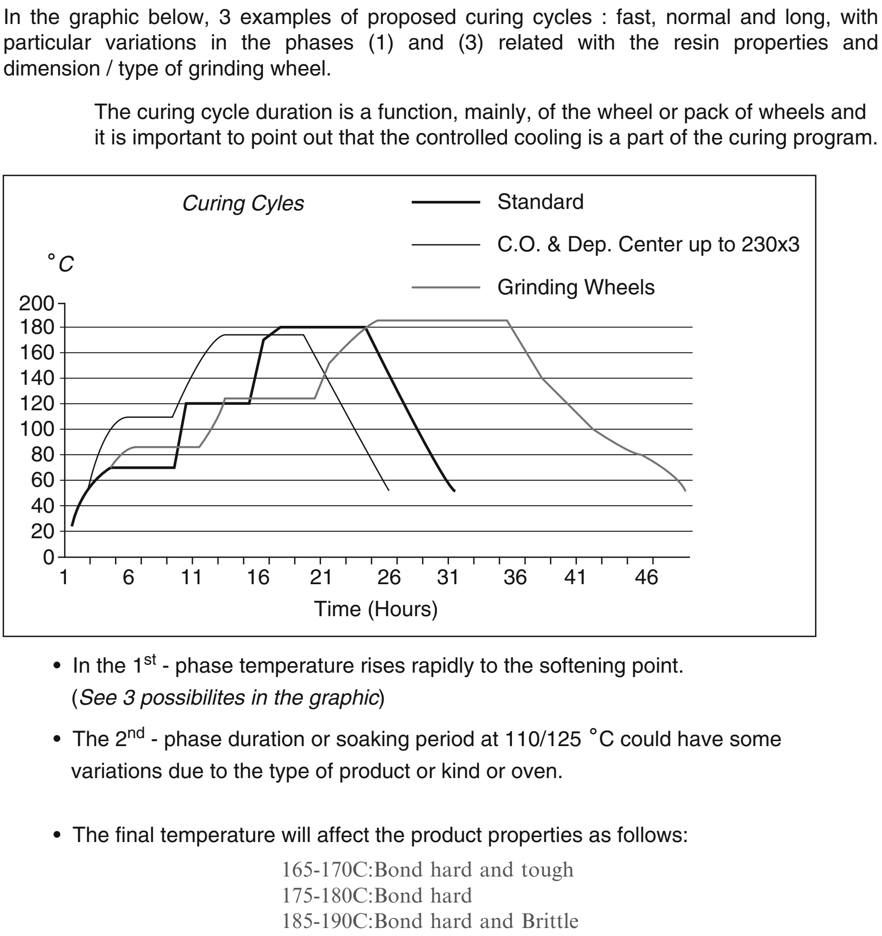


Fig. 13.16 Heating process for grinding wheel (photo: Noritake company limited co., Ltd, Japan)



In the graphic below, 3 examples of proposed curing cycles : fast, normal and long, with particular variations in the phases (1) and (3) related with the resin properties and dimension / type of grinding wheel.

The curing cycle duration is a function, mainly, of the wheel or pack of wheels and it is important to point out that the controlled cooling is a part of the curing program.

- In the 1st - phase temperature rises rapidly to the softening point. (*See 3 possibilites in the graphic*)
- The 2nd - phase duration or soaking period at 110/125 °C could have some variations due to the type of product or kind or oven.
- The final temperature will affect the product properties as follows:

165-170C:Bond hard and tough
175-180C:Bond hard
185-190C:Bond hard and Brittle

Fig. 13.17 Curing program (to show 3 typical examples)
Source: Sumitomo Bakelite Europe co., Ltd, Spain

onset of cure from 80°C to 120°C. Equally important for satisfactory grinding performance properties is that the final cure temperature is from 150°C to 200°C and an extended holding time is from 5 h to 10 h. This ensures proper heat resistance with the cured desired density furnished by the phenolic resin.

13.5.2 Phenolic Resin for Bonded Abrasive

Both liquid and powdered resins are used in the manufacture of bonded abrasives. Tables 13.13 and 13.14 show typical resins.

Table 13.13 Liquid resin product line for grinding wheel

No.	Resin type	Solvent	Viscosity (mPa s/25°C)	Resin content (%/135°C)	Cut-off	Depressed center	Coolant use	Heavy-duty	Diamond
LA	Low MW water soluble alkaline catalyst resin	Water	~200	~72			XX		
LB	Medium MW alkaline catalyst	Water	~400	~70	XX	XX	X		
LC	Medium MW amine catalyst	Water	~200	~69	X	X	XX		
LD	Medium MW alkaline catalyst	Furan group	~200	~60	X		XX	X	X
LE	High MW alkaline catalyst	Water	~400	~70	XX	XX			

XX: strongly recommend; X: recommend

Source: Sumitomo Bakelite co., Ltd, Japan

Table 13.14 Powder resin product line for grinding wheel

No.	Resin type	Melting point (C)	Flow (mm/l25°C)	Hexamine content	Cut-off	Depressed center	Coolant use	Heavy-duty	Diamond
PA	Straight resin	~95	~20	Low	XX	XX	X		XX
PB	Straight resin	~85	~45	Low	X	X	XX		
PC	Straight resin	~90	~28	Medium	XX	XX	X		
PD	Straight resin	~85	~40	Medium–high	X	X	X	X	
PE	Straight resin with HAP technology	~102	~12	High				XX	XX
PF	Straight resin with HAP technology	~95	~33	High				XX	
PG	NBR modified resin	~80	~40	Low		X	XX		
PH	Phenoxy resin modified resin	~100	~27	High	X	X	X	X	

XX: strongly recommend; X: recommend

Source: Sumitomo Bakelite co., Ltd, Japan

13.5.2.1 Liquid Resin

Liquid resole phenolic resin is used as a wetting agent to uniformly coat the grain. Table 13.13 lists various liquid resins. Figure 13.18 presents an approximate relationship between liquid resin and the properties of the grinding wheel. The main role of the wetting agent is that it helps dissolve the powdered resin and evenly coat the surface of the individual grains. Liquid resole phenolic resins can affect the degree of wetting during mixing, the strength after molding, the flow and the degree of cross-link density at curing. A typical liquid phenolic resin for this application is prepared using a base catalyst, and has a final viscosity range of 100–1,000 mPa s at 25°C, resin content of typically 70% and free phenol content between 10% and 100%.

Figure 13.18 shows the relationship of viscosity and molecular weight of the resin with the condition of the coated grain and the strength of the finished product. In the case of a water soluble resole resin, the resin that is low viscosity and low molecular weight generally gives a high strength product suitable for low density wheels, but the coated grain has less flow and less stability in storage. Conversely, a resin that is high viscosity and high molecular weight generally gives a coated grain with better flow and better stability in storage. The strength of this product is low and is suitable for cut-off wheels and depressed center grinding wheels.

The liquid resins that use furan-group solvent like furfural or furfuryl alcohol as solvent have low moisture content and result in high strength grinding wheels. This resin system is suitable for grinding wheels with high hardness. However, these solvents quickly dissolve the powdered resin and the coated grain has less flow and less stability in storage.

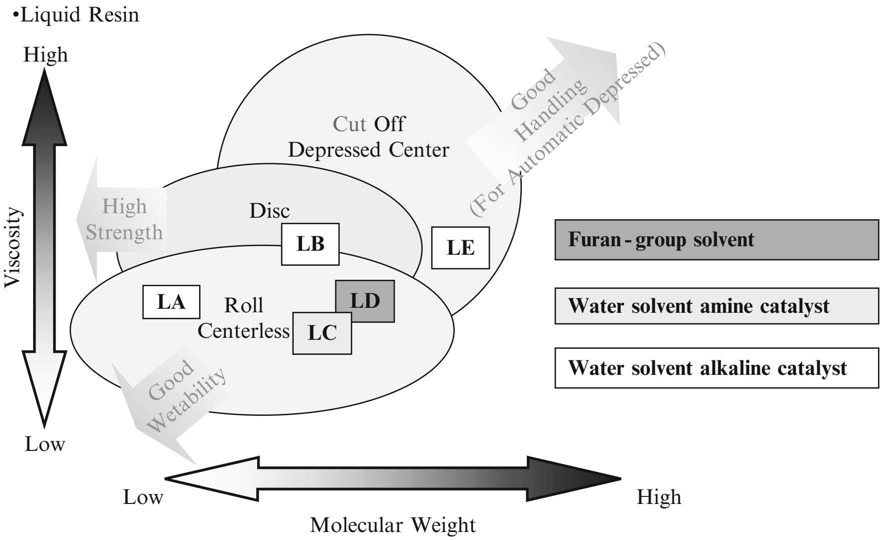


Fig. 13.18 Approximate relationship of liquid resins with different types of grinding wheels
Source: Sumitomo Bakelite co., Ltd, Japan

The resin that is prepared with neutralized base catalyst or amine catalyst provides water resistance to the grinding wheel. It is suitable for a grinding wheel used with coolant water.

13.5.2.2 Powder Resin

Powdered resin is used as the principal resin binder. Table 13.14 shows a listing of powdered resins. Figure 13.19 shows an approximate relationship between properties of resin and the resulting properties of the grinding wheel. Powdered phenolic resin affects the degree of wetting during mixing, the strength after molding, the flow and the degree of cross-link density at curing, and helps determine abrasive properties, strength, and heat resistance. Commercial powdered novolac phenolic resins are made in two steps. The first step is the preparation of solid novolac resin using acid catalyst, and the second step involves the combining of the solid novolac resin with hexamine.

The performance of powdered phenolic resin is roughly determined by the molecular weight, which directly influences flow, hexamine content, and particle size (see Fig. 13.19). The wide range of powdered phenolic resins available can

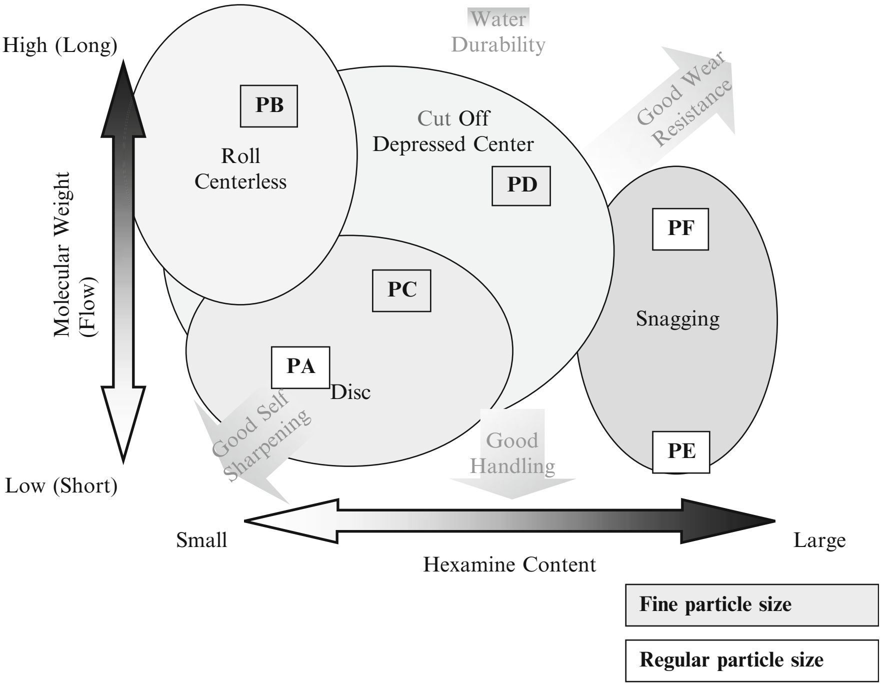


Fig. 13.19 Approximate relationship of powder resins with different types of grinding wheels *Source*: Sumitomo Bakelite co., Ltd, Japan

produce an equally wide range of grinding wheels and customer needs. For example, a resin that has high hexamine content has high heat, and is suitable for making high density, heavy-duty grinding wheels. A resin with low hexamine content has good cutting efficiency, which is caused by accelerated wearing, and is suitable for making grinding wheels for precise grinding. A resin that has low molecular weight, provides high water resistance, and is suitable for making grinding wheels used with coolant water.

13.5.3 Cut-off Wheels

Cut-off wheels are used in construction and machinery manufacture. Cut-off wheels can cut various metals, organic and inorganic materials. There are many types of cut-off wheels for cutting different materials of different shapes and sizes. These are usually used in a cutting machine and used for dry grinding without coolant (see Fig. 13.20).

The grain size most commonly used is #80–#20. Glass cloth insert is used as a reinforcement to increase rotational speed and safety, but glass cloth insert is not used in precision wheels. The molding method is usually semi-hot molding and automated molding machines are used for mass production of standardized products.

Tables 13.13 and 13.14 show liquid resin and powdered resin for cut-off wheels. There are many resins to meet specific application needs. Powdered resins with a short flow and low hexamine content like PA give good cutting properties. Resins

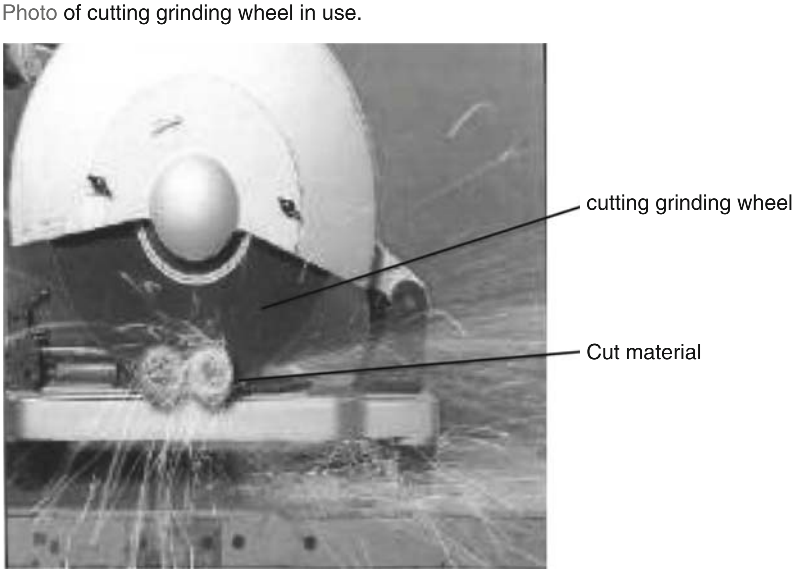


Fig. 13.20 Photo of cutting grinding wheel in use (photo: Noritake company limited co., Ltd, Japan)

with long flow and high hexamine like PB give high wear resistance during cutting due to its high strength and high heat resistance.

13.5.4 Depressed Center Grinding Wheels (Rough Grinding Wheels)

Depressed center grinding wheels are used for clearing burrs and rough leveling on work surfaces of steel and aluminum in construction and machinery manufacture. Depressed center grinding wheels are used on hand held grinders (see Fig. 13.21). These are used under dry conditions without coolant. For depressed center grinding wheels, the face is used for grinding horizontal to the surface and the edge is used as a cut-off wheel. The production process and structure of depressed center grinding wheels are similar to those of cut-off wheels. The molding method is usually semi-hot molding. An automated machine is used for mass production of standardized products.

Depressed center grinding wheels need more strength than cut-off wheels. Generally two sheets of glass cloth are used for reinforcement. There is a difference in structure between the upper side and the underside that is used in grinding. The upper side needs flexibility and strength and the underside that is actually grinding needs strength and efficiency.

Tables 13.13 and 13.14 show liquid resins and powdered resins for depressed center grinding wheels. There are many resins to meet specific application needs. Powdered resins with medium flow and medium hexamine content like PC provide good working properties and strength during grinding. Resins with long flow and high hexamine content, like PB offer high wear resistance. PG is rubber-modified resin. PG has flexibility and high strength and is suitable as a binder for the upper side of the wheel.

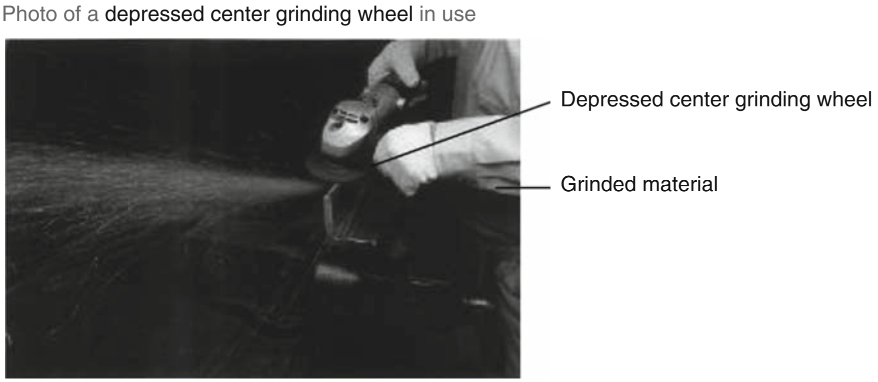


Fig. 13.21 Photo of a depressed center grinding wheel in use (photo: Noritake company limited co., Ltd, Japan)

13.5.5 Grinding Wheel with Coolant Water

Cylindrical grinding wheels, center-less grinding wheels, roll grinding wheels, and surface grinding wheels are used in high precision grinding in machinery and automobile manufacture. Most grinding wheels are used with coolant water (see Fig. 13.22). The grain size of these is typically in the range of #10–#3,000, and depends on application and surface roughness. This kind of grinding wheel is designed to meet the end-user's process requirement and equipment. Both resinoid grinding wheels and vitrified grinding wheels are used dependent on application and material to be processed.

The production process for these grinding wheels is usually cold or semi-hot molding and curing process time is dependent on wheel size.

Tables 13.13 and 13.14 show liquid resins and powdered resins for depressed center grinding wheels with coolant water. There are many resins to meet specific application needs. Powdered resins with short flow and low hexamine content like PA provide good working properties during grinding. Resins that have long flow and low hexamine content like PB offer high water resistance. PG has flexibility and high strength and is suitable for use as a binder for absorbing vibration during grinding. LB is standard liquid resin for high strength and LC has water resistance.

13.5.6 Heavy-Duty Grinding Wheel

Heavy-duty grinding wheels are used for cutting and grinding foundry iron in the steel industry (see Fig. 13.23). These grinding wheels do not need precision but need excellent heat resistance and high strength. The grain is usually a sintered type and the grain size usually #10–#40. The molding method is hot molding.

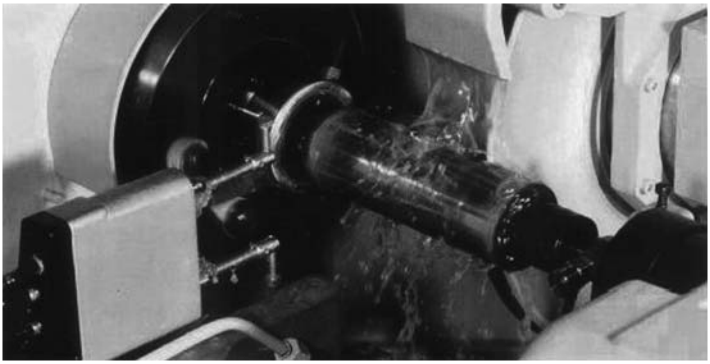


Fig. 13.22 Photo of precise grinding wheel in use with coolant water (photo: Noritake company limited co., Ltd, Japan)

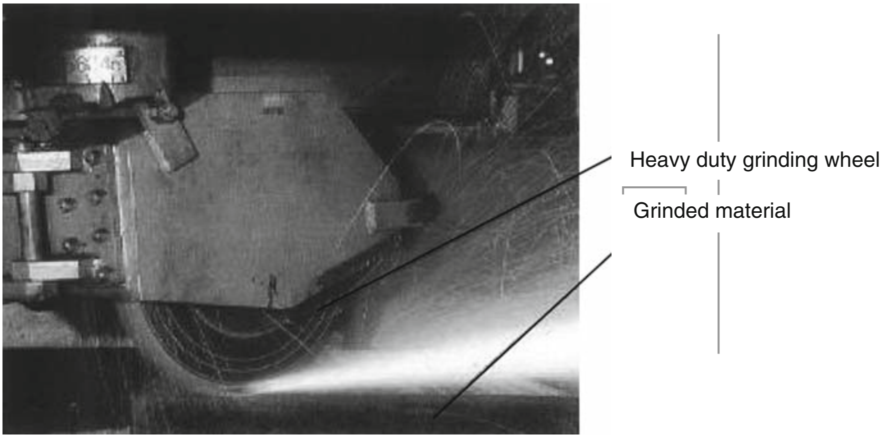


Fig. 13.23 Photo of a heavy duty grinding wheel in use (photo: Noritake company limited co., Ltd, Japan)

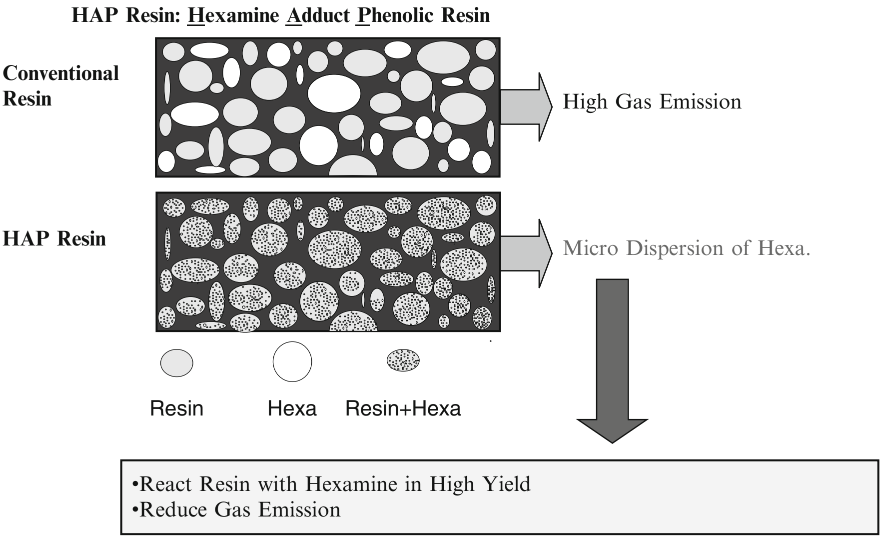


Fig. 13.24 Comparison of HAP resin with conventional powder resin
Source: Sumitomo Bakelite co., Ltd, Japan

The structure of the grinding wheel differs from other general resinoid grinding wheels. There are little or no voids and they have high hardness.

Tables 13.13 and 13.14 show powdered resins for this application. Liquid resins are not used. The resins used have high heat resistance. These resins have short flow and high hexamine content. PE gives good molding properties. Resins with long flow and high hexamine content, like PF can be used with high filler content. These resins utilize HAP technology shown in Fig. 13.24. In the hot molding process utilizing HAP technology, the reaction of resin with hexamine is more efficient and the amount of gas-emission during cure is lower [12].

13.5.7 Diamond Grinding Wheels and CBN Grinding Wheels

Diamond grinding wheels and CBN grinding wheels are classified as different from general grinding wheels due to their special grain. These are called super abrasives. They are used when grinding stone or ultra hard materials. Lately, these are being used for precision grinding in machinery and automobile manufacture. These grinding wheels can cut down maintenance and the frequency of dressing and replacement for the end user. Their structure is different from other grinding wheels. The abrasive component is made by hot press molding and is 1–10 mm thick. The resulting abrasive composition is attached to a metal hub (Fig. 13.25).

Tables 13.13 and 13.14 provide powdered resins for this application. Liquid resins are not used. The resin is usually short in flow. In this application, the resin content is high which makes hot molding difficult. Resins with short flow and low hexamine content, like PA give a soft grinding action. Resins with short flow and high hexamine content, like PE provide high heat resistance.

13.5.8 Others

There are other types of low volume phenolic grinding wheels that are not discussed. For example, there are precision thin cutting wheels, segment grinding wheels, axial deposition grinding wheels, lap grinding wheels, etc. Liquid and powdered phenolic resins are used for these types of grinding wheels.

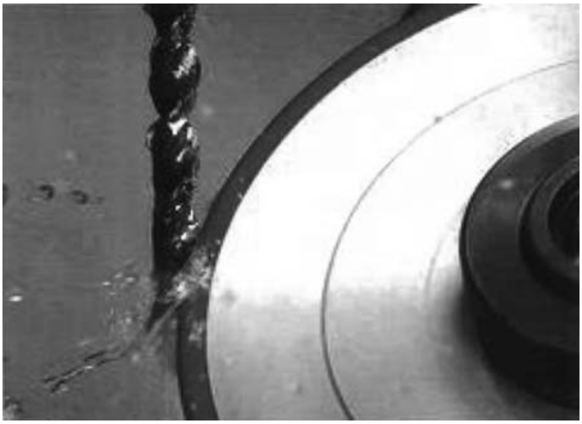


Fig. 13.25 Photo of a diamond grinding wheel in use (photo: Noritake company limited co., Ltd, Japan)

13.6 Coated Abrasives

Coated abrasives consist of backing, binder, and grain. Backings used are paper, vulcanized paper, cloth, and nonwoven fabric. The binder component that holds the grain is mainly phenolic resin. Urea resin, epoxy resin, urethane resin, and hide glue are also used as binders. Epoxy resin and urethane resin are used mainly when the coated abrasive product requires water resistance and flexibility. Urea resin is used in coated abrasive products that are used in wood sanding where heat resistance is not critical. Phenolic resin is used primarily in coated abrasives for metal grinding under both dry and wet conditions.

Coated abrasives were developed in the 1910s and their use has expanded due to their high grinding efficiency and safety. Today many types of coated abrasive products are available commercially (see Fig. 13.26).

13.6.1 Manufacturing Process

Figure 13.27 shows the manufacturing process for coated abrasives. The treated backing is applied with a solution of mixed phenolic resin with filler. Grain is then sprinkled over the wet backing. The layer, which is applied to this solution, is called the "make coat." The coated backing with the make coat and grain is dried in an

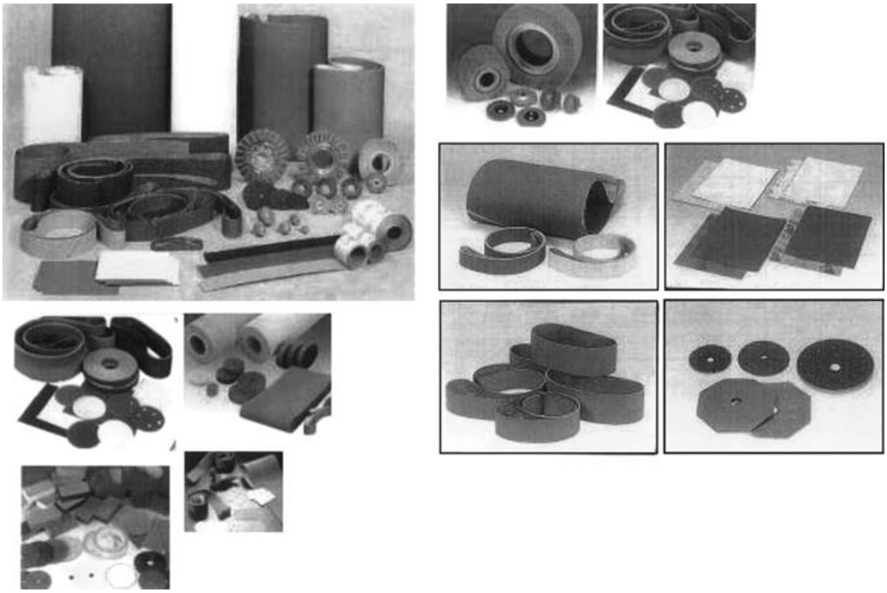


Fig. 13.26 Coated abrasives product line (photo: Noritake company limited co., Ltd, Japan)

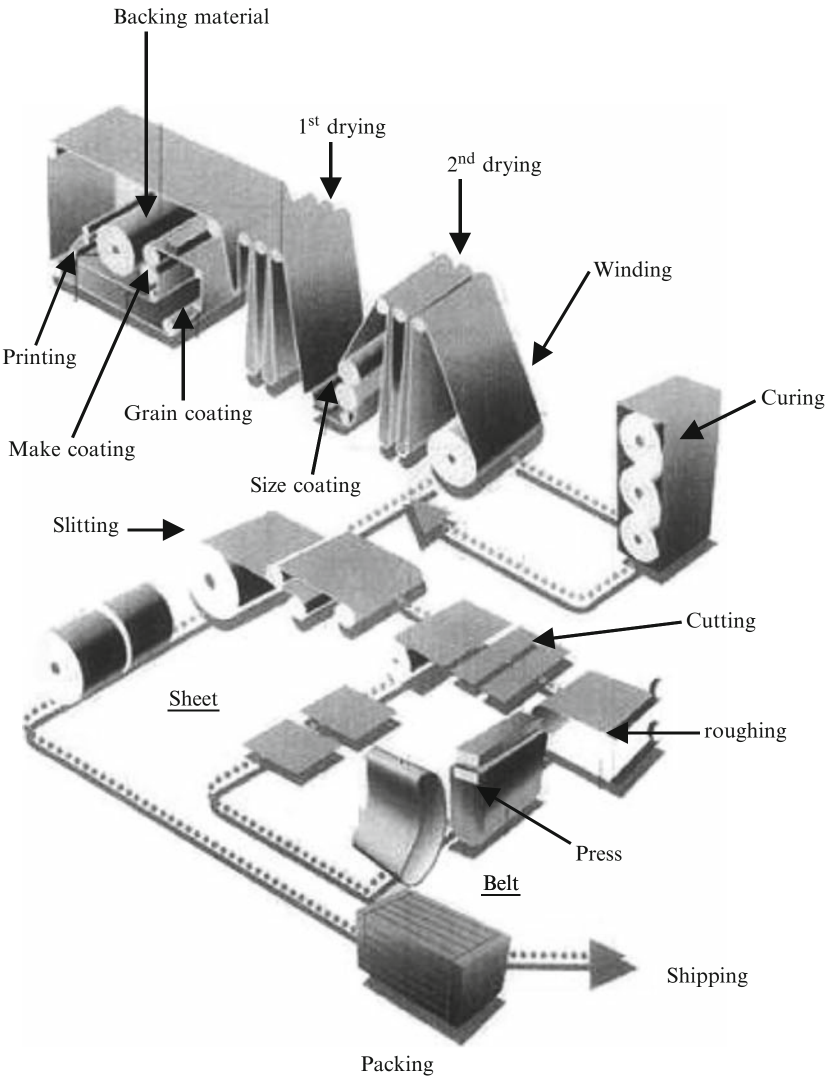


Fig. 13.27 Production flow process of coated abrasive (photo: Noritake company limited co., Ltd, Japan)

oven. Next the dried backing is coated with a solution of mixed phenolic resin and filler. This second coating layer is called the "size coat." The coated backing with the size coat is again dried in an oven. The dried flat backing is rolled up. The roll is placed in an oven to develop final cure. The cured roll is opened up and undergoes a cracking treatment to conform easily to a curved surface. After the cracking treatment, it is rolled up again. This is called a "jumbo roll." The jumbo roll is cut and slit into a wide variety of shapes and sizes. Solvent based resin is mainly used for sandpaper for wood sanding, and is fast drying and quick curing. The water based resin is used primarily for metal grinding. It has high heat resistance and is slightly water soluble.

13.6.1.1 Make Coat

The make coat bonds the grain to the backing. It is important for this layer to bond both materials and to spread over the backing evenly to wet the grain. The solution for the make coat is made from phenolic resin mixed uniformly with fillers like calcium carbonate. The solution is kept at a constant temperature, which is between 20°C and 40°C, and its viscosity is controlled to a set value by adding water or solvent. The solution is applied to the backing by means of a spreading roll (see Fig. 13.28). Then the grain is immediately sprinkled over it. This is done under a static electrical charge. Static electrical application allows the sprinkled grain to align vertically. Coated abrasive is then dried in an oven which is controlled between 80°C and 120°C, for about 30 min–1 h until tack free. Blistering must be avoided by gradually increasing the drying temperature. This is usually accomplished in a multi zone oven. Table 13.15 shows liquid resins for the make coat. The resin is a water soluble resole resin, and its viscosity is 100–1,000 mPa at 25°C.

13.6.1.2 Size Coat

A size coat is then coated over the make coat and grain. It is important for this to bind strongly to the grain. The solution for the size coat is made in the same way that the make coat is made. Phenolic resin is mixed uniformly with filler, which is typically calcium carbonate or cryolite. The solution is kept at constant temperature, between 20°C and 40°C, and the viscosity is controlled to a set value by adding water or solvent. The solution is applied using the same method as the make coat.

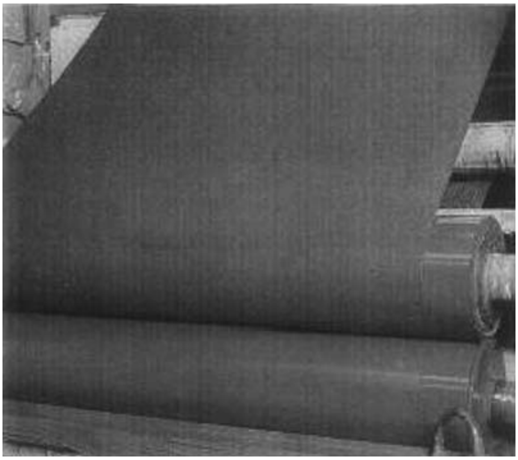


Fig. 13.28 Size coating process (photo: Noritake company limited co., Ltd, Japan)

Table 13.15 Liquid resin product line for coated abrasive

No.	Resin type	Solvent	Viscosity (mPa s/25°C)	Resin content (%/135°C)	Gel time (s/150°C)	Water solubility (times)	Use
X	Water soluble resin	Water	~700	~74	~135	~3	For make coat and size coat
Y	Low viscosity resin	Water	~300	~67	~90	~0.5	For mainly make coat
Z	High viscosity resin	Water	~2,500	~78	~90	~0.5	For mainly size coat
ZA	Modified resin	Water	~350	~73	~100	~0.5	For make coat and size coat for heavy duty type
ZB	Fast cue	Water	~1,500	~75	~80	~2	For make coat and size coat
ZC	Pale color	Water	~1,000	~75	~170	~2	For size coat and super-size coat

Source: Sumitomo Bakelite co., Ltd, Japan

The thickness of the layer of the size coat is usually two to three times as thick as that of the make coat. The material is then heated in an oven to a temperature which is controlled between 80°C and 120°C for about 30 min–2 h, until tack free. Again gradual heat up is necessary to control blistering. Table 13.15 shows liquid resins for the size coat. The resin is a water soluble resole resin, and its viscosity is 100–1,000 mPa at 25°C.

13.6.1.3 Heating

The jumbo roll is cured by final heating in an oven set at between 100°C and 140°C for 10–30 h. The jumbo roll has a tendency to be slow in heat penetration so there is a long cure time. This is a low curing temperature for a phenolic resin but is necessary for finished product flexibility. It is also necessary as the backing is made of cotton or polyester which has low heat resistance.

13.6.1.4 Processing

The jumbo roll is an interim product and it must be processed to make the necessary and specific product types. Examples are: belt, roll, sheet, flap wheel etc. (see

Fig. 13.26). These abrasive products are made from the jumbo roll through the various procedures of slitting, cutting, shaping, and bonding.

13.6.1.5 Phenolic Resin for Coated Abrasive

Phenolic resin for coated abrasive is generally a liquid resole. Table 13.15 shows typical resins. Typical liquid phenolic resins for this application are prepared using a base catalyst, and their viscosity is from 100 mPa s to 10,000 mPa s at 25°C, Resin content is around 50–85% and phenol content is about 1–10%. The solvent is water and an organic solvent (methanol). To help prevent blistering, the resin content of the resin is generally high and sometimes an anti-blister agent, like a high-boiling-point solvent is added.

13.6.2 Abrasive Cloth (Abrasive Belt, Roll, Sheet, Flap Wheel)

Abrasive cloth is used for metal grinding in construction, wood, automobile, and machinery manufacture. The grain size used is from #30 to #400. Abrasive cloth is used as backing for heavy duty grinding. Generally it is used in heavy duty grinding of metal. Phenolic resin is used for its ability to survive heavy duty grinding. Phenolic resin is the preferred resin and provides the best performance for cloth backed applications (see Fig. 13.29).

The types of phenolic resin for this application are water based phenolic resole resins. Table 13.15 shows resole resins for abrasive cloth. X, in Table 13.15, is a standard resin and its water-tolerance is over 200%, so it can be diluted with water for

Fig. 13.29 Photo of a coated abrasive for heavy duty grinding in use (photo: Noritake company limited co., Ltd, Japan)

use. ZA, in Table 13.15, is suitable for heavy duty grinding. ZB, in Table 13.15, is fast curing with low monomer content. ZC, in Table 13.15, develops color after cure.

13.6.3 Abrasive Paper (Sandpaper)

Abrasive paper (Sandpaper) uses kraft paper for the backing. There are several types: belt, roll, sheet, etc. Generally it is used for waterproof finishing. The binders are not usually phenolic. Urea, epoxy, and urethane are used. The grain size used is from #60 to #2,000. The applications are primarily for wood sanding.

The phenolic resin for this application is a resole phenolic resin, either organic solvent based or water based. The application layer is thin and its fast drying speed is important for productivity.

13.6.4 Non-woven Fabric

Non-woven fabric is usually nylon or polyester (see Fig. 13.30). Many types of products are made with this backing: sheet, abrasive wheels, etc. The application technique used is both dipping and spraying. The binder used is typically phenolic resin and epoxy resin. Epoxy resin is used mainly in products for household use. It is important for light color and water resistance. Phenolic resin is used in heavy duty industrial applications. The phenolic resin for this application is a resole phenolic resin, either organic solvent based or water based.

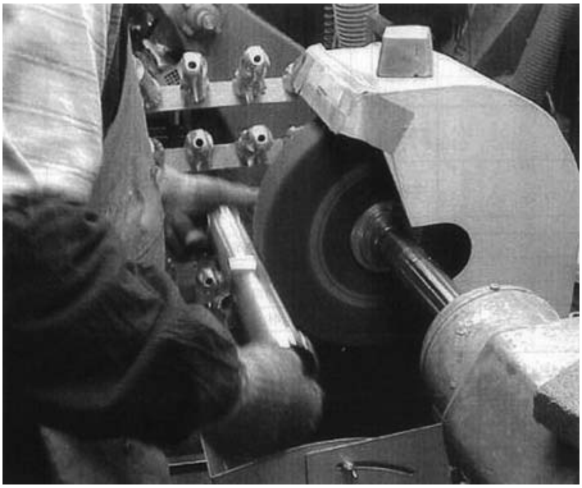


Fig. 13.30 Photo of a non-woven fabric abrasive product in use (photo: Noritake company limited co., Ltd, Japan)

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Chapter 14
Friction

Yoshihiro Matsuo, Daryl D. Clarke, and Shinichi Ozeki

Abstract Friction materials such as disk pads, brake linings, and clutch facings are widely used for automotive applications. Friction materials function during braking due to frictional resistance that transforms kinetic energy into thermal energy. There has been a rudimentary evolution, from materials like leather or wood to asbestos fabric or asbestos fabric saturated with various resins such as asphalt or resin combined with pitch. These efforts were further developed by the use of woven asbestos material saturated by either rubber solution or liquid resin binder and functioned as an internal expanding brake, similar to brake lining system. The role of asbestos continued through the use of chopped asbestos saturated by rubber, but none was entirely successful due to the poor rubber heat resistance required for increased speeds and heavy gearing demands of the automobile industry. The use of phenolic resins as binder for asbestos friction materials provided the necessary thermal resistance and performance characteristics. Thus, the utility of asbestos as the main friction component, for over 100 years, has been significantly reduced in friction materials due to asbestos identity as a carcinogen. Steel and other fibrous components have displaced asbestos in disk pads. Currently, non-asbestos organics are the predominate friction material. Phenolic resins continue to be the preferred binder, and increased amounts are necessary to meet the requirements of highly functional asbestos-free disk pads for the automotive industry. With annual

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automobile production exceeding 70 million vehicles and additional automobile production occurring in developing countries worldwide and increasing yearly, the amount of phenolic resin for friction material is also increasing (Fig. 14.1). In recent years, increased fuel efficiency of passenger car is required due to the CO_2 emission issue. One of the solutions to improve fuel efficiency is to lower the car body weight. It means that the weight of car components must be decreased. In the case of reduced weight for friction parts, the load applied to the friction parts would be higher (more heat also) and trend would lead to phenolic resins with improved heat resistance.

14.1 Introduction

Disk pads, brake linings, and clutch facings are called "Friction Materials," which are widely used for automotive applications. The function of friction materials during transferring and braking is to take advantage of friction resistance, while playing an important role in transforming kinetic energy to thermal energy.

Before the introduction of friction materials as we know them today, leather or wood was often used for stopping vehicles or machinery. Then asbestos fabric or asbestos fabric saturated by asphalt, later followed by resin and pitch, were used as braking materials.

Later, woven material saturated by rubber solution or a liquid resin binder was used for an internal expanding brake, which operated similar to a brake lining system.

Afterward, chopped asbestos bound by rubber solution was used. However, the rubber lacked the heat resistance required for the increasing speeds and heavy gearing of the automotive industry.

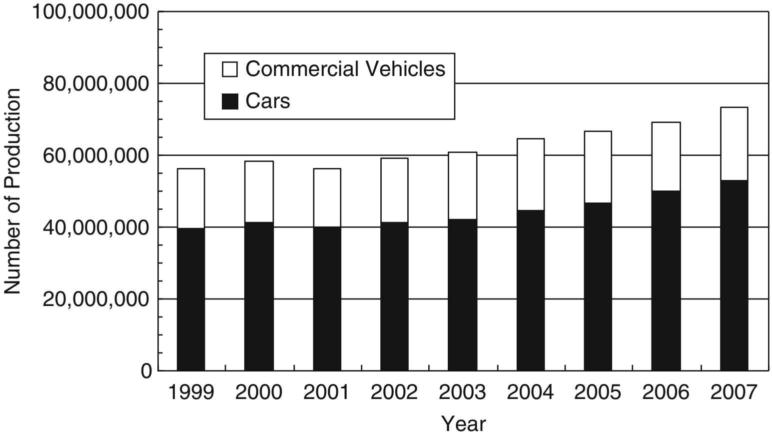


Fig. 14.1 Worldwide commercial vehicle production

Although asbestos had been used for over 100 years as the main material of brake linings, restrictions were imposed for most applications when it was identified as a carcinogenic material. Subsequently, steel type and other fibrous containing disk pads were used in place of asbestos.

In order to maintain quality, car manufacturers introduce an approval system. The car parts are classified into Original Equipment (OE) parts and after-market parts. OE parts are assembled for the new car and require car manufacturer's approval. On the other hand, after-market parts can be sold with 'parts' manufacturer's approval. In general, the quality of OE parts is higher than that of the after-market parts, but the quality of after-market parts has improved in recent years.

14.2 Application of Friction

In this section, various types of friction materials will be discussed. Disk brake system is shown in Fig. 14.2 while only disk pads are shown in Fig. 14.3.

Fig. 14.2 Appearance of disk brake system (Photo: Akebono Brake Industry Co., Ltd.)

Fig. 14.3 Appearance of disk pads (Photo: Akebono Brake Industry Co., Ltd.)

14.2.1 Disk Pads are Classified into Five Types

14.2.1.1 Asbestos Type of Disk Pads

Asbestos type disk pads are molded using asbestos, friction adjuster, lubricant and phenolic resin. Today, using asbestos type disk pads is forbidden or restricted in nearly every country due to potential health and environmental issues.

14.2.1.2 Semi-Metallic Type of Disk Pads

Semi-metallic disk pads are categorized by their steel content, which is above 50%. This type of disk pad is excellent for wear resistance [1]. On the other hand, this pad contains iron and graphite, which means good heat conductivity. Therefore heat is transferred to the brake fluid and may cause vapor lock phenomena resulting in damage to the rubber parts of the disk pad system [2]. Other weaknesses of semi-metallic pads are more noise, corrosion, and dark color wheel dust. Higher metallic content pads are mainly used for heavy-duty industrial vehicles in the North American market.

14.2.1.3 Low Steel Type of Disk Pads

The amount of steel fiber reinforcement used in "low steel" type disk pads is generally 10–40%. Metal powder and friction adjuster are utilized as well as metallic fillers. As a result of lowering the steel content, heat conductivity is reduced and friction properties are improved [3]. On the other hand, the degree of rotor attack is much higher due to the addition of abrasive material in the formulation for increasing the friction coefficient. Weaknesses of low steel type disc brake pads are excessive noise and higher wear of rotors [4–8]. At present, this type of disk pad is mainly used in the EU market.

14.2.1.4 Non-Asbestos Organic Type of Disk Pads

Aramid fabric is used as the reinforcement for non-asbestos organics (NAO) disk pads. The advantage of NAO disk pads are comfort properties, such as noise, and less wheel dust. Requirements such as brake noise, pad wear, and other performance properties are well balanced. NAO type frictions have been widely developed in Japan, where the number of passenger cars equipped with this type of brake pad is increasing. The main reason NAO pads are preferred is that wear properties have improved [9]. Recently this type of disk pad has gained acceptance in the US market for passenger cars.

14.2.1.5 Carbon Silicon Brakes (SGL Carbon, Germany)

Carbon Silicon brake is mainly used for aircraft or racing car applications. The features of this brake are high friction coefficient and its stability/heat resistance, and are also much higher than the brakes for passenger car. Carbon silicon brakes have not been adopted fully because they are quite costly due to the expensive raw materials, production cost, high rotor attack causing frequent rotor replacement as well as wheel dust, brake noise. However, they are installed in sports cars and luxury, exotic cars. Phenolic resin is used as the binder and is transformed into a carbon carbon composite followed by liquid silicon infiltration at high temperatures. Carbonization to the carbon carbon composite occurs under the inert conditions at elevated temperatures.

14.2.2 Brake Linings

Brake lining system and brake lining are shown in Figs. 14.4 and 14.5, respectively.

The majority of drum type brake linings are classified into two types: “asbestos” and “non-asbestos.” Only a few applications use semi-metallic type or low steel type linings.

14.2.3 Clutch Facings

Clutch facings transfer power from engine to the tire when moving vehicles shift gears. A typical clutch facing is shown in Fig. 14.6. Historically, manual transmission systems were adopted for automotive applications. “Dry type” clutch facings are used for manual transmission systems. In recent years, manual transmission systems have been replaced with automatic transmission, double clutch and CVT (Continuously Variable Transmission), resulting in an annual decrease of using dry clutch facings in automobiles. Dry clutch is mainly used for truck, bus and industrial machines.

Fig. 14.4 Appearance of brake lining system (Photo: Akebono Brake Industry Co., Ltd.)

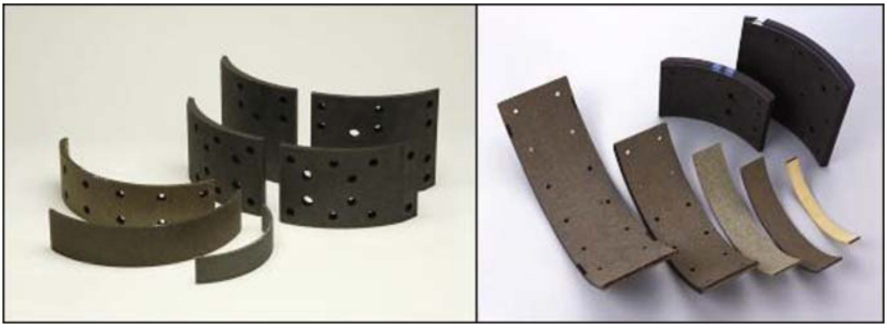


Fig. 14.5 Appearance of brake lining (Photo: Akebono Brake Industry Co., Ltd.)

Fig. 14.6 Appearance of clutch facing (Photo: Akebono Brake Industry Co., Ltd.)

A “wet type” clutch facing is used for automatic transmission systems. This type of clutch was adopted in the United States in the 1940s, and today, its usage has increased to over 90% in the US and Japan. On the other hand, the number of on board using automatic transmission systems is still very low in the EU market.

14.3 Raw Materials

14.3.1 Disk Pads

A typical disk brake pad consists of binder, fabric, filler, friction adjuster and lubricant as shown in Table 14.1. The raw materials chosen for a friction formulation depend on the type of disk pad being made. Phenolic resins are often used as

Table 14.1 Typical formulation of disk pad [10]

Function	Material	Non-steel	Low-steel	Semimetallic	Asbestos
Reinforcement	Steel wool	–	5–30	40–65	–
	Aramid fiber, acrylic fiber	3–15	0–5	–	–
	Ceramic wool	1–15	1–10	–	–
	Copper, brass fiber	1–10	1–10	–	–
	Asbestos	–	–	–	20–40
Friction adjuster	Rubber (NBR, SBR)	1–10	0–10	0–5	5–15
	Cashew dust	5–15	2–10	–	5–15
	Metal powder (copper, brass)	0–5	–	0–5	5–10
	Abrasive	1–5	1–5	1–5	0–5
	Filler (barium sulfate, mica etc.)	5–35	5–35	5–25	5–15
Lubricant	Graphite, antimony sulfide, tin sulfide, molybdenum disulfide	5–15	5–20	5–25	5–15
Binder	Phenolic resin	8–15	8–15	8–15	10–20

the binder component in the formulation for disk pads. Various types of phenolic resins have been developed; non-modified phenolic resin, oil modified, cashew modified, cresol modified, and rubber-modified resins have been utilized.

For over 100 years asbestos was used as the reinforcement material in brake formulations. Today, its use is restricted or forbidden in most countries due to carcinogenic behavior linked to the development of lung cancer. Therefore, based on the situation, new fibers were tested and developed as asbestos substitutes. The typical fibers are steel wool, ceramic wool, and organic fibers such as aramid or acrylic.

Commonly used organic friction modifiers are cashew dust and rubber materials such as NBR, SBR and acrylic. Inorganic metallic powders such as copper and brass are used as well. In addition, to increase abrasiveness, metallic oxides such as silica or aluminum oxide are used. Barium sulfate and calcium carbonate are used as fillers for the disk pad.

The coefficient of friction increases with increasing temperature of the substrate [11]. To maintain the friction coefficient close to the preset desired value, formulations include lubricants such as graphite or sulfate.

14.3.2 Brake Lining

Drum brakes are classified as either asbestos type or non-asbestos type as shown in Table 14.2. Asbestos based brake lining formulations also contain a phenolic resin binder and mixture of organic and inorganic materials that act as friction agents [12].

The reinforcement materials for non-asbestos type drum brakes include heat resistance organic fibers such as aramid and acrylic fiber as well as inorganic fibers such as glass, mineral, and others.

Table 14.2 Typical formulation of brake lining

Function	Material	Non-asbestos	Asbestos
Reinforcement	Organic fiber	2–10	–
	Non-steel, inorganic fiber	3–30	–
	Asbestos	–	40–50
Friction	Organics (rubber, friction dust)	5–20	10–30
	Metallic (brass, copper)	0–10	2–10
	Filler (lime stone, mica)	10–25	10–25
	Metal oxide	1–5	0–5
Lubricant	Graphite, petroleum cokes	0–15	0–5
Binder	Phenolic resin, modified-phenolic resin	10–20	15–20

14.3.3 Clutch Facing

Historically asbestos was used as the reinforcement, but woven glass is being used today. Clutch facing consists of glass yarn as the reinforcement, rubber, resin and additives. Non-modified and melamine modified phenolic resins are commonly used as the binder. Alternatively, a "wet type" clutch facing consists of paper impregnated with resin as the reinforcement.

14.4 Manufacturing Process

14.4.1 Disk Pad

Figure 14.7 is a flow diagram for "dry mix" and "wet mix" manufacturing process of disk brake pads. Today, because of health and environmental concerns, the dry mix process is most often applied in manufacturing plants. Raw materials are weighed and mixed. The mixture is then pre-molded at room temperature into a friction material preform. Next, an adhesive coated steel backing plate is put into a mold cavity followed by the preform. The mold cavity containing preform and backing plate is then pressed under heat and pressure. Molding time is generally 3–10 min depending on the thickness of the preform. Molding temperature is generally 130°C–180°C.

While molding, several "bump" steps are included in the mold cycle in which the press opens for a few seconds to release gas. Generally, the gas released is water vapor, which the raw materials have absorbed, and ammonia gas, which is formed by the reaction of phenolic resin and hexamine. In most applications, friction materials are not completely cured after the molding process is finished. Therefore, post-curing in an open bake oven is required. Generally, the post-curing temperature is 180°C–220°C and the time required is 1–6 h. Some disk brake pad manufacturing processes have specific formulations that do not require post-curing. After the post-curing process, polishing and scorching is done and finished products are obtained [13].

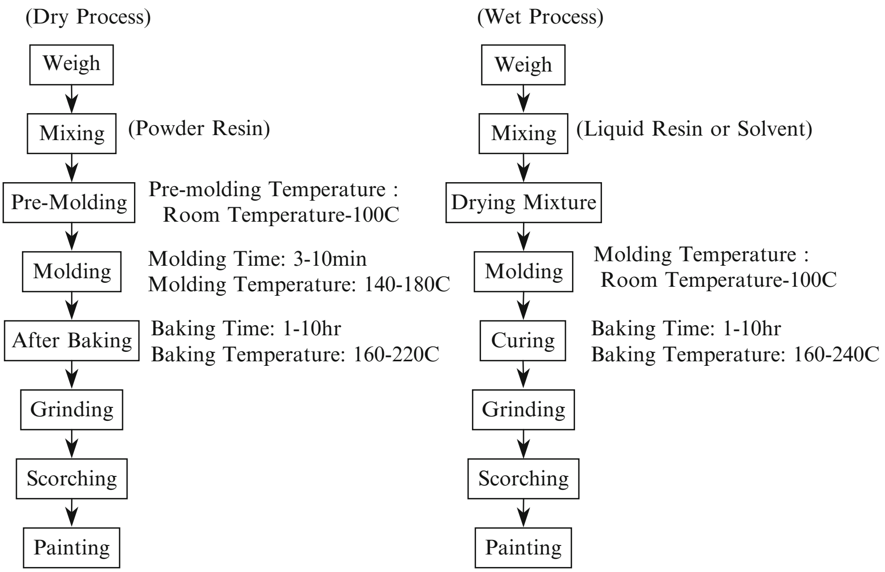


Fig. 14.7 Manufacturing process of disk pad

14.4.2 Brake Lining

The two manufacturing methods for brake linings are “dry” mix and “wet” mix as shown in Fig. 14.8.

For the “dry” manufacturing method, fiber, powdered phenolic resin, and other additives are mixed together under dry conditions. After mixing, a preform part is made by preliminary compression (pre-molding) and shaping. This can be done at room temperature or in a mold warmed to 50°C–80°C. The preform is then placed in a mold cavity and press cured under heat (140°C–180°C) and pressure. An open oven post bake at 160°C–220°C normally follows molding, to completely cure the brake lining.

For the “wet” manufacturing method, fiber, binder and other additives are mixed under wet conditions and then the mixture is kneaded and extruded. The extruded material is cut into the desired shape followed by a drying process. Finally, parts are compression molded under heat until a finished brake lining is obtained.

14.4.3 Clutch Facing

There are two manufacturing methods: “dry” process and “wet” process.

For the “dry” manufacturing method, glass fiber, powdered phenolic resin binder and filler are mixed under high shear. Next, the clutch lining friction mix is pre-molded and shaped at ambient temperature. The pre-molded parts are hot

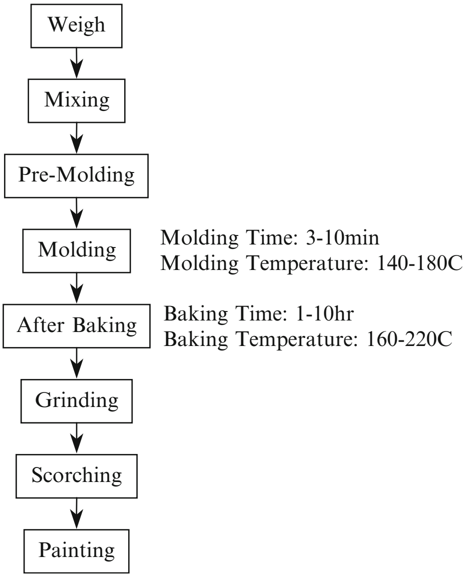


Fig. 14.8 Manufacturing process of brake lining

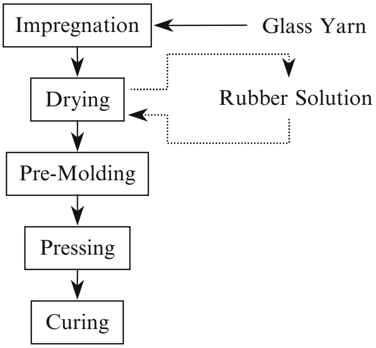


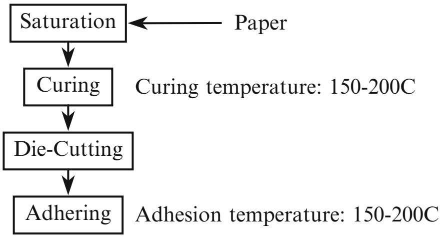
Fig. 14.9 Manufacturing process of wet type yarn clutch facing

compression molded, and post baked, to form the finished clutch lining. This process is similar to the manufacturing process for disk brake pads.

The flow diagram for the "wet" manufacturing process is shown in Fig. 14.9. A clutch facing is obtained by saturation of glass fiber in liquid phenolic resin, followed by drying, winding, molding and curing. In this method, it is possible to use a liquid phenolic resin and rubber solution together.

The manufacturing process of paper clutch facing is shown in Fig. 14.10. Paper that contains aramid fiber and friction modifiers is saturated with liquid type of phenolic resin. Curing temperature depends on the phenolic resin, but is normally 150°C–200°C. After curing, the saturated paper is cut to the ring shape and bonded to the steel plate.

Fig. 14.10 Manufacturing process of wet type paper clutch facing



14.5 Friction Requirements

Friction materials requirements are as follows:

14.5.1 Stability of Friction Coefficient in Each Temperature Region

Friction materials must be designed to maintain mechanical strength at high temperatures. It is possible for the surface temperature of brake pads to exceed 400°C during a period of continuous braking. On the other hand, the working temperature of friction materials can be below −20°C in colder climates. Therefore, it is necessary that friction properties are stable over a wide range of temperature. Specifically, stability of friction coefficient at the low and high operating temperatures is required. North America, EU and Japan have their own standards for braking properties. Friction materials are manufactured, tested, and approved based on these standards [14, 15].

14.5.2 Low Wear

The surface of a disc brake pad is gradually worn away with repeated braking. Low wear (longest possible service life) of disc brake pads is desired. Excessive wear of brake pads will result in a short service life and require numerous brake pad replacements. Additionally, a higher amount of wear dust emissions will be released into the environment.

14.5.3 Reduced Noise and Judder

Recently, as passenger vehicles have become tranquil and quiet during operation, brake noise and judder is easily recognized and scrutinized by drivers. The emphasis to reduce brake noise and judder has increased yearly. In addition to brake noise that occurs during normal operation, there is a morning effect of squeaking that formulators are working to reduce. This squeaking occurs due to condensed water that settles overnight along with brake dust on the surface of the disk pads.

For the clutch facings, the benefit of a melamine-modified phenolic resin is to increase fade resistance. During operation, the clutch temperature increases and organic material decomposes. For non-modified phenolic resins, thermal decomposition by-products are both gaseous and liquid. Liquid products cause the decrease of friction coefficient, which is referred to as fade. Alternatively, thermal decomposition of melamine modified phenolic resins generate gaseous by-products solely and fade resistance is increased.

14.5.4 Reduced Damage to the Rotor

Excessive rotor wear will result in damage and eventually a short service life. Replacement of the rotors is expensive and difficult for car owners. One of the main reasons for rotor scarring is due to dirt and sand. Another reason is the hardness or reduced flexibility of the friction material. In the brake pad formulation, abrasives are added in order to increase the friction coefficient and decrease the wear of the friction material. Unfortunately, increased rotor wear is the trade-off. In order to reduce the damage to the rotor, softer, more flexible, NAO type brake pads are recommended.

14.5.5 Reduce the Burden on the Environment

Disk brake pads generate abnormal odors when operated at high temperatures because they contain organic components which decompose or sublime. In order to resolve the above issue, low monomer content phenolic resins are recommended. Very low monomer content phenolic resins are used predominantly in the EU. The use of asbestos is forbidden or limited in friction materials due to reasons stated earlier.

For clutch facing applications, solvent based phenolic resins are being replaced by water based resins to improve working conditions and minimize the potential for environmental pollution.

14.6 Design and Control of Phenolic Resin Properties

Figure 14.11 shows the relationship between the requirements of disk brake pads and the requirements of phenolic resins. In order to meet performance requirements of friction materials, various kinds of phenolic resins have been developed.

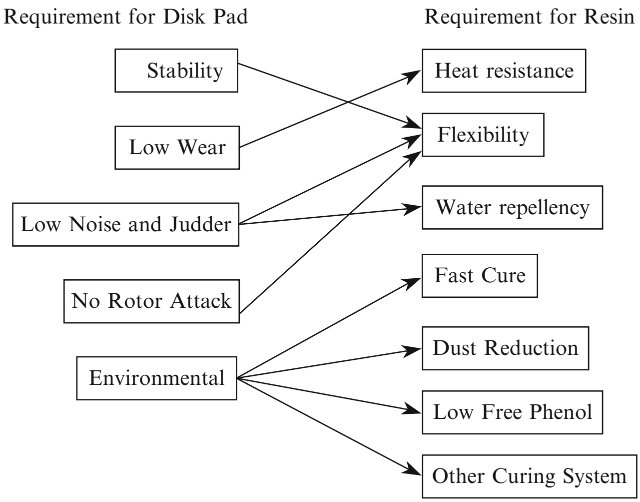


Fig. 14.11 Relationship between disk pad properties and resin properties

Non-modified phenolic resins have been widely used because of their low cost and high performance. Brake manufacturers select the resin with specific inclined plate flow and hexa content best suited to optimize the performance of brake formulations. Flow and hexa content directly impact physical properties such as porosity, mechanical strength, hardness, and elastic modulus. Table 14.3 shows a listing of typical straight resins. Aralkyl modified phenolic resin has been developed to improve heat resistance such as disk pad wear due to thermal decomposition of resin binder during high temperature braking (Table 14.4) [16].

Recently, as the engine noise in passenger vehicles has been reduced, brake noise has become more noticeable to drivers. In order to reduce brake noise, various kinds of elastomer-modified phenolic resins have been developed. By adding an elastomeric material, it is possible to obtain the phenolic resin with increased flexibility. The concept of contact area on the friction surface is shown in Fig. 14.12. It is assumed that true contact area increases with increased flexibility. Additionally, flexible resins are effective for decreasing brake noise because the contact between the disk pad and rotor is more uniform [11, 17].

Another reason for brake noise and judder is the existence of water on the friction surface. In order to prevent the influence of water on brake performance, phenolic resins modified with silicone gel have high water repellency.

Improvements in the environmental responsibility of phenolic resins is on-going, especially the requirement for phenolic resins to be low and free of phenol content. On the other hand, improving the productivity of disk pad manufacturing plants is a high priority as well. Fast curing phenolic resins are required more often today than ever before. New fast cure press molding equipment requires a fast cure resin for this purpose. Some fast cure resins contain an organic acid such as benzoic acid and

Table 14.3 Resin list for brake application (non-modified resin)

Product code	PR-50099	PR-217	PR-51794	PR-311	PR-50590	PR-54364
Molecular weight	High	High	High	Middle	Middle	Low
Gel time (150°C/s)	110	110	82	74	120	100
Flow (125°C/mm)	19	20	13	55	29	42
Hexa content (%)	9	7	12	9	9	9
Free phenol (%)	2.5	2.5	2.5	6	2.5	1>

Table 14.4 Resin list for brake application (modified resin)

Product code	PR-55453	PR-55291	PR-54529	PR-55170	PR-54458A
Modifier	Acid-modified	Acrylic rubber	Silicone gel	Aralkyl	Aralkyl
Effect	Moldability	Flexibility	Water repellency	Heat resistance	Heat resistance
Gel time (150°C/s)	59	125	125	42	200
Flow (125°C/mm)	21	40	38	29	39
Hexa content (%)	11	11	10	13	11
Free monomer (%)	1>	1>	1>	1>	3

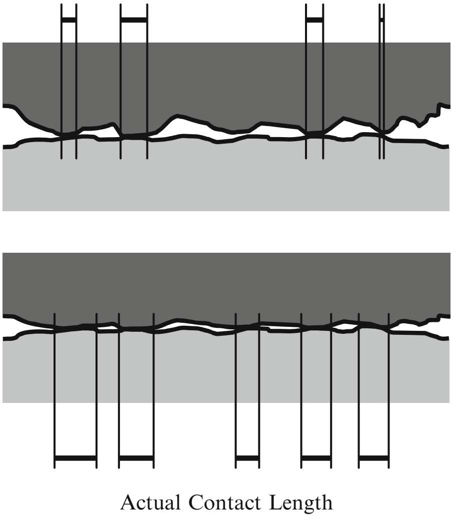


Fig. 14.12 Concept of true contact area

salicylic acid and/or resorcinol as a curing accelerator to shorten the molding time. High ortho phenolic resins are also applicable to shorten molding cycles [18].

Most ingredients for disk brake pads are dry ingredients mixed together in a dry process which can be very dusty. Some brake manufacturers have requested resins that reduce dust during the mixing process. In response to the industry request, some phenolic resin manufacturers have developed dust-free phenolic resins [19].

Non-hexamine curing systems, such as benzoxazine resins, have been studied for years. Commercialization has not been practical yet due to the requirements for high temperature curing to achieve acceptable crosslink density. Many phenolic resin manufacturers and universities have been studying new curing systems for phenolic resins but as yet are not commercial [20].

For many years, solvent-based phenolic resins have been used in clutch facing formulations. Recently, clutch facing manufacturers have been trying to substitute with water-based phenolic resins due to the environmental issues solvents create.

Phenolic resins must be stored under controlled conditions to maintain performance characteristics. Improper storage, under conditions that are not suitable for the phenolic resin, will jeopardize the performance of the friction materials in which the resin is used.

Porosity is one of the most important physical properties of any friction material. The porosity of friction materials influences the friction coefficient, noise, and wear. The resin property which most influences porosity of friction materials is the resin inclined plate flow. Before hot pressing, the mold has a large amount of porosity. Once premold is hot-pressed, the thickness of the premold is lower because the resin flows and fills in the porosity. If the plate flow is long, the resin can easily flow and fill in the porosity. As a result, porosity would be lower.

It is important to understand the relationship between resin physical properties and performance of friction materials as summarized in Fig. 14.13. Moisture content affects the flow of powdered phenolic resins. Therefore, storage conditions are important to control moisture pickup and maintain low moisture content. Keeping the resin away from storage at high temperatures and humidity is also recommended to minimize the amount of rejected parts.

Finally, Tables 14.3–14.5 show the phenolic resins used by friction manufacturers for disk brake pads, brake lining and clutch facings, available from Sumitomo Bakelite.

The friction manufacturers have their own friction formulations and manufacturing conditions. As a result, the phenolic resins they use are chosen based on properties such as flow, hexa content, and gel time to optimize their processes. In addition, non-modified phenolic resins have some limitations which affect friction properties mentioned in Sect. 14.6. To meet these requirements, phenolic resin manufacturers have developed various kinds of modified resins as shown in Tables 14.4 and 14.5.

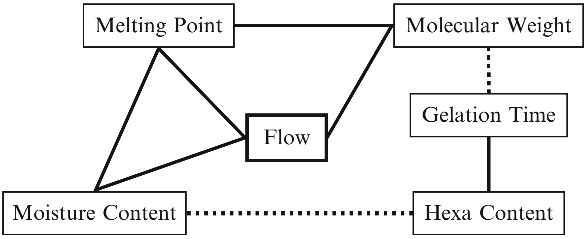


Fig. 14.13 Relationship between resin properties

Table 14.5 Resin list for clutch application

Product code	PR-54562	PR-53123	PR-55386	PR-54139
Modifier	Non-modified	Alkyl benzene	Melamine	Melamine
Solvent	Methanol	Methanol	Water	Methanol
Non-volatile (135°C/%)	48	45	40	13
Viscosity (mPas)	14	12	9	4
Gel time(165°C/s)	50	75	35	55
Specific gravity (25°C/-)	1.03	0.98	1.16	0.88
Free monomer (%)	15	4	1>	1

Table 14.6 Comparison of each standard

Item	JIS/JASO	SAE	ISO
Specific gravity	JIS D4417-86	J380	–
Porosity	JIS D4418-96	–	–
Shear strength	JIS D4422-90	J840–98	6312-01
PH	JASO C458-86	–	–
Compressive strain	JIS D4413-98	J2468	6310-01
Heat expansion	JIS D4416-98	J160	6313-80
Dyno test	JASO C406-00	J212	11157
Wear test	JASO C427-88	EDB5O17	–

At present, NAO have been the mainstream for friction materials. The importance and use of phenolic resins continues to increase, to meet the requirements of highly functional asbestos-free disk pads for automotive applications. Annual automotive production is over 60 million vehicles. Recently, automotive production in the developing countries around the world has been rapidly increasing which is expected to increase the demand for quantity and performance of phenolic resins.

14.7 Evaluation Method of Brake

Brake standards in the automotive field are mainly JIS/JASO, which is the Japanese standard, SAE, which is the United State standard, and ISO, which is international standard. Table 14.6 shows the comparison of each standard. These standards are expected to be unified worldwide in the near future. So far, standards are adopted in their own respective countries.

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Chapter 15
Photoresists

Fumitaka Saimura and Michael Santorelli

Abstract Lithographic technology by photoresist is an important technique for today's electronic industries. In the manufacture of a semiconductor and a liquid crystal display (LCD), a photoresist is used as the key photo sensitive material. Phenolic resin is the base polymer that controls photoresist characteristics and plays an active role in these vital electronic industries.

In this chapter, we discuss phenolic resins for photoresists, meta–para cresol novolaks, important properties for photoresist such as meta–para ratio, molecular weight, and alkali dissolution rate. Moreover, various types of phenolic resins for photoresists and production technology are also discussed.

15.1 History of Photoresists

In 1822, Joseph Nicephore Niepce, France, made a photo-image by coating asphalt on a metal sheet. It is claimed that this was the first time that photo sensitive materials were recognized worldwide. This technique led to the development of photosensitive silver halide compounds and evolved into our present knowledge of silver halide photograph technology.

During the intervening years, various materials and photo systems were studied and developed. In the1950s, Kodak developed a cinnamic acid vinyl polymer as a photo sensitive compound, and the word "photoresist" emerged as a trademark for

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this compound. At present, “photoresist” has become a common word and is used as a synonym for any photo sensitive compound.

In 1949, Oskar Suss discovered the phenomenon that a novolak with diazo quinone derivatives was difficult to dissolve in an alkali aqueous solution, but by photo irradiation, this novolak compound lost its inhibition effect to alkali dissolution. This led to the design and proposal of the first positive photoresist system using novolak with diazo naphtho quinone (DNQ) [1, 2].

During that time, a contact exposure system was mainly used in a lithography system for the manufacturing of semiconductors. Negative photoresist compounds such as cinnamic acid vinyl polymer and cyclic rubber – bis azido compounds were common at this time.

Although positive photoresist compounds using novolaks showed good properties for resolution and resistance for etching, they exhibited very poor adhesion properties to wafers with corresponding fragile film strength. So for a contact exposure system, a novolak photoresist was of minimal use.

The use of positive photoresist compounds consisting of novolaks with DNQ was reestablished for two reasons: (1) the progress of semiconductor high integration and fine pitch patterns required high resolution properties, and (2) a projection exposure system was developed in the 1970s.

An interesting historical presentation of the use of novolak resins in photolithography and the micro-electronics market was recently published by Rahman and coworkers [3].

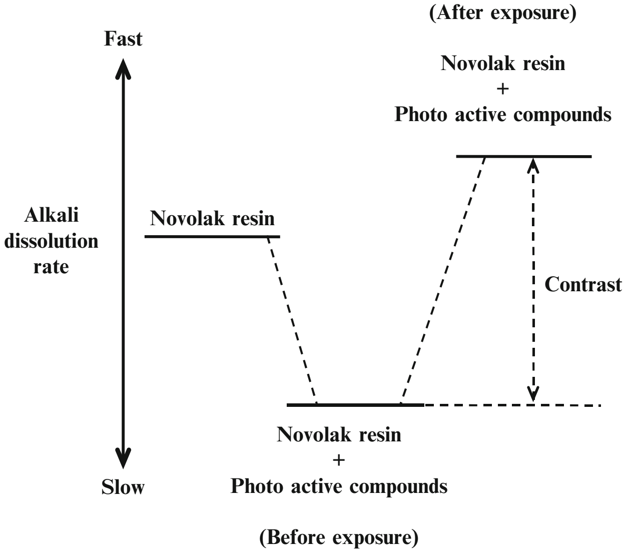
Presently, photoresist plays an important role in the field of patterning for devices of large scaled integrated circuits (LSI) or LCD, and making printing plates, etc.

15.2 DNQ – Novolak Photoresists

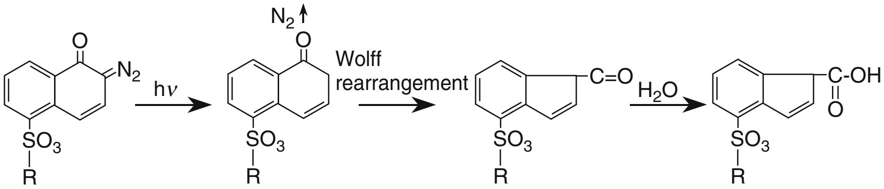
DNQ – novolak photoresists generally consists of novolak (about 25%), DNQ derivatives (about 10%), solvent (about 65%), and selective additives which provide various properties. The mechanism of this photoresist is said to be based on the difference of alkali dissolution rate between the exposed part and the unexposed part. When unexposed, the inhibition effect to alkali dissolution results from the interaction of DNQ and novolak. When exposed the acceleration effect to alkali dissolution results from DNQ’s photo chemical reaction (Scheme 15.1).

DNQ’s photo chemical reaction is said to occur as shown in Scheme 15.2. By photo exposure, after expelling nitrogen, DNQ is transformed into indene ketene by Wolff rearrangement and emerges as indene carboxylic acid by reaction with water. This carboxylic acid becomes soluble in alkali [4].

Near UV and deep UV are mainly used as light sources for photoresists. G-line (436 nm), and i-line (365 nm) are especially desirable for DNQ – novolak photoresists. Moreover, KrF (248 nm) and ArF (193 nm) excimer lasers are used in order to achieve good fine patterning of semiconductors. When using laser light source,



Scheme 15.1 Photo lithography mechanism of DNQ-Novolak photoresist



Scheme 15.2 Photo reaction mechanisms of diazonaphthoquinone

novolaks cannot be used due to their lack of transparency. Instead polyhydroxystyrene or acrylic polymers are used with this light source.

As for the inhibition effect by DNQ, various theories have been reported, but even now a firm theory has yet to be established.

For example,

(1) Cluster (octopus pot model), which is generated by the hydrogen bond of the hydroxy group of the phenolic resin and DNQ, shields hydrophilic parts [5]. This is a proposed model of a macromolecular complex of ortho–ortho bonded novolak microstructure with photo active compound, PAC. PAC is compared to the "Octopus" part, and novolak is compared to the "Pot" part.

(2) When unexposed the novolak reacts with the PAC by a diazocoupling reaction and the product becomes insoluble in alkali [6].

(3) Three complex factors exist. One is interaction of the hydrogen bond, the second is an azoxy-bond made from the novolak and DNQ, and the third is formulation of a protective layer by the hydrophobic part of DNQ [7].

15.3 Phenolic Resins for Photoresist

Meta–para cresol novolaks are generally used as phenolic resins for photoresist. The reasons that cresols are selected as monomers are due to having adequate solubility in alkali and good heat resistance by virtue of the high softening point of novolaks made from them. Moreover, meta-cresol has the tendency to dissolve easily in an alkali aqueous solution while *p*-cresol is difficult to dissolve. So, by adjusting the ratio of meta–para, it is possible to control and achieve the target properties.

Ortho cresol novolaks are not used for photoresist due to low softening points and insufficient heat resistance even though they dissolve in alkali rapidly.

Unsubstituted phenol novolaks are not suitable because they dissolve rapidly in alkali to pattern the required images. Furthermore they have low heat resistance due to low softening points.

The market of novolak for photoresist is monopolized by Japanese companies. The sales volume was about 3,500 tons in 2007. Of the 3,500 tons, about 1,000 tons was for semiconductor applications and about 2,500 tons was for LCD applications. This market had grown in pace with the growth of LCD market in recent years. However, it has become a mature market and is estimated to be quite static overall.

15.4 Meta–Para Cresol Novolaks

A study of synthesis and properties of meta–para cresol novolaks was reported by Bogan [8] and Arita [9]. In this section [1], the relation of meta–para ratio between feed and in the resin [2], the relation of synthesis conditions of meta–para cresol novolaks (reaction temperature and meta–para ratio) and resin properties (ADR, molecular weight) are introduced.

Under fixed reaction conditions, novolaks are synthesized by changing only the meta–para cresol feed ratio. By ^{13}C-NMR analysis method, the meta–para cresol ratio in resin is calculated and analyzed using the integral value of methyl groups on the aromatic ring [10]. The result is shown in Fig. 15.1. There is a tendency that the amount of *m*-cresol in the resin is higher than that in feed. This tendency seems to occur due to the different relativities of cresols with formalin or the fact that *m*-cresol reacts with formalin faster than *p*-cresol [11].

The relationship of weight average molecular weight and alkali dissolution time with varying the meta–para cresol ratio in feed is shown on the Fig. 15.2. The measurement method of ADR is accomplished after coating a resin solution on a silicon wafer with a film thickness of about 1 μm. The dissolution time is measured visually by using a developer of tetra methyl ammonium hydroxide aqueous solution. Weight average molecular weight (M_w) is analyzed using gel permeation chromatography (GPC) by conversion to polystyrene standard M_w.

The result is that as M_w increases, ADR becomes slower, and as *m*-cresol ratio in feed increases, ADR becomes slower.

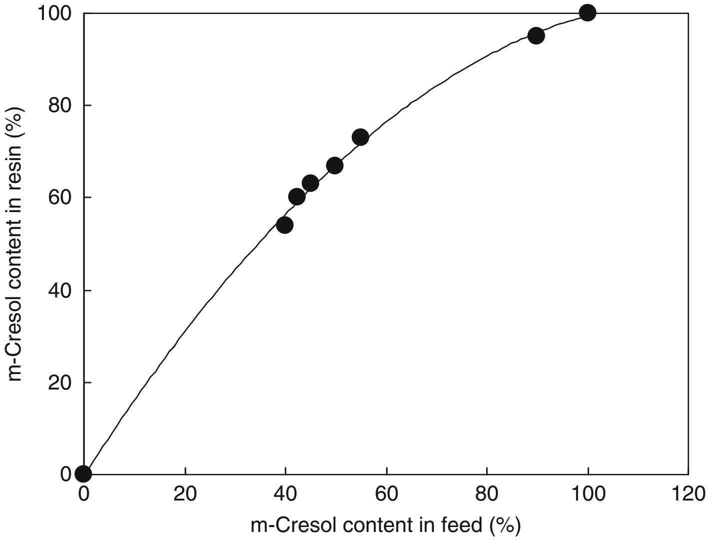


Fig. 15.1 Relation of *m*-cresol content between *m*/*p* ratio in feed and in resin on *m*, *p*-cresol novolak resin

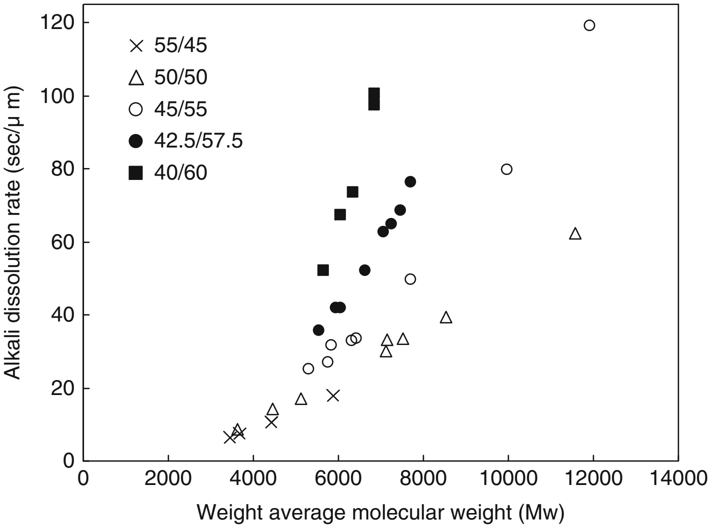


Fig. 15.2 Effect of *m*/*p* ratio in feed on alkali dissolution rate and weight average molecular weight

Figure 15.3 shows the relationship of M_w and ADR in resin synthesized with a change of reaction temperature with formaldehyde, whose meta–para ratio in feed is constant at 60/40. At the same M_w, as the reaction temperature increases, ADR has a tendency to become slower. Generally as the temperature is increased in the

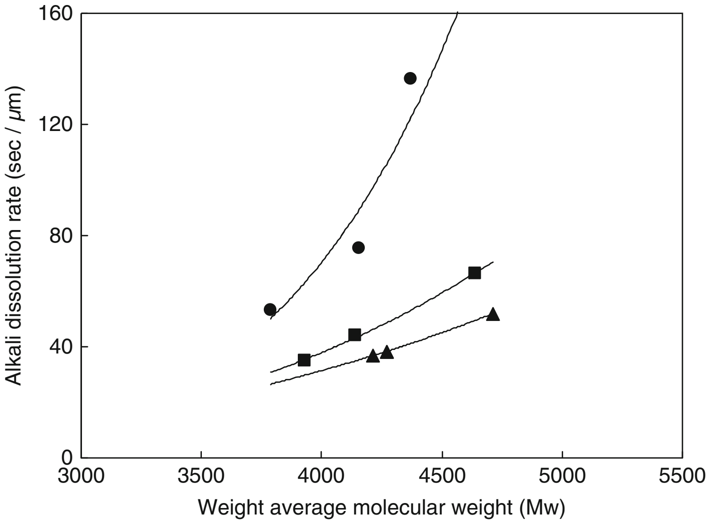


Fig. 15.3 Effect of reaction temperature on alkali dissolution rate and weight average molecular weight. Reaction temperature *filled triangles*: 140°C, *filled squares*: 145°C, *filled circles*: 150°C. *m*/*p* ratio in feed: 6/4

Table 15.1 Effect of reaction temperature on methylene bond composition in *m*, *p*-cresol novolak resin (*m*/*p* ratio in feed: 6/4)

Reaction temp.	o–o′ bond (%)	o–p′ bond (%)	p–p′ bond (%)
145	58.4	35.8	5.8
150	63.0	32.5	4.5

preparation of phenolic resins, the ortho–ortho bond ratio of the methylene unit increases and a high-ortho structure resin is obtained [12]. When a novolak has a large amount of high-ortho structures, hydroxyl groups form ring like (cyclic) structures with each other due to the effect of hydrogen bonding. As a result, it is assumed that alkali developer cannot penetrate the hydroxyl group easily, and that ADR becomes slow. Ortho–ortho bond ratio can be determined by ^{13}C-NMR method [13]. Table 15.1 shows that as reaction temperature becomes higher the ortho–ortho bond ratio becomes higher also.

15.5 Analysis of Phenolic Resins for Photoresist

Novolak analytical methods for photoresists are discussed in several reports [10,14,15]. For example, NMR methods can show the meta–para cresol ratio in resin and the ratio of methylene bond position, pyrolysis gas chromatography can show phenolic monomer composition, HPLC (GPC) can show molecular weight and molecular weight distribution, especially GPC–LALLS (Low Angle Laser

Light Scattering) can show the absolute value of molecular weight and accurate molecular weight distribution, and GC-FT-IR can detect the dimer content in resin.

15.6 Relationship of Resin Properties and Photoresist Properties

Required properties for the photoresist and its related phenolic resin properties are shown in Table 15.2.

These required properties can be classified into three categories such as (1) the improvement of photoresist properties, (2) consistency (minimal variation in resin properties) of the photoresist, (3) photoresist purity. Based on these categories, studies of phenolic resins for photoresists are discussed in the next section.

15.7 Improvement of Photoresist Properties

15.7.1 Improvement by Changing the Type of Phenol Monomers

In an early study of DNQ-novolak photoresist, a meta–para cresol novolak was used. There are some reports detailing the relationship between meta–para cresol ratio and photoresist properties. Asaumi reported that a photoresist in which a novolak with a *p*-cresol ratio of 60% was used was suitable, because the photoresist had properties of providing a sharp pattern edge, no tailing pattern, and good depth of focus [16]. Resolution is expressed by the following equation, known as the "Rayleigh equation."

$$R = k\lambda/\mathrm{NA}$$

(R: Resolution, k: constant determined by process condition and/or materials, λ: wavelength of exposure, NA: numerical aperture).

Table 15.2 Relationship of phenolic resin properties and photoresist properties

Photoresist properties	Phenolic resin properties
High resolution	Phenolic monomer composition
High sensitivity	Alkali dissolution rate
High heat resistance	Molecular weight
Good adhesion	Molecular weight distribution
Low film thickness loss	Structure (branch or linear, block or random etc.)
Consistency	Constant molecular weight Constant alkali dissolution rate
High purity	Low metal impurities (ppb level)
Low sublimates	Low dimer

Asaumi made photoresist test patterns using cresol novolak with *m*/*p* ratio 60/40, 50/50, 40/60, and found experimentally that novolak with *m*/*p* ratio 40/60 the *k* value was the smallest among them.

Hanabata also reported studies of photoresist properties related to meta–para cresol ratio [17]. He found that high containing *p*-cresol content in novolak led to lower sensitivity, higher film thickness retention, higher heat resistance and higher resolution. He considered that high content *p*-cresol composition gave rigidity and regulation in novolak's chemical structure, and this structure caused both poor solubility in the developer and good heat resistance. He also speculated that they attributed this to the improvement of film thickness retention and resolution. The main reason was that higher containing *p*-cresol unit facilitated the appearance of indene carboxylic acid which was from DNQ derivatives by light exposure, so the contrast of exposed and unexposed part became definite. Further the novolak of high content *p*-cresol unit did indeed exhibit good film thickness retention and high resolution.

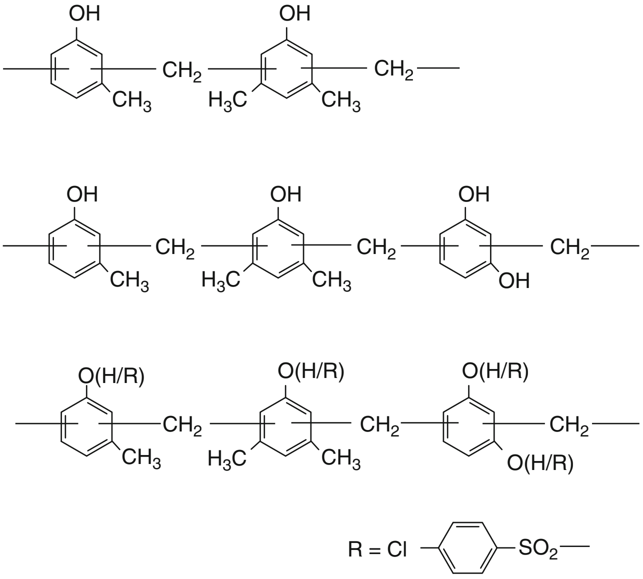
But as semiconductor integration continues in increased density, higher resolution and higher sensitivity for increased production throughput is mandated. Further some production operations have become more severe, that is, the etching method has changed from a wet to a dry system and baking temperatures have increased. Under these conditions, meta–para cresol novolaks have not been able to satisfy the required performance characteristics.

For the improvement of photoresist properties, Kajita studied the use of poly-substituted phenols (3,5-xylenol and 2,3,5-trimethylphenol) and achieved high sensitivity while maintaining heat resistance. These poly-substituted phenol monomers have low reactivity at the para position due to their structural characteristics and electron density resulting in a high methylene ortho bonding ratio. Moreover, it is reported that 3,4-xylenol, where the para position is substituted by a methyl unit exhibits the same effect [18].

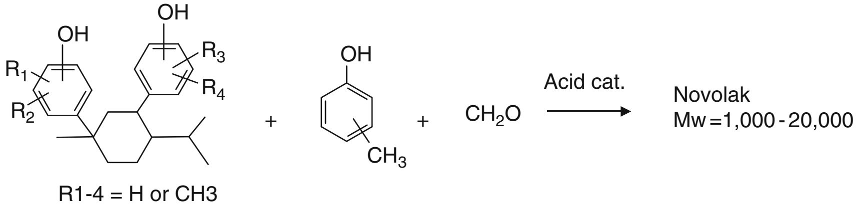
Khanna advanced the study of tri-component novolaks. He synthesized several novolaks consisting of (1) *m*-cresol, 3,5-xylenol and resorcinol, (2) *m*-cresol, 3,5-xylenol and (3) *m*-cresol, 3,5-xylenol and resorcinol whose hydroxyl group was esterified. He showed the novolak consisting of *m*-cresol, 3,5-xylenol and resorcinol had good properties of resolution, heat resistance, and adhesion in photoresist [19] (Scheme 15.3).

Many patents using xylenol and trimethylphenol have been filed. These photoresist compositions are being optimized based on the manufacturer's expertise and process.

Yu synthesized resins containing a variety of phenol monomers to prepare a positive photoresist. Various categories such as hydroxyl unit density, molecular weight, molecular weight distribution, and ortho–ortho ratio were investigated. As the result, it was reported that co-monomer resins of resorcinol and divinylbenzene provided the best properties for a photoresist [20]. He synthesized the addition polymerization resin with resorcinol and divinyl benzene using oxalic acid as catalyst, and found that the resin showed good performance of sensitivity, film



Scheme 15.3 Structure of the tri-component novolaks



Scheme 15.4 Reaction of the terpene-diphenols

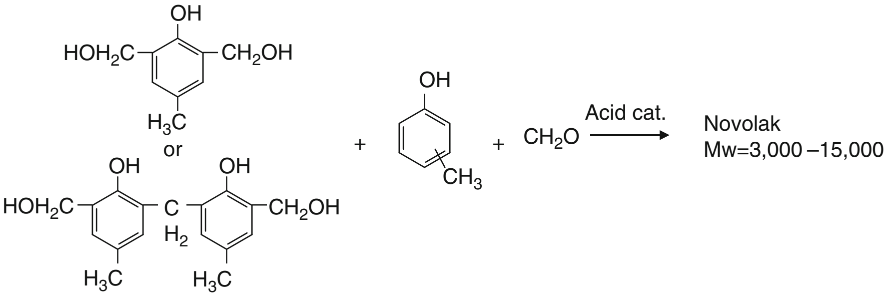
thickness retention and resolution when the molar ratio of resorcinol/divinyl benzene was from 1:1 to 1:1.2.

In order to achieve improved photoresist pattern profiles with the accompanying improvement of heat resistance, resolution, and sensitivity, Morikawa used terpene-diphenols as one of phenol components [21] (Scheme 15.4).

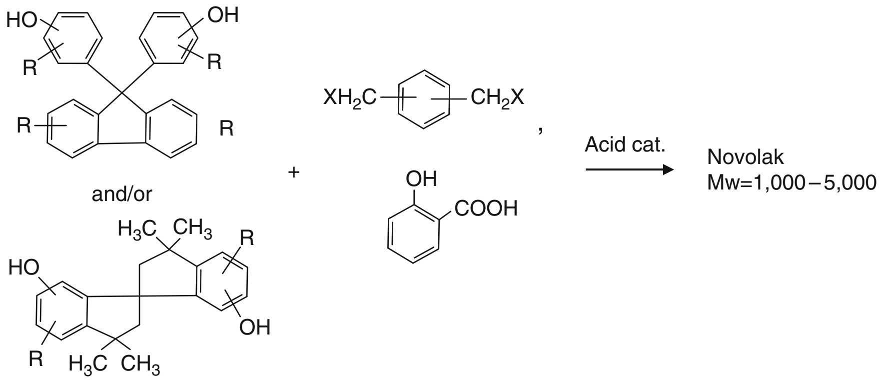
Kurimoto used a dimethylol of *p*-cresol or a dimethylol of *p*-cresol dimer as the starting monomers for the resulting novolak [22] (Scheme 15.5).

Ito applied dihydroxy phenyl indenes and tetra methyl tetra hydro spiro indene diols and achieved high heat resistance [23] (Scheme 15.6).

As etching methods have changed from wet to dry (reactive ion etching), improvement of the etching resistance of the photoresist is required. During etching the photoresist film is subjected to high temperatures and in some cases a portion of photoresist surface may be charred.



Scheme 15.5 Reaction of dimethylol of para cresol or dimethylol of *p*-cresol dimer



Scheme 15.6 Reaction of dihydroxy phenyl indenes and tetra methyl tetra hydro spiro indene diols

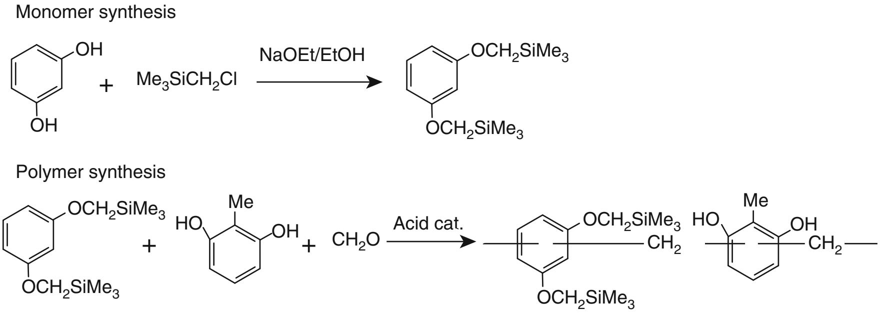
Photoresists containing silicon were studied under the premise that the surface after burning possesses better heat resistance due to the presence of silicon on the surface of the coating.

Tarascon synthesized a modified resorcinol monomer with the hydroxyl group functionalized with the trimethyl-silyl group and achieved high etching resistance by using it as one of the monomers for the novolak [24] (Scheme 15.7).

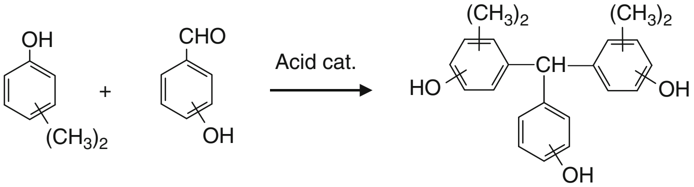
15.7.2 Enhanced Behavior with Different Aldehydes

A study for enhanced behavior of novolaks for photoresists was initiated by not only changing phenol monomers, but also the aldehyde monomers which react with phenols by condensation polymerization.

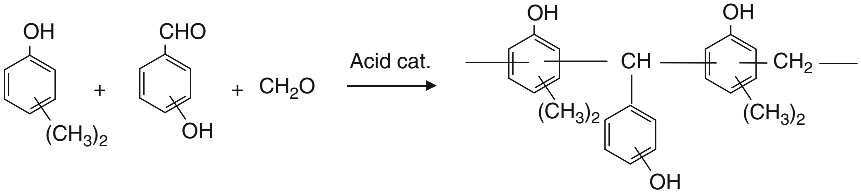
Ida achieved high sensitivity and heat resistance by using aromatic compounds such as xylenol and hydroxy benzaldehyde [25] (Scheme 15.8).



Scheme 15.7 Reaction of the silicon contained novolak



Scheme 15.8 Reaction of aromatic compounds which consisted of xylenol and hydroxy benzaldehyde



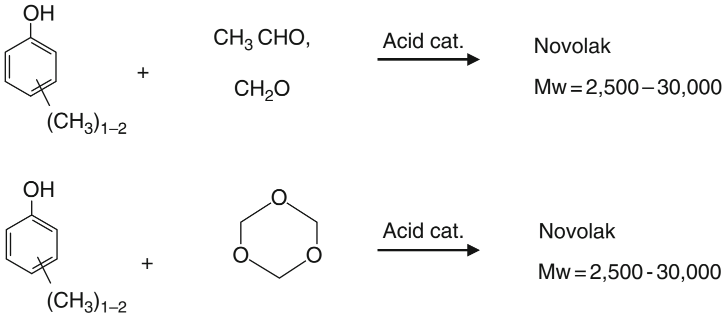
Scheme 15.9 Reaction of xylenol, hydroxy benzaldehyde and formaldehyde

Lazarus designed an improved novolak which consisted of xylenol, hydroxy benzaldehyde and formaldehyde [26] (Scheme 15.9).

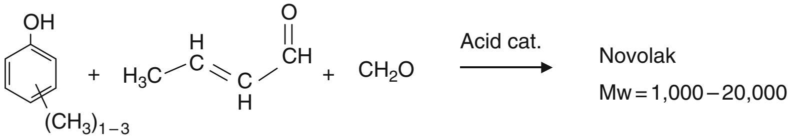
Nakano examined both acetaldehyde and formaldehyde [27] or used trioxane instead of formaldehyde [28] and found that the resulting materials showed high sensitivity, high resolution and excellent pattern profiles for the photoresist (Scheme 15.10).

Kouno prepared a photoresist with improved sensitivity, film thickness, and depth of focus by using a novolak containing an aldehyde with unsaturation such as crotonaldehyde [29] (Scheme 15.11).

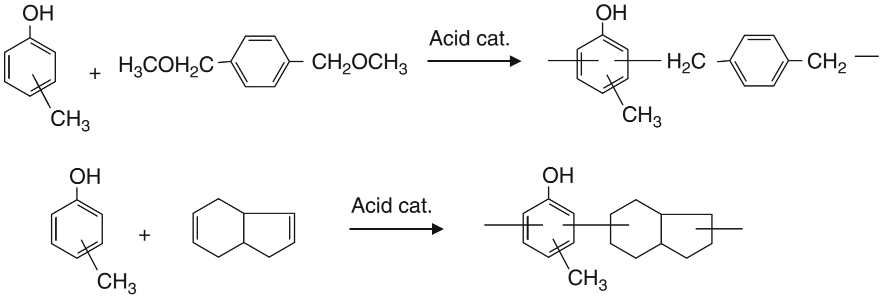
Urakami reported that novolaks using xylylene glycol dimethyl ether or dicyclopentadiene exhibited good transparency with high sensitivity and high resolution. Thus these resins could be utilized not only for g, i-line but also for KrF laser [30] (Scheme 15.12).



Scheme 15.10 Reaction of acetaldehyde or trioxane modified novolak



Scheme 15.11 Reaction of crotonaldehyde modified novolak

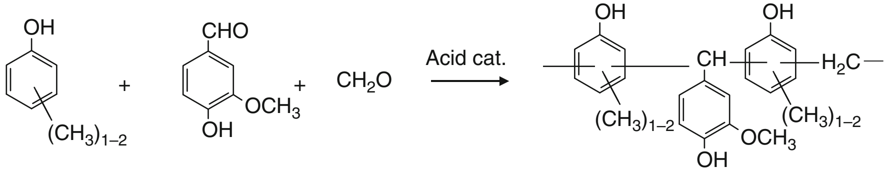


Scheme 15.12 Reaction of xylylene glycol dimethyl ether or dicyclopentadiene modified novolak

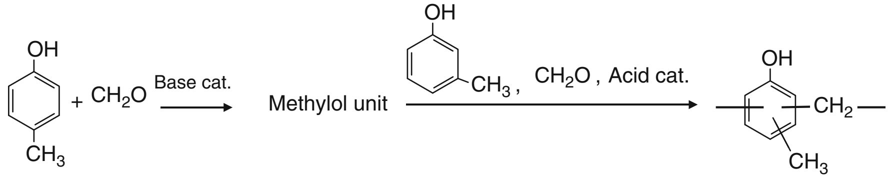
Tan used methoxybenzaldehyde (vanillin), as the aldehyde group for a novolak, and achieved high resolution, high heat resistance and a wide focus latitude which is the range for making the proper photoresist pattern when focus adjustment becomes far from the best point [31] (Scheme 15.13).

15.7.3 Improvement in the Control of Resin Structure

As a method for controlling the resin structure, a novolak was synthesized by a two-step reaction. During the first step, meta–para cresol novolak was synthesized



Scheme 15.13 Reaction of methoxybenzaldehyde (vanillin) modified novolak



Scheme 15.14 Reaction of two-step process using a novolak followed by a resole

followed by a second step by adding *p*-cresol monomer and formaldehyde to the first step novolak. The resulting novolak was obtained after this sequence of reactions. The final novolak showed high heat resistance, high sensitivity and good resolution by adjusting the cresol monomer ratio [32].

Gokan developed a method of preparing novolaks by adding *m*-cresol and formaldehyde to a resole oligomer of *p*-cresol and formaldehyde under basic conditions. An improved photoresist possessing high sensitivity, heat resistance, and resolution was obtained [33]. This is a two-step process consisting of a resole followed by a novolak (Scheme 15.14).

Sizensky developed a high resolution photoresist by synthesizing a high ortho novolak. This novolak, whose ortho–ortho bonding ratio was 55–75%, was made at a temperature range of 100°C–200°C and high pressure, without utilizing a catalyst. He achieved a high ortho structure by using *m*-cresol and paraformaldehyde by this method [34].

Hanabata studied the relationship between ortho–ortho ratio in cresol novolaks and their photoresist properties using high ortho novolaks. He reported that an optimum ortho–ortho ratio existed for both sensitivity and remaining film thickness. At a high ortho–ortho ratio, resolution was greatly improved and heat resistance was lower. He proposed that high ortho structure increased the non substituted para position of the phenolic ring and the diazocoupling reaction with PAC showed increased inhibition to solubility [35].

Douki proposed the concept of complex branched structures with a high ortho bonded end group and studied base catalyzed phenolic resins. He found that this resin showed excellent photoresist contrast [36]. Contrast is generally shown as a slope in the graph between exposure energy and film thickness after development. When a slope is near vertical, a small difference of exposure energy clearly can distinguish the patterning of the exposed part from that of the unexposed part.

High contrast generally leads to high resolution. Following this concept, he synthesized a compound which was formed from six phenolic rings with tetra methylol and *p*-cresol, and confirmed an improvement of photoresist contrast [13].

Generally phenolic resins with narrow molecular weight distribution are proposed to improve the resolution of a photoresist because the resin properties approach that of a pure compound. Kamimura synthesized a cresol novolak with a narrow molecular weight distribution and developed a photoresist with good sensitivity and heat resistance [37]. Miyashita developed a novolak whose low molecular weight component was removed by a solvent extraction method and achieved improvement of the photoresist properties [38].

In a study of molecular weight distribution, Hanabata proposed the theory of a stone-wall model. High molecular weight novolak (H), low molecular weight novolak (L), and naphthoquinonediazide (N) constitute a photoresist. Small L and N molecules seem to fill in spaces among large H molecules. He compared it to a stone-wall. In exposed parts, the indene carboxylic acids are formed from N molecule, and L molecule begins to dissolve. This increases the surface area of H molecules and enlarges their contact area to the developer. In unexposed parts, the azocoupling reaction between L molecule and N molecule prevents the stone wall from being disrupted by the developer. He suggested that L molecule affected sensitivity and resolution, and H molecule determined the heat resistance of the photoresist [39]. He then proposed that a tandem type consisting of H and L molecule components was ideal, and reported that a novolak with a tandem type of molecular weight distribution showed the best performance of sensitivity, heat resistance, and film thickness retention in his experiments.

15.8 Consistency

Photoresists used in semiconductor and LCD applications require fine patterning in micro to nano meter range. This requires the variation of photoresist properties to be very narrow and necessitates strict control. This in turn requires the novolak resin which is the key material as the base polymer to be controlled to within very narrow specifications. Precise novolak production techniques are needed.

Exact charging of phenolic monomers to achieve the exact desired ratio in the final structure may be obtained by the use of precise measurement with highly accurate gages. The control of molecular weight to a narrow M_w range is very difficult due to variations in the formalin content which can change during storage. Various methods have been studied in order to minimize the variation of molecular weight. An example is to analyze the molecular weight midway through the process during the preparation of a meta–para cresol novolak and adjusting the cresol or formalin to meet the final desired structure [40]. An alternate method that can be considered is that molecular weight increases at a high temperature so that the molecular weight can be manipulated by the application of heat [41].

15.9 Photoresist Purity

The main contamination issue for a photoresist is particle and metal contamination. Metal contamination is critical and is required to be strictly controlled below 10 ppb in concentration. Particle contamination is generally controlled by the removal by filtration before packaging of the photoresist product so the control of particle level is dependent on the filter quality. It is difficult to remove metal contamination during filtration as the contamination can exist as ions or metal particles.

Several methods for the removal of metal contamination have been developed. Kotani reported that strong acid ion exchange resins were effective for removing metal contamination. He showed the data that Na was reduced from 29 to 4 ppb and Fe was reduced from 60 to 2 ppb by using ion exchange resins [42].

Rahman developed a method for using both acid and base ion exchange resins. He reported the method reduced Na and Fe content in novolak below 100 ppb. After dissolving novolak in a mixed solvent of polar and nonpolar components, he passed the solution through a filter from 0.04 to 0.50 μm pore size. Then he treated it with base ion exchange resins which were free of Na and Fe content below 200 ppb. Moreover he treated it with acid ion exchange resins which were similarly free of these ions below 100 ppb [43].

Once the contaminate is present, some metals are difficult to remove so it is important to prevent metals from contaminating the phenolic resin during their manufacture.

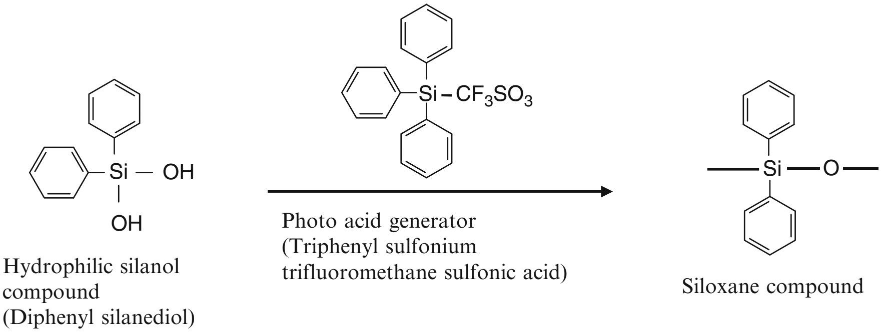
Novolaks for general industrial use are normally produced in stainless steel reactors. During manufacture the reactor material is slightly corroded by the acid catalyst used for the synthesis of the novolak, and traces of the stainless steel components contaminate the novolak resin. Test results show the presence of iron, chromium and nickel with levels up to 10 ppm. The amount and type of acid catalyst determines the degree of contamination.

In order to produce a novolak with low metal contamination in the ppb range, it is necessary to design the resin reactor with material that is resistant to acid catalysts. Special materials such as tantalum, hafnium, niobium, and zirconium are used as materials for nuclear reactors. Novolaks were synthesized in a small reactor which was made from these materials and examined for metal contamination. The test results are shown in Table 15.3. Metals which are strictly prohibited for photoresist material, such as sodium, iron, calcium, potassium, magnesium, nickel, were confirmed to be in the ppb range.

Reactors coated with polytetrafluoroethylene [44] or glass [45] are also effective in removing metal contamination but teflon does not have high thermal resistance and glass does not have high impact resistance so they have limited the production value. Materials such as tantalum, hafnium, niobium, and zirconium have both high thermal and high impact resistance similar to stainless steel so they are suitable as reactor material and can control contamination to low ppb levels [46].

Table 15.3 Metal contamination in novolak resins prepared in reactors made from special metals (unit: ppb)

Metal composition	Na	Ca	Fe	K	Sn	Ni	Mg	Si
Tantalum	120	110	200	130	50	180	150	210
Hafnium	100	150	110	60	100	80	200	90
Zirconium	50	90	100	180	70	130	150	190
Niobium	200	150	140	90	120	100	90	110
Titanium	160	120	100	180	50	110	120	60
Zirconium + Hafnium	60	80	150	210	200	150	160	130
SUS316	300	280	6,210	200	360	1,150	120	190
Glass lining	3,550	1,350	300	190	250	300	900	1,050
Hastelloy C	250	180	590	180	150	3,310	160	250



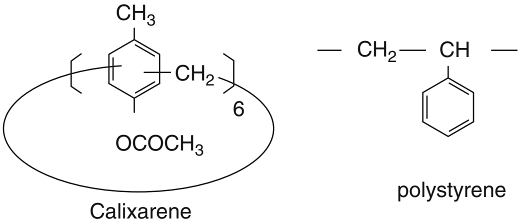
Scheme 15.15 Reaction from a hydrophilic silanol compound to a siloxane compound

15.10 Phenolic Resins for Semiconductor Photoresist

In the field of semiconductor photoresists, the light source is evolving from g, i-line to KrF, ArF excimer laser in order to achieve fine patterning. Novolaks are not used because of their poor transparency to excimer lasers. Poly hydroxy styrene (for KrF lasers) and poly acrylic ester with cyclic monomers such as adamantane (for ArF lasers) are used for these applications. Though there are many publications concerning the study of novolaks for photoresists using excimer lasers such as KrF, ArF, novolaks are not used due to their poor transparency. But in future there is a possibility that electron beam or X-ray may be used as the light source. For these, novolaks may be necessary. Studies are already in progress.

Feely discussed a negative photoresist which involved a cross linking reaction of hexa methoxy methylol melamine and a novolak by use of an acid from a photo acid generator [47]. Aoki reported an electron beam photoresist, with a novolak as a base polymer, which used a chemical change from a hydrophilic silanol compound to a siloxane compound by the use of an acid from a photo acid generator [48] (Scheme 15.15).

Scheme 15.16 Structure of calixarene and poly-styrene



There are some reports that relate to the use of calixarene which is a cyclic phenolic oligomer, as the material for an EB or X-ray photoresist. Onishi developed a photoresist, to improve heat resistance which consisted of a calixarene and cross-linking agent of bis-azide compounds [49]. Ochiai developed an EB photoresist which consisted of calixarene and a low molecular weight poly-styrene to achieve 10 nm scale lithography [50] (Scheme 15.16).

15.11 Phenolic Resin for LCD Photoresist

The basic properties required for a phenolic resin for LCD photoresists are achieved by the use of similar photoresist technology for semiconductor application. Here the characteristic technologies of phenolic resins for LCD photoresists will be covered [51].

During the production process of a LCD panel, the problem of yield decrease occurs when volatiles from the photoresist contaminate the production line. It has been found by analytical methods that the volatile was the dimer of the novolak. Thus the novolak for LCD photoresist requires a low dimer, content. Low dimer novolaks have been developed by removing the dimer content from cresol novolaks by steam distillation methods [52]. A GPC chart is shown in Fig. 15.4 of a “before” and “after” steam treatment of cresol novolak.

By adding a mixture of water and some selective solvents, instead of steam, the production method of a low dimer novolak with small energy consumption has been developed [53].

Inatomi developed a phase separation reaction in the preparation of novolaks by using a phosphoric acid as the catalyst (PAPS novolak technology). In the water phase, low molecular weight components such as monomer and dimer are in the catalyst phase, and they react with formaldehyde. As the molecular weight increases, these materials are transformed into the organic phase. As a result, novolak with low dimer content can be obtained [54] see Chap. 4, new PAPS novolak technology.

Low dimer novolaks with not only low volatile characteristics but also high heat resistance and high film thickness retention have been developed by the method of adding formaldehyde and an acid catalyst to a novolak which was previously steam distilled and dissolved in a solvent [55].

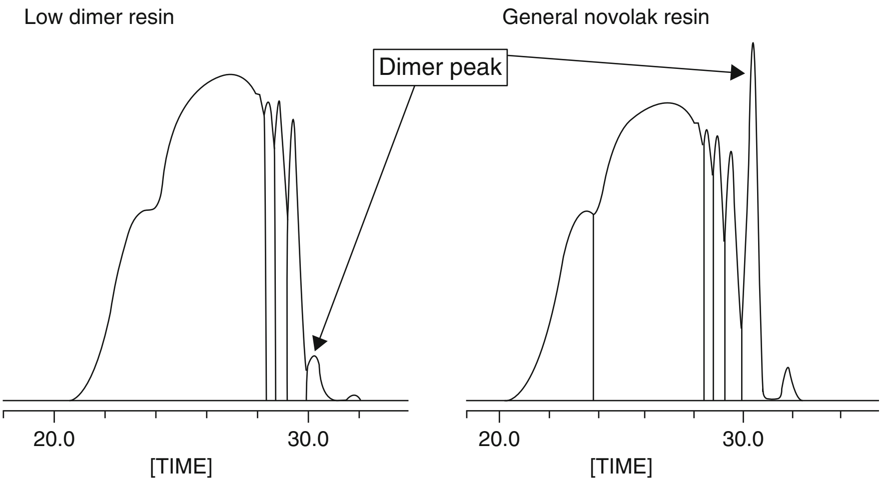


Fig. 15.4 GPC charts of low dimer resin and general cresol novolak resin

As the size of the glass plate becomes larger, uniformity of film thickness after coating the photoresist becomes increasingly important. During the production of semiconductor devices, a silicon wafer disk with a diameter of 70–300 mm is used. During the production of LCD thin film transistor, a square glass plate with a side length of 1–3 m is used. The dimensions of these plates are quite different between these two applications.

The coating method has been modified from a spin method to a spin & slit or a slit method according to the size of plate. For this reason uniformity of film thickness becomes important.

Some studies have been successful in coating photoresist film on the whole large glass plate with a uniform thickness. For example, Kato developed a photoresist with good coating uniformity by adding a phenolic compound of 2–5 ring structures [56]. Lee achieved not only good uniformity but also high sensitivity by specifying the ratio of resin, PAC, photo-accelerator and organic solvent [57]. For photoresist for color filters, Suzuki developed a photoresist containing a specific fluoride surface-active agent for coating uniformity without "mura" (surface roughness) [58].

To achieve uniformity in the coating thickness it is expected that additional developments in materials and equipment will occur.

15.12 Summary

For the application of g, i-line photoresists for semiconductors and LCDs, phenolic resins, primarily cresol novolaks are used. For semiconductor lithography, the light source has been changed from g, i-line to KrF, ArF excimer laser. Novolaks are not used due to their lack of transparency to these laser light sources.

For LCD applications g, h, i-line light sources continue to be used.

Photoresist lithography for these light sources is essential, so phenolic resins are expected to be widely used for this application in the future. Recently, fine patterning has been required for the displays for cellular phones and mobile devices. i-line lithography seems to be suitable for this application and phenolic resins will be required for the technology. As the size of the glass plate becomes larger and the patterning of lithography becomes finer, the required properties for phenolic resins for photoresists will become narrower. Phenolic resins are expected to continue to play an important role and contribute to the photoresist technology and the electronics material industry.

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Chapter 16
Phenolic Molding Compounds

Koji Koizumi, Ted Charles, and Hendrik De Keyser

Abstract Phenolic Molding Compounds continue to exhibit well balanced properties such as heat resistance, chemical resistance, dimensional stability, and creep resistance. They are widely applied in electrical, appliance, small engine, commutator, and automotive applications. As the focus of the automotive industry is weight reduction for greater fuel efficiency, phenolic molding compounds become appealing alternatives to metals. Current market volumes and trends, formulation components and its impact on properties, and a review of common manufacturing methods are presented. Molding processes as well as unique advanced techniques such as high temperature molding, live sprue, and injection/compression technique provide additional benefits in improving the performance characterisitics of phenolic molding compounds. Of special interest are descriptions of some of the latest innovations in automotive components, such as the phenolic intake manifold and valve block for dual clutch transmissions. The chapter also characterizes the most recent developments in new materials, including long glass phenolic molding compounds and carbon fiber reinforced phenolic molding compounds exhibiting a 10–20-fold increase in Charpy impact strength when compared to short fiber filled materials. The role of fatigue testing and fatigue fracture behavior presents some insight into long-term reliability and durability of glass-filled phenolic molding compounds. A section on new technology outlines the important factors to consider in modeling phenolic parts by finite element analysis and flow simulation.

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16.1 Introduction

One of the most important applications of phenolic resins is the manufacture of phenolic molding compounds. There are few suitable roles for unfilled phenolic resins molded to neat shape, but by compounding phenolic resins with fillers and/or reinforcements, a diverse range of products has been established for use in thousands of ways. Thermosetting phenolic molding compounds are the oldest in plastics, the very first of the engineering plastics as they are recognized today. The development of phenolic molding compounds closely followed Dr. Leo H. Baekeland's pioneering work in 1907 that established the first industrialized resin. Phenolic molding compounds continue to play an important role in the application of plastics, testimony to an enduring technology and continuing innovation in new materials and molding processes. Phenolic molding compounds have well balanced properties of heat resistance, chemical resistance, dimensional stability, and creep resistance. They are widely applied in electrical, appliance, small engine, commutator, and automotive applications. As the automotive industry focuses more on weight reduction as a means to drive fuel savings, phenolic molding compounds become appealing alternatives to metals. Technological advances have enabled them to expand in the aviation field as well.

Phenolic molding compounds have a long history and have sustained their viability in the market through the years by advances in technology. They continue to have enormous growth potential because of recent technical innovations and the continuing desire for weight reduction through metal replacement.

Despite the growth potential, phenolic molding compounds continue to suffer periodic market erosion due to part obsolescence and replacement by high performance thermoplastics, especially in appliances, where color and impact resistance are important considerations. This trend accounts for a volume decline of about 5%/ year, particularly in general purpose grades (Table 16.1). In the last decade, consolidation of suppliers has continued and some capacity retired.

More recently, chaotic developments in the economy, beginning in the second half of 2008 and continuing in the 2009 calendar year, have reduced global sales volumes for all plastic and metal materials, including phenolic molding compounds. Expected volume losses of 30–40% are expected through 2009. It is anticipated that global sales volumes will improve in 2010.

Table 16.1 Global production of phenolic molding compounds

Region	Production (in thousands of tons)				
	2004	2005	2006	2007	2008
Asia	108	106	103	98	88
North America	62	55	53	49	44
Western Europe	59	53	50	48	43
Totals	229	214	206	195	175

16.2 Characteristics and Formulations

Phenolic molding compounds are composite matrices which have phenolic resin as the primary binder and inorganic and/or organic fillers and reinforcements. They are commonly produced in granular or pellet form. Before molding, the molecular weight of the phenolic resin component is generally much lower (around 500–5,000) in comparison to thermoplastic resins. The resins have superior affinity to many fillers and reinforcements and, unlike thermoplastics, are typically designed with several fillers in each formulation to impart a balance of properties. Hexamethylenetetramine (HMTA) is generally compounded with novolak based formulations as the curing agent, providing enough formaldehyde to complete the reaction. The novolak based molding compounds are relatively easy to mold and provide excellent dimensional stability and shelf life compared to the resole resin based materials. One-step based compounds can be cured without HMTA, and thus do not emit ammonia. These compounds have excellent heat resistance and are noncorrosive to mating metal parts.

Phenolic molding compounds have been developed to provide a wide range of properties by optimizing combinations of these two resin types with various reinforcements. These formulations are designed to take advantage of phenolic's heat resistance, microbial resistance, electrical insulation, rigidity, and long-term reliability.

16.2.1 Novolak Phenolic Resins (Two-Stage Phenolic)

A novolak resin (two-step) is produced by condensing phenol with an insufficient amount of formaldehyde to complete the reaction (ratios of formaldehyde to the phenol, F/P, are from 0.5 to 1) in the presence of an acid catalyst (sulfuric acid, oxalic acid, etc.). This produces a thermoplastic resin. To cure this resin, a hardening agent is used, HMTA (or hexa). Hexa is made from ammonia and formaldehyde. Under heat and pressure, it yields ammonia and formaldehyde as methylene groups to cure the resin, hence the term "two-step," because of the two formaldehyde additions. A novolak phenolic resin has an infinite shelf life under normal storage conditions.

A novolak phenolic compound emits ammonia molecules; therefore, it is not used in electronic parts where corrosion of mating metal components is an issue. These materials are more stable than single-stage materials by a factor of two-to-one for materials of similar filler formulation. A two-stage compound offers a controlled cure and lower water absorption. Most two-stage molding compounds are formulated with a combination of resins, primarily random and ortho novolaks with different molecular weights and/or structures, targeting specific viscosity, cure speed, and performance properties.

16.2.2 Single-Stage Phenolic Resin

A resole resin (single-step) is produced by condensing phenol and an excess (more than 110%) of formaldehyde in the presence of a basic catalyst, ammonium or sodium hydroxide. This produces a thermosetting resin which is reactive when subjected to heat and will polymerize, cure (set up), advance or stiffen in storage at room temperature. Because it stiffens under normal storage conditions, molding compounds made from resole resins normally have a limited shelf life. In most cases, changes in the molding character are acceptable over the course of 3–12 months, depending on the formulation and application process. The shelf life may be extended by refrigerated storage.

The use of a resole or novolak resin determines many of the properties of the molding compound due to different cure mechanisms. Since a resole molding compound contains no ammonia, it is odor-free and is typically used in such applications as bottle caps and refrigerator switch boxes.

The resole compounds are ideally suited for hermetically sealed switches. There is no corrosion of beryllium copper components since there is no ammonia present to react with water vapor in the presence of an arc to form nitrous acid.

Wet/dry applications, where one side of the part is wet and the other dry (such as pumps or vaporizers), require the use of specific impact grades of resole materials.

Applications that need resistance to thermal shock, such as automotive pulleys with metal inserts, require the use of specific heat resistant grades of resole materials.

As in the case of novolaks, most resole molding compounds are formulated with a combination of resins designed to impart molding and/or performance properties important to specific applications.

16.2.3 Organic Fillers

Organic fillers such as wood flour, bark flour, shell flours, and cotton or paper fibers are used in molding compounds. Large volumes of these fillers are compounded because they are low in specific gravity and relatively inexpensive. Cellulose fibers, especially cotton and paper, are used to improve impact resistance. Materials reinforced with organic fillers are typically applied in appliances, knobs, and pan handles, as well as electrical devices such as switches, outlets, and circuit breakers, taking advantage of the fillers' relatively low specific gravity.

16.2.4 Inorganic Fillers

Inorganic fillers such as fiberglass, glass beads, calcium carbonate, clay, mica, silica, talc, wollastonite, and metallic hydroxide are used for improving various properties:

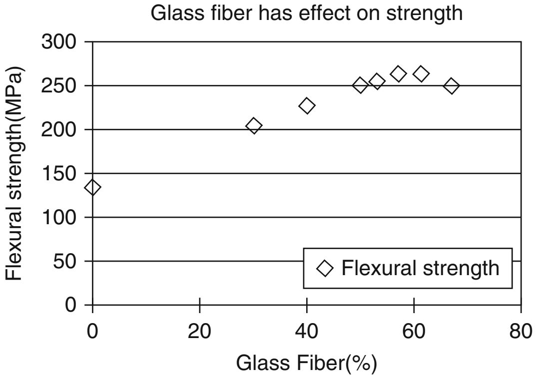


Fig. 16.1 Quantity of glass fibers has effect on strength molding compounds

1. Strength and stiffness
2. Heat resistance
3. Dimensional stability
4. Less molded shrinkage
5. Electrical properties
6. Flammability
7. Chemical resistance
8. Cost reduction

Fiberglass is compounded in phenolic molding compounds because it is effective in improving strength and stiffness. Generally, strength and stiffness can be increased linearly by increasing the quantity of glass fibers up to 60 wt% (Fig. 16.1). Other inorganic fillers are compounded for heat resistance, dimensional stability, and lower molded shrinkage. Addition of these fillers must be carefully considered, as they have a profound effect on the molding character of the material and on mold wear, depending on the type of mineral and its impurities. Metallic hydroxides, such as alumina trihydrate, are compounded to improve flammability properties. Inorganic fillers, especially in combination with fiberglass and other reinforcements, can provide strength, heat resistance, and dimensional stability in molding compounds. These properties make phenolic molding compounds particularly well suited for commutator and automotive applications.

16.2.5 Other Fillers

16.2.5.1 Lubricating Fillers

Addition of solid lubricant fillers, such as graphite and molybdenum disulfide powder, can give sliding properties to the molded surface of phenolic molding compounds. Figure 16.2 shows the dynamic friction coefficient decreasing in comparison with the normal phenolic molding compounds by adding graphite.

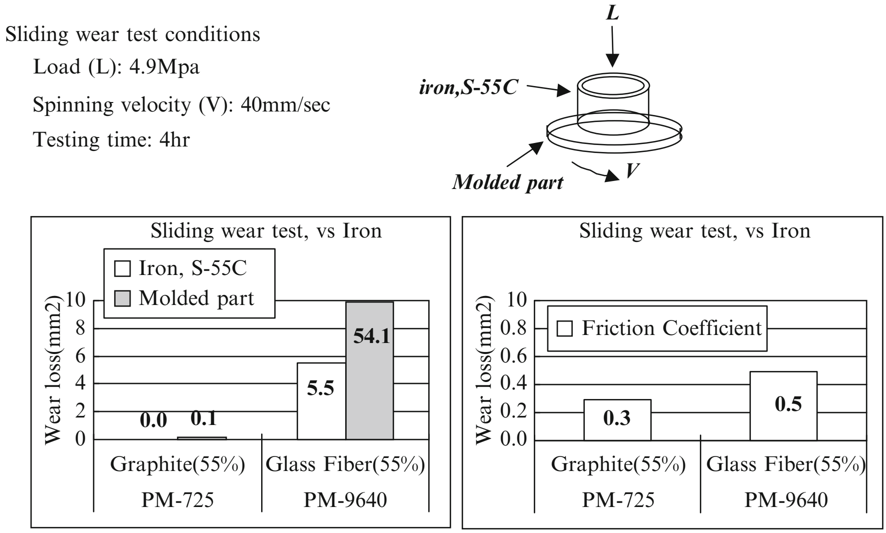


Fig. 16.2 Sliding wear test results

There is a compromise, however, in that graphite-modified materials have lower mechanical and electrical properties.

Sliding Wear Test Conditions

- Load (L): 4.9 Mpa.
- Spinning velocity (V): 40 mm/s.
- Testing time: 4 h.

16.2.5.2 Fillers to Improve Toughness

Phenolic molding compounds have excellent rigidity properties, but they are not particularly "tough," as exemplified by high resistance to impact or high hoop strength. Elastomers and rubbers, such as acrylonitrile-butadiene rubber (NBR) and polyvinyl acetate (PVA) can be used to improve these properties. Figure 16.3 shows the strain-stress curve for a typical glass-filled phenolic with and without NBR. Elongation of the molded part can be increased by adding NBR. However, higher wt% loading of these modifiers results in lower heat resistance and dimensional stability. Additionally, the material viscosity is often increased, affecting the moldability. As a result, use of these modifiers is always carefully considered.

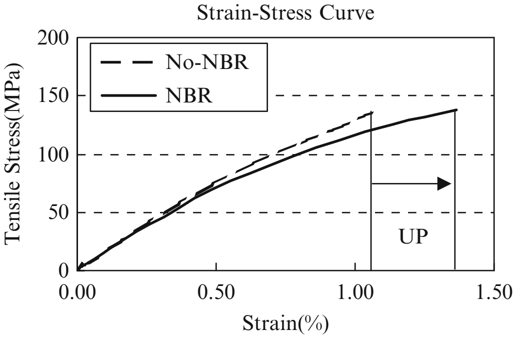


Fig. 16.3 Strain-stress curve in presence or absence of NBR

16.2.5.3 Colorant Fillers

Phenolic molding compounds are not colorfast. In the cured state, phenolic resin is easily oxidized, resulting in a yellow surface color. For this reason, phenolic molding compounds are not generally dyed in bright colors. Most producers prefer black, brown, or dark green colors. Dyes and/or pigments can be used, typically in wt% loadings at 0.5–1.5%. Better electrical properties can usually be attained using pigments, but better appearance is typical of many dyes. Part and cost requirements dictate the balance of colorants.

16.2.5.4 Lubricants

Phenolic molding compounds invariably contain 0.5–2 wt% lubricants. The bulk of these lubricants is compounded with the other raw materials, but it is common practice to blend external oils and/or waxes on the finished product, especially for those materials that are injection molded. The external lubricants are added to reduce adhesion of the material to the barrel and screw and they tend to improve the powder feeding characteristics, as well. Internal lubricants improve the viscosity or flow of the molding compound and promote good mold release. Typical lubricants are fatty acids such as stearic acid, stearates such as magnesium, calcium, or zinc, and esters and amides of fatty acids. These lubricants have a profound effect on appearance, strength, and moldability, so producers usually guard this information as a trade secret.

The general properties of representative phenolic molding compounds using inorganic and organic fillers, graphite, etc., are shown in Table 16.2.

16.3 Production of Phenolic Molding Compounds

Molding compounds have been manufactured in many ways, some with great imagination. Early methods were typically wet processes using liquid resoles. Some adaptations of those early processes exist today. Phenolic molding compounds consist

Table 16.2 General properties of representative phenolic molding compounds

Grade			PM-9640	PM-6630	PM-3075	PM-8180	PM-8200	PM-9820	PM-725
Application			Automotive/ Mechanical	Commutator	Pulley	Ashtray	Electric components	Electronic components	Sliding
Characteristic			High mechanical strength	High mechanical strength	High mechanical strength and thermal shock resistance	Low specific gravity	General purpose	Ammonia free	Excellent wear resistance and low friction coefficient
Resin			Novolak	Novolak	Single stage	Novolak	Novolak	Single stage	Novolak
Main fillers	Unit	Test method	Inorganic	Inorganic	Inorganic	Organic	Organic	Organic	Graphite
Specific density	–	JIS K6911	1.78	1.78	1.73	1.42	1.41	1.45	1.66
Molding shrinkage factor	%	JIS K6911	0.25	0.20	0.35	1.00	1.00	0.90	0.45
Water absorption	%	JIS K6911	0.05	0.05	0.10	0.30	0.30	0.35	0.04
Linear expansion coefficient	1/°C	TMA	2.5E–05	2.2E–05	3.5E–05	–	5.0E–05	3.5E–05	3.2E–05
Heat deflection temperature	°C	JIS K6911	210	230	280	180	170	175	175
Dielectric strength	MV/m,S/S	JIS K6911	15	10	–	19	11	11	–
Insulation resistance dry	Ω	JIS K6911	1.0E + 12	1.0E + 12	1.0E + 12	1.0E + 10	1.0E + 11	1.0E + 12	–
Tracking resistance	V	IEC pub.112	175	175	–	–	150	175	–
Flexural strength	MPa	JIS K6911	230	220	210	80	90	125	80
Flexural modulus	GPa	JIS K6911	17.0	17.0	13.0	6.5	6.5	7.4	12.5
Compression strength	MPa	JIS K6911	300	230	230	200	210	220	130
Charpy impact strength	KJ/mm2	JIS K6911	5.0	5.5	5.3	3.0	2.5	3.5	2.5
Grade			29502B*	29502*	X655	2940W	X680	X613	X6952
Application			Piston	Piston	Brake systems, commutators, clutch systems, fuel pumps	Idlers and pulley systems	Turbohousings and EGR systems, clutch systems, idlers, and pulley systems	Cooling systems and solenoid covers	Transmission, lubrication, cooling, and EGR systems
Characteristic			Heat resistance and dimensional stability	Heat resistance and dimensional stability	High dimensional stability, high thermo/ electrical shock resistant	High mechanical strength and stifness	Outstanding performance at high temperature and isotropic dimensional stability	Excellent thermal/ chemical resistance	Superior strength and excellent thermal/ chemical resistance

Resin			Novolak	Novolak	Novolak	Novolak	Novolak	Novolak	Novolak
Main fillers	Unit	Test method	Inorganic	Inorganic	Inorganic	Inorganic	Inorganic	Inorganic	Inorganic
Specific density	–	ISO 1183	2.10	2.10	2.08	1.83	1.68	1.60	1.70
Molding shrinkage factor	%	ISO 2577	0.15 − 0.35	0.10 − 0.25	0.15	0.27	0.36	0.35	0.14
Water absorption	%	ISO 62	0.03	0.03	0.06	0.10	0.05	0.08	0.06
Linear expansion coefficient	1/°C	TMA	1.6E − 05	1.6E − 05	1.7E − 05	2.9E − 05	3.3E − 05	3.7E − 05	2.5E − 05
Heat deflection temperature	°C	ISO 75 − Af	>275	>275	210	185	188	213	224
Dielectric strength	kV/mm	IEC 60243	12	12	25	25	36	17	38
Volume resistivity	Ω cm	IEC 60093			1.7E + 15	1.19E + 15	3.2E + 13	7.0E + 14	7.0E + 14
Comparative tracking index	V	IEC 60112	225	225	300	250	175	175	175
Flexural strength	MPa	ISO 178	135	105	185	124	185	190	255
Flexural modulus	GPa	ISO 178	23.6	24.2	25.0	12.0	13.0	12.0	17.0
Compression strength	MPa	ISO 604	355	250	360	212	270	260	300
Charpy impact strength notched	kJ/mm2	ISO 179	1.2	1.2	2.7	3.1	3.5	3.8	4.9

generally of 6–10 components. Most of today's processes employ some method of dry-mixing these, then apply heat and shear to fuse the resins with the fillers and reinforcements. Many processes reduce the resin intermediates, lubricants, and curing agents to fine powders, which are subsequently mixed by paddle, sigma blade or ribbon blenders, mullers, ball mills, high shear plow mixers, V-blenders, cone blenders, or other means to assure a homogeneous blend of raw materials. Precise control of the charging process is generally regarded as critical to the manufacture of high quality phenolic molding compounds. The initial blending step is usually followed by a kneading process, many times using extruders and/or roll mills adapted specifically for the production of phenolic molding compounds. Extruders and kneaders are employed in a vast variety of diameters, screw configurations and speeds, and can be co-rotating or counter-rotating. Die head extruders force the mix through a die plate, producing a nodular product form. Roll processes most commonly employ differential roll mills, where one roll is designed to turn faster than the other, creating a shearing zone. This process typically calls for the rolls to operate at different temperatures, as well, and the combination of shear ratio and temperature difference forces the molding compound to adhere to one roll and to be repelled by the other, such that the phenolic molding compound forms a sheet on the forming roll. Extruders and roll mills can be deployed in tandem or serve as stand-alone kneading steps. The kneading process can be followed by many secondary devices such as grinders, sifters, dryers, air classifiers, and compactors aimed at adding quality and value to the product. The aim, no matter what process is used, is to manufacture products that can be converted to the molded shape in the most cost effective manner. Output is typically in granular, pellet, or flake form. Each production line configuration targets very specific properties important to the customer, weighing performance and ease of use against product cost.

16.4 Molding Process

16.4.1 Basic Molding Methods

Nearly every customer molding facility has some unique variation of the molding process, but the basic molding methods can be grouped by injection, transfer, or compression. Selecting the proper molding material is an essential step to produce an acceptable finished product; however, selecting the right molding method is equally important.

16.4.1.1 Compression Molding

Compression molding is the oldest form of processing thermoset molding compounds (Fig. 16.4). In its simplest form, the molds used for compression molding consist of a force and a cavity that form a two-piece mold.

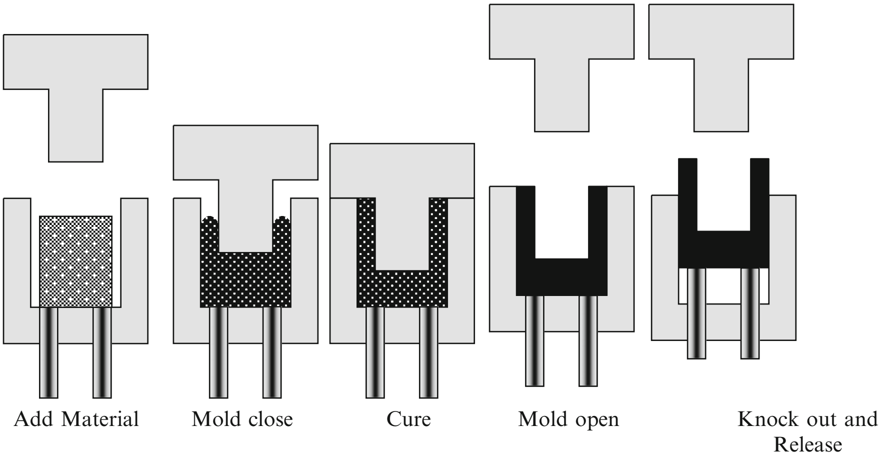


Fig. 16.4 Compression molding system

The mold contains one or more cavities in the shape of the part that is molded. The mold is heated to 160–190°C, the proper amount of material is added to the cavity (a preform heated 80–120°C might be used), and the two halves of the mold are brought together under 500–2000 psi of pressure. The compound is softened by the heat, and flows to form the shape of the cavity.

Advantages

- Mold shrinkage is minimized and reproducible, functional parts of accurate dimensions.
- Pressure is applied evenly throughout the mold, resulting in lower internal stress and warpage on the molded part.
- Dimensional accuracy perpendicular to the direction of close is possible with full positive molds.
- Minimum material is wasted.

Limitations

- Uneven parting lines may pose design problems.
- When processing full positive molds, weight control is critical.
- Dimensions across the parting line cannot be held precisely as in closed mold processing.

16.4.1.2 Transfer Molding

A transfer mold consists of a pot or chamber that is separated from the cavities, but connected to them through a system of runners and gates (Fig. 16.5). The mold is

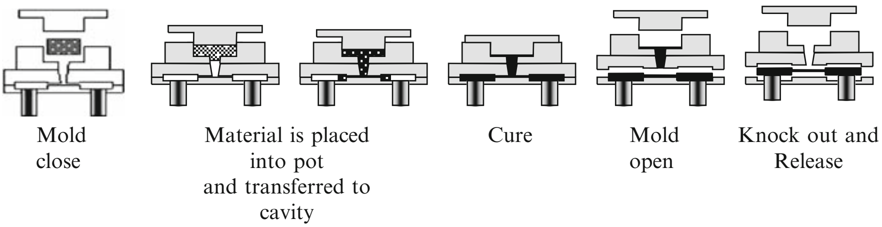


Fig. 16.5 Transfer molding system

closed and the material in the form of a preheated preform is put into the pot or chamber. Then, an auxiliary ram pushes the material through the runner and gates and into the cavities, completing the transfer process and forming the molded part.

Advantages

- A good transfer of heat throughout the mold coupled with the heat generated by friction that occurs during molding contributes to the short molding cycles.
- Higher tensile and flexural strengths can be obtained with transfer molding than with compression molding.
- The transfer process is good for molding delicate inserts and sections because the mold is closed before the process commences.
- Automatic gate-cutting of the mold's tunnel-gates is possible, providing appearance advantages and allowing for better flow and venting of the cavity.

Limitations

- The cull and runner system are scrap material.
- High molding pressures are required for the transfer process, so fewer cavities can be put into a press of the same tonnage.

16.4.1.3 Injection Molding

Injection molding is the most popular molding method (Fig. 16.6). With the ability to preheat, convey and inject plasticized material directly into a closed mold, material handling is minimized in the screw injection process. That can be a big advantage over other molding methods.

Injection molding eliminates the need for a preform, preform storage and preheating stages of compression and transfer molding. The granular molding compound is poured or conveyed directly into the injection machine hopper. Then, the

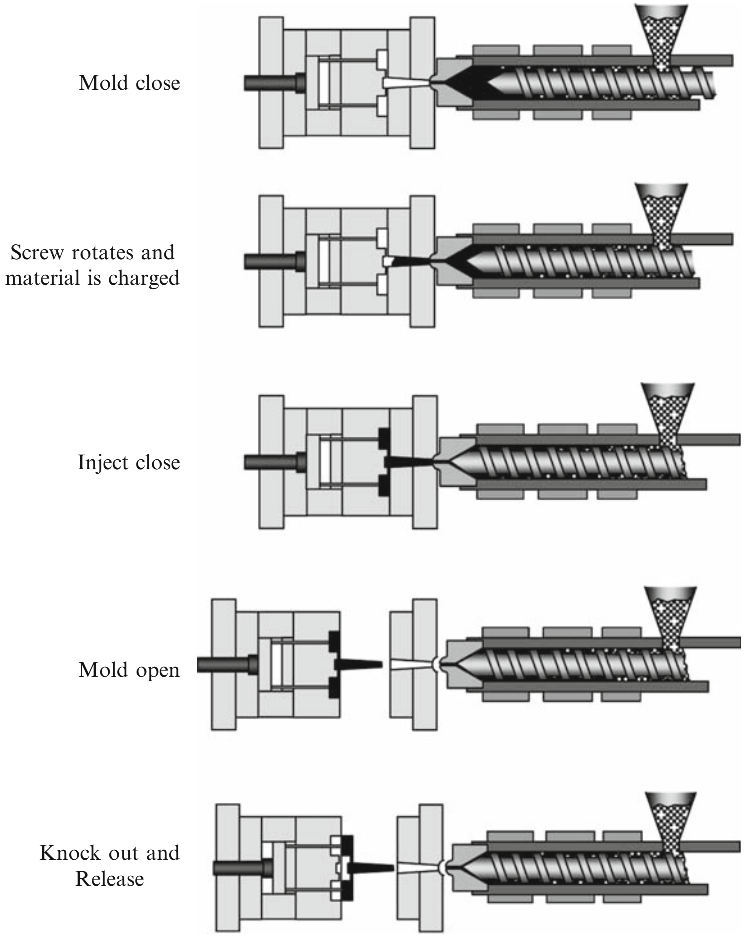


Fig. 16.6 Injection molding system

screw begins rotating and moves backward, drawing the material in from the hopper. When the required volume of molding compound has been plasticized into a soft, putty-like mass, the screw stops rotating. It moves forward, acting as a ram, and forces the plasticized compound through the sprue, runners, and gates, and into the mold cavities. After the required cure time, the mold opens and discharges the finished parts.

Most thermoplastic injection machines can be converted to mold thermosets by installing a new screw and barrel unit specially designed for thermoset materials. Most injection presses designed to mold phenolic molding compounds employ the use of 1:1 compression screws (no compression zone) and a water jacketed barrel with at least two or three heating zones.

Advantages

- Fast cure time and high productivity can be achieved with injection molding.
- The injection molding process has close tolerances, particularly when it is center-gated.
- Parts that are injection molded have an excellent surface finish, particularly when the process is fan-gated.
- Preforming and preheating stages are eliminated because the material is fed directly into the press.

Limitations

- The injection molding process generates scrap in the sprue and runner system.
- Tooling costs are generally higher than in compression molding.
- Dimensional stability is not as good as compression molding.
- In the automatic mode, insert molding requires robotics.

16.4.2 High Advantage Molding Process

As mentioned above, the molding process for thermoset materials is selected based on the part requirement. There are several ways to modify these processes, though, aimed at reducing the molding cost, improving quality and accuracy, or reducing waste. We refer to these modifications as High Advantage Molding Processes and they are based on refinement of the basic injection molding process.

16.4.2.1 High Temperature Molding

High temperature molding (HTM) has proved to be a highly effective injection molding process (Fig. 16.7). This technique superheats the thermoset material as it passes through the sprue and runner, showing significant improvements over conventional injection molding.

Conversion to HTM from a conventional injection molding process will show immediate returns. It is a low-cost method that increases output while molding parts of the highest quality.

Advantages

- HTM can improve the molded properties, for example, flexural strength, tensile modulus, Rockwell hardness, while reducing the cycle time of injection molding.
- Superior surface appearance can be achieved with HTM.

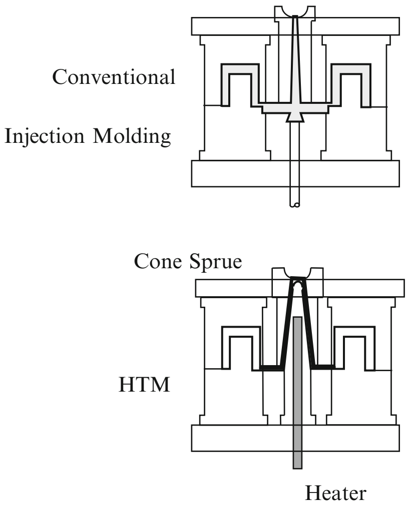


Fig. 16.7 High temperature molding

- Little to no flashing is produced across the mold surface. Runner, sprue, and gate scrap is also reduced.
- HTM reduces the risk of incomplete mold filling and gas entrapment.
- HTM can cure thicker walled parts with no increase in cycle time.
- Postbake shrinkage is reduced with HTM technique.
- Part release from the mold is improved with HTM.
- Existing conventional injection molds can be converted to the HTM process.

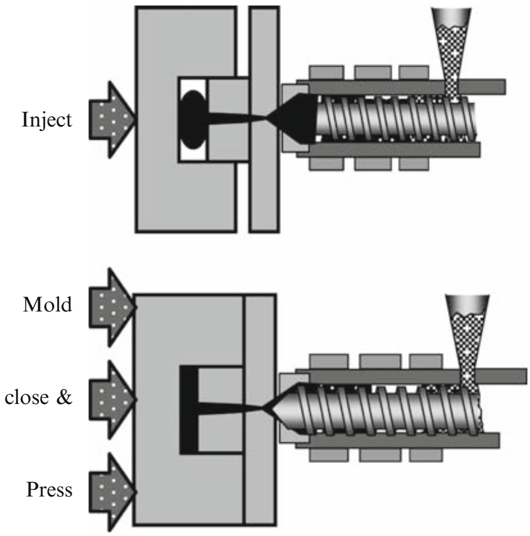
16.4.2.2 Live Sprue Molding

The conventional sprue bushing can be replaced with an oil or/water-cooled sprue bushing. This permits the sprue portion of the runner system to remain plasticized to be molded in succeeding shots. This approach is one that can be applied to existing molds in any facility on existing equipment. The cost of changeover is minimal. It is also reversible in that it can be changed back to conventional injection molding if molding requirements and customer needs dictate. Conventional injection molding materials can be used. Therefore, its use in production can generate a scrap saving that would compensate for the conversion costs. On those applications with thin sections, where sprue size dictates the cure time, a cycle time improvement may be realized because the plasticized material in the sprue remains in suspension from shot to shot.

16.4.2.3 Injection Compression

One of the best molding techniques to improve mechanical properties and accuracy is “Injection Compression Molding” (Fig. 16.8). The purpose of this molding

Fig. 16.8 Injection compression



method is to improve strength and dimensional accuracy by improving the filling density while maintaining the advantages of compression molding, such as less fiber orientation and lower molded-in stresses. This process enjoys many important benefits of both the injection and compression processes.

16.5 Test Methods for Phenolic Molding Materials

There are dozens of test methods for evaluation of properties of phenolic molding materials. Most exist under the jurisdiction of several influential standards producing organizations.

16.5.1 Standard Test Methods

International Organization for Standardization (ISO), American Society for Testing and Materials (ASTM), International Electrotechnical Commission (IEC), Japanese Industrial Standard (JIS), Deutsche Industrie Normen (DIN), and Underwriters Laboratories (U.L.) develop and publish standards affecting the characterization of phenolic molding compounds. Test methods for physical, thermal, electrical, and chemical properties are included in these standards. Comparison of many commonly used test methods from these standards is shown in Table 16.3. Although there exist many similarities among the methods, specimen shape, test speed, or

Table 16.3 Comparison of each test method

	ISO			ASTM			JIS K6911			DIN		
	No.	Test specimens	Test method	No.	Test specimens	Test method	No.	Test specimens	Test Method	No.	Test specimens	Test Method
Bulk factor	60	Compounds	Measuring cylinder	–	–	–	5.2.1	Compounds	Measuring cylinder	–	–	–
Specific gravity	1,183	Molded parts	Sink–float method	D1,505	Molded parts	Sink–float method	5.28	Molded parts	Sink–float method	53,479	Molded parts	Sink–float method
Molding shrinkage	2,577	SG 170 × 10 × 4 mm P 120 × 10 × 4 mm	23°C/24 h length change	D955	165 × 13 × 7 mm 115 × 6 × 4 mm	23°C/24 h length change	5.7	ϕ 90 × 5 mm∧t	23°C/24 h diameter change	53,464	120 × 15 × 10 mm	23°C/24 h length change
Water absorption	62	ϕ 50 × 3 mm∧t others	50°C/24 h in water weight change	D1242	ϕ 51 × 3.2 mm∧t others	23°C × 24 h in water weight change	5.26	ϕ 50 × 3 mm∧t	23°C × 24 h in water weight change	53,495	ϕ50 × 3 mm∧t others	23°C × 24 h in water weight change
Rockwell hardness	2,039/2	Molded parts	M scale: Load = 1000 N Time = after 30 s	D1822	Molded parts	M scale: Load = 1000 N Time = after 30 s	5.16.1	d = 6 mm<	M scale: Load = 980 N Time = after 30 s	–	–	–
Heat deflection temperature	75	110 × 10 × 4 mm 80 × 10 × 4 mm	Load = 1.8 MPa Speed = 2°C/min	D648	127 × 13 × 3 ~ 13 mm	Load = 1.82 MPa Speed = 2°C/min	5.35	127 × 13 × 3 ~ 13 mm	Load = 1.81 MPa Speed = 2°C/min	53,461	110 × 10 × 4 mm	Load = 1.82 MPa Speed = 2°C/min
Flexural strength Flexural modulus	178	80 × 10 × 4 mm	3-point loading Speed = d/2 = 2 mm/min	D790	130 × 13 × 6.4 mm	3-point loading Speed = 2.8 mm/min	5.17	80 × 10 × 4 mm	3-point loading Speed = d/2t	53,452	80 × 10 × 4 mm	3-point loading Speed = 1,2,5, 10, 20,50,100,200 mm/min
Tensile strength Tensile modulus Tensile elongation at break	527	Type A (ISO3167)	Speed = 1,5,50, 100,500 mm/min	D638	Type I, II, III, and V	Speed = 5,50, 500 mm/min	5.18	Fig. 30 in 5.18 (110 × 45 × 6.5 mm)	Speed = 5 mm/min	53,455 (EN61)	No. 3 in Fig. 2 in 53,455 (150 × 20 × 4 mm)	Speed = 1,5,10, 50,100,200, 500 mm/min
Compressive strength	604	10 × 10 × 4 mm	Arbitrary speed	D695	12.7 × 12.7 × 25.4 mm	Speed = 1.3 mm/min	5.19	12.7 × 12.7 × 25.4 mm	Speed = 1 mm/min	53,554	10 × 10 × 10 mm	Speed = 1,2,5,10, 20,50,100 mm/min
Impact strength (notched and unnotched): Charpy/Izod	179/180	Charpy: 80 × 10 × 4 or 50 × 6 × 4 mm Izod: 63.5 × 12.7 × 3.2(6.4) or 80 × 10 × 4 mm (Notch: V-form)	Pendulum capacity = 0.5, 1, 4, 15 J	/D256	63 × 12.7 × 12.7 mm (Notch: V-form)	Pendulum capacity = 2.71 – 21.68 J	5.2/	90 × 15 × 15 mm Notch: U-form (notched only)	Not defined	53,453/	120 × 15 × 10 or 50 × 6 × 4 mm (Notch: U-form)	Pendulum capacity = 0.5, 1, 4, 15 J

(*continued*)

Table 16.3 (continued)

	ISO			ASTM			JIS K6911			DIN		
	No.	Test specimens	Test method	No.	Test specimens	Test method	No.	Test specimens	Test Method	No.	Test specimens	Test Method
Dielectric strength	EC243-	Plate, foils (No prescription of thickness)	Stepwise in air or oil at 23°C	D149	No prescrition	Short time (500 V/s) in air, gas, or oil at 23°C	5.11.3	ϕ 100 × 2 mm∧t or 100 × 100 × 0.8 ∼ 3 mm∧t	Short time, stepwise (20 s step) in oil at 20 or 90°C	53,481/ VDE03 03 part2	Plate up to 3 mm∧t	0.5 ∼ 1 kV/s in air at 20°C
Surface resistance Volume resistance	93	Plate	–	D257	Plate	–	5.13	ϕ 100 × 2 mm∧t	–	53,482/ VDE03 03 part3	120 × 120 mm No prescription of thickness	–
Arc resistance	–	–	–	D495	Plate 3.2 mm∧t	90–130 V/steps of 1 min Tungsten bar	5.15	ϕ100 × 3 mm∧t	12.5 kV Tungsten bar	53,484/ VDE03 03 part5	120 × 120 mm No prescription of thickness	220 V Carbon ϕmm
Flame retardance	UL94	–	–	UL94	–	–	UL94	–	–	UL94	–	–

other test conditions may lead to different determinations. For this reason, migration to ISO standards has been encouraged globally. This has proven to be a difficult process, as each governing body has a long history and each country affected has a testing and reporting infrastructure built around their existing methods.

16.5.2 Flowability Test

The flow of phenolic molding materials is a measure of the combination of molten viscosity and cure speed. Unlike thermoplastics, the behavior is a very complex because molecular weight increases with temperature and time [1]. As a result, precise characterization of the molding properties of phenolic molding compounds can present a challenge for the manufacturer and user. Manufacturers and molders have developed many tests, over the years, to determine the molding character of materials, and each one has its strengths and weaknesses. Many producers have more than one method and adapt their test plan, in agreement with the product users, around the most discerning method for each grade. Some of the more common test methods are presented.

16.5.2.1 Orifice Flow Method [2]

Figure 16.9 is a depiction of an orifice flow die. This method derives data based on the flow rate of molten material. Material (specified weight: 50 g ± within 0.1 g) is charged to the cavity which is heated to a predetermined temperature (usually 165°C). The mold is closed under closely controlled pressure and the material extrudes through two diagonally opposed v-notches. The flow rate is calculated by weighing the material remaining in the cavity at the end of the test. Test pressure can be changed to accommodate materials in a wide range of plasticities.

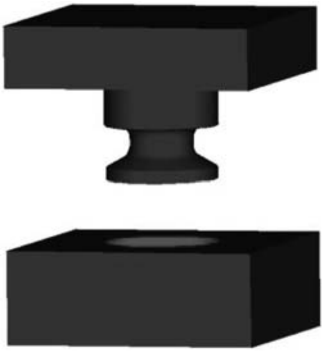


Fig. 16.9 Orifice flow die

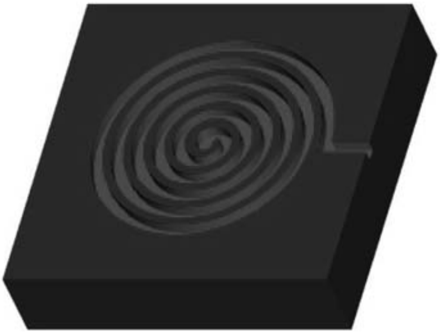


Fig. 16.10 Spiral flow die

16.5.2.2 Spiral Flow (Farrell Flow) Method [3]

This method uses a die with a spiral-shaped cavity like Fig. 16.10. Flow value is derived from the length of flow in the spiral cavity.

16.5.2.3 Disk Flow Method [4]

Expansion of material that is sandwiched between flat surface dies is measured in this method. Material weight, die temperature, compression pressure, and compression time have to be carefully controlled. The flow value is derived by measuring the diameter of the glossy part on the molded disk.

16.5.2.4 Cup Flow Method [4, 5]

This method uses a die with a cup shaped cavity. A carefully weighed sample is molded under prescribed pressure at a constant die temperature. Flow value is based on the close time of the die, the flash thickness, and part appearance.

16.5.2.5 Torque Rheometer Method [6]

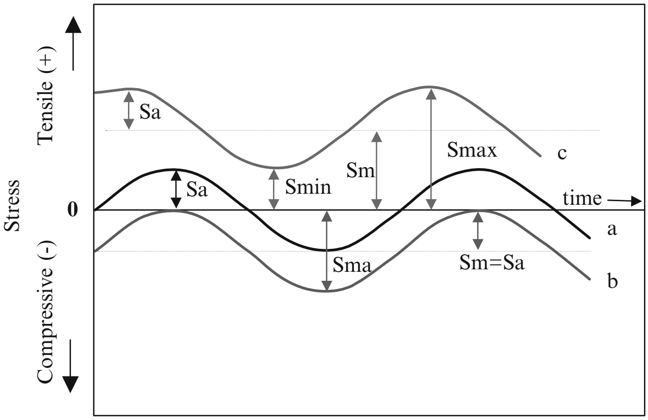
In this method, a sample of phenolic molding compound is charged into a temperature controlled mixer/measuring head, in which the material is compacted, melted, cross-linked, hardened, and crushed under constant shear. The output data are the minimum torque value measured after the resin has been fused, before the compound increases in molecular weight during the curing process. This test also generates a cure time value that is often useful as a troubleshooting tool where side-by-side comparison of materials is possible.

16.5.3 Reliability Test

In recent years, phenolic molding compounds have become attractive alternatives to metals and the use of glass reinforced materials in such applications has increased. Dramatic weight reductions have been realized, but development of more reliable phenolic materials is necessary for the expansion of this industry segment to continue. It is important that mechanical properties are not degraded over the expected life of the component. In case of metal materials, a respectable database has already been established related to fatigue, creep, thermal properties, and more. However, plastics have not developed such an extensive body of knowledge, and this applies to phenolic molding compounds, too. In order to make further advances in the field of metal replacement, it is imperative that these data be made available in the marketplace.

16.5.3.1 Fatigue Test

Fatigue testing is performed by subjecting a test part to sine wave oscillation, as shown by Fig. 16.11. Each test cycle is completed when the test specimen breaks as stress amplitude (Sa) is added under constant mean stress (Sm). The data are plotted on a graph (horizontal axis: cycle numbers, vertical axis: Sa). This graph is called "S-N curve." An S-N curve of a glass-filled phenolic material is shown in Fig. 16.12. In the case of steel, the upper stress limit of unbroken specimens at



S_a : Stress amplitude
S_{max} : Maximum stress
S_m : Mean stress
S_{min} : Maximum stress

"a" is reversed stress (tensile-compressive).
"b" and "c" are repeated stress (tensile or compressive).

Fig. 16.11 Stress cycle for fatigue test

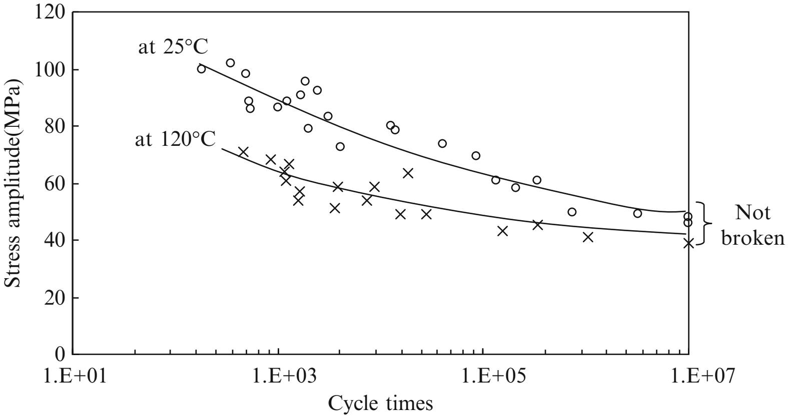


Fig. 16.12 S-N curve of glass-filled phenolic molding compound

10^7 cycles becomes the fatigue limit because the flat part of the curve is found around 10^6–10^7 cycles on the graph. In case of plastics, the flat portion is not found in many cases. So, the Sa value of unbroken specimens at 10^7 cycles is generally recognized to be the fatigue limit for plastics. The test frequency for plastics is generally set at less than 30 Hz, because test specimen can be affected by the heat generated at higher frequencies.

The fatigue limit diagram is a used to visualize the relationship between fatigue strength and Sm. A Goodman diagram, which is shown in Fig. 16.13, is a typical fatigue limit diagram. Line At is the fatigue strength line that was derived from fatigue testing. In the case of steel, the yield limit line FYt (FYc) is the 45° line from yield stress Yt (compressive side: Yc) on X-axis. However, as phenolic molding compounds do not have a yield point, a stress level at 0.2% strain % is assumed for yield stress. As the result, the combination of Sa and Sm in the quadrangle bounded by YcBEYt represents the safe application conditions for fatigue.

16.6 Applications

16.6.1 Electrical Applications

One of the principal applications of phenolic molding compounds is in electric switch gear such as circuit breakers and magnetic switches (Fig. 16.14). These parts provide the outstanding phenolic resin characteristics such as excellent electrical insulation, heat resistance, and strength properties. But many other thermosetting materials exhibit better tracking resistance than phenolic molding compounds, which are generally in the 150 V range. The reason may relate to the phenolic

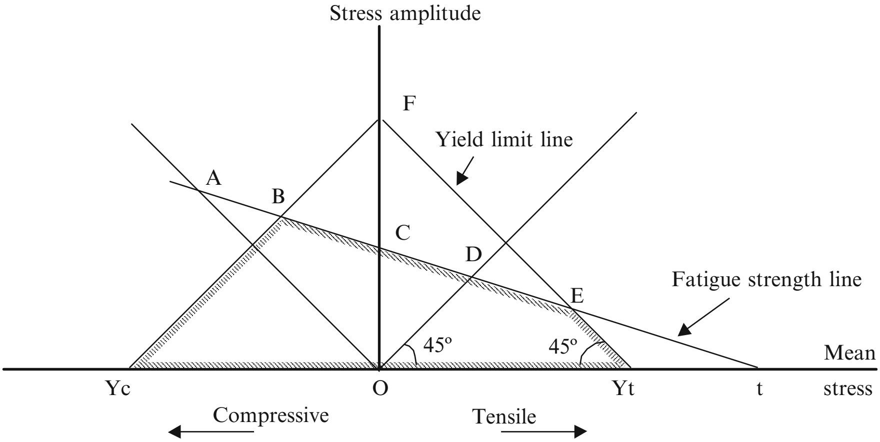


Fig. 16.13 Goodman diagram

Fig. 16.14 Breaker and magnet switch

resin which forms a char when pyrolytically decomposed. Since the tracking resistance property is linked to the basic chemistry of the phenolic resin, it is difficult to improve this behavior. But, this property is offset by better price performance compared with other thermosetting materials. Thermoplastic materials are generally inferior in glow wire properties. So, it is anticipated that the market's preference for phenolic molding compounds in these applications will continue.

In recent years phenolic molding compounds have been developed with a Comparative Tracking Index of 250 V for use in high voltage applications.

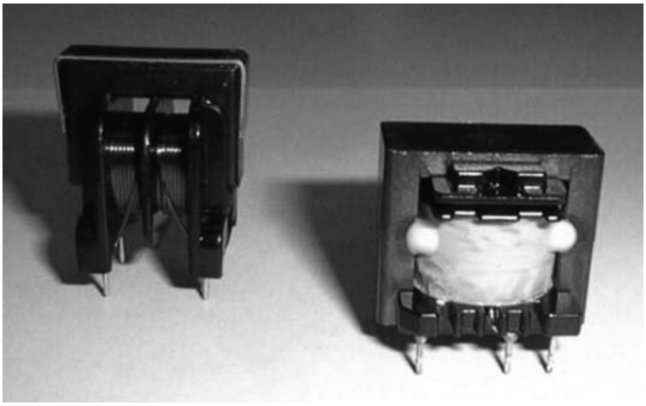


Fig. 16.15 Coil bobbin

16.6.2 Electronics Applications

The main application for phenolic molding compounds in the electronics market is the coil bobbin which is used for transformers in such devices as televisions and personal computers (Fig. 16.15). Superior heat resistance is required when the bobbin wiring is soldered to the circuit board. Compatibility with metal components is another important property, so resole based materials are used in many cases to the avoid ammonia gas, which will corrode the metal. The life of copper wire is longer using one-step resins, rather than two-step.

As electronic parts continue to diminish in size, customers have reduced the wall thicknesses of their coil bobbins. In recent years, liquid crystal display (LCD) televisions have become very popular consumer products. The LCD display uses a coil bobbin in the inverter component. These thin-walled coil bobbins require high strength and toughness. Traditionally, these applications call for liquid crystal polymers, rather than phenolics. In recent years, though, toughened phenolic molding compounds have gained acceptance.

16.6.3 Commutator Applications

One of the most common applications of phenolic molding compounds in electric motors is in commutators (Fig. 16.16). Commutators are used in motors for household, automotive, industrial, and heavy equipment markets and require high performance materials. There are a number of small electric motors in each auto and truck. Examples are motors for the starter, power windows, wipers, fuel pump, and electric power steering. The typical luxury car contains even more options such as the power antenna, power trunk, sun roof, and seats, to name a few. Commutators consist of insulating bodies that possess a large number of laminar copper segments.

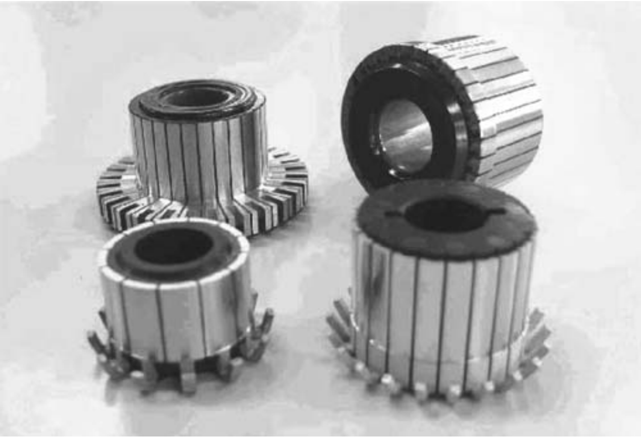


Fig. 16.16 Commutator

Copper sections must be solidly anchored in the commutator body and have no contact with other segments. The commutator is mounted on the drive shaft of the motor. The mounting method depends on the expected performance demands, where the commutator may be bonded with a metal insert before assembly or where it is pressed directly on the motor shaft. In this case, the material requires a tolerance for mechanical stresses of press fit; otherwise it may burst in assembly or fail in service. Unlike the press fit commutators, the bonded commutators generally have a metal insert that reduces the expansion forces on the phenolic body of the commutator. In addition, the commutator must withstand thermal stresses during assembly. In the fusing process the wire terminals of the windings are welded and attached to the copper segments of the commutator, a process during which extremely high temperatures and force can develop for a short period. During this assembly step, the temperature on the surface of the copper components may reach 600°C or more and the temperature of the molding compound may exceed 300°C.

The commutator is exposed to two main forms of stress when the electric motor is in operation: (1) centrifugal force and (2) thermal stresses due to the frictional heat with the motor brushes.

The criteria for phenolic molding compound in commutator applications require properties that may be summarized as: (1) good electrical insulating strength, (2) high mechanical strength, (3) high thermal resistance, (4) high expansion resistance, and (5) forgiving processing properties. Regarding this last item, the user needs a molding compound with low abrasion to minimize the wear on cutting tools during the slotting operation, an assembly step that separates the copper segments in shell type commutators. Most commutator materials are fiberglass filled. Other fillers and reinforcements may be added to the formula to assure high dimensional stability and the materials are generally formulated with low resin content for the same reason. To improve the dimensional stability even further, and to improve performance at elevated temperatures, a postbake step is nearly always employed. Postcure is important to satisfy two objectives: (1) completion of the curing reaction and (2) release of volatile reaction products. Additionally, various characteristics improve: (1) electrical properties, (2) a desirable coefficient of thermal expansion, (3) thermal shock resistance, and (4) a high mechanical strength.

16.6.4 Automotive Applications

Phenolic molding compounds require good heat resistance, good creep properties, chemical resistance, and other critical properties to satisfy the demands of under-the-hood applications.

The high performance phenolic molding compounds meet the requirements of current and future automotive systems such as air/fuel management, exhaust, cooling, and lubricating components. The exceptional combination of heat resistance, chemical resistance, and mechanical strength makes them the preferred materials for such systems. The substitution of these materials for steel and aluminum alloys contributes to significant cost and weight reduction.

The following are examples of successful applications:

16.6.4.1 Air Supply Systems

The advantages of high performance phenolics in air supply systems was, at first, not so apparent to automotive engineers, as the application temperature was relatively low and there was no exposure to aggressive chemicals. But eventually, high performance phenolic molding compounds were selected over other polymers because they combined low creep and warpage, high dimensional capability, and high mechanical strength with weight and cost savings compared to aluminum or magnesium components.

Intake Manifold

The fully variable air intake manifold was developed for the German 8-cylinder gasoline engine. The main purpose for this development was to increase torque level over that of its predecessor. This was achieved by using a newly developed, unique, continuously variable intake manifold molded in glass fiber reinforced phenolics. The engineering thermoplastics, such as glass fiber reinforced PPS and PPA were evaluated in this application, but failed due to the complexity of the construction and their lack of necessary dimensional stability at high temperature. Glass fiber reinforced phenolics solved the problems (Fig. 16.17).

Fig. 16.17 Intake manifold

Fig. 16.18 Throttle bodies

Throttle Bodies

“Drive-by-Wire” system throttle body produced in phenolic meets the requirements for high dimensional stability in order to maintain the desired air–fuel ratio at all engine temperatures over the life of the vehicle (Fig. 16.18)

Exhaust Gas Recycling Thermal Insulation

High performance phenolics are used as thermal insulation between metal and thermoplastic engine components. We believe that high performance phenolics could play an even bigger role in such applications in the future (Fig. 16.19).

Fig. 16.19 Exhaust gas recycling thermal insulation

Fig. 16.20 Cooling systems

16.6.4.2 Cooling Systems

High performance phenolics provide enhanced performance in cooling systems. Weight and cost savings are combined with improved cooling efficiency in water pumps, impellers, thermostat housings, water inlets, and outlets. They can be molded into complex shapes and withstand hot coolants based on glycol/water mixtures. In water pumps, their high mechanical strength and creep resistance withstand the severe side load caused by belt tension and the compressive loads generated by bolting directly to the engine block without metal inserts (Fig. 16.20).

Fig. 16.21 Fuel systems

16.6.4.3 Fuel Systems

Worldwide, regulatory emission requirements and customer expectations are becoming ever more stringent. The automotive industry is continuously developing lower emission, noise, and fuel consuming engine systems. High performance phenolics play a significant role in today's advanced fuel systems. Their high dimensional stability, tight molding tolerances and low fuel absorption properties contribute to increased pump efficiency (Fig. 16.21).

Fuel Pump Housing/Impeller

Since the introduction of the synthetic fuels and biofuels, the fuel absorption of most engineering thermoplastics is too high, causing problems with dimensional stability. High performance phenolics are proven performers and are used worldwide in automotive fuel pump systems (Fig. 16.22).

16.6.4.4 Brake Systems

Disc Brake Caliper Piston

High performance phenolics are widely used in disc brake calipers, combining high heat resistance, high mechanical strength, good chemical resistance, and other advantages to contribute to weight and cost savings. The excellent insulating properties of phenolics can prevent brake loss due to fluid boil. Several studies have shown advantages for noise/vibration/harshness (NVH) performance in brake systems (Fig. 16.23).

Fig. 16.22 Fuel pump housing/impeller

Fig. 16.23 Disc brake caliper piston

Antilock Braking System Components

High performance phenolics are used to produce the precision components for Antilock Braking Systems (ABS). ABS pistons, ABS-activating parts, guides, and spacers are all examples of these applications. They offer good resistance to hydraulic brake fluids and meet the critical requirements for heat resistance, dimensional stability, and mechanical loading. Complicated parts can be molded to tight tolerances so that machining of the parts is not necessary (Fig. 16.24).

Fig. 16.24 ABS system components

Fig. 16.25 Pulleys

16.6.4.5 Pulleys

Multi-V pulleys, cog belt pulleys, idlers, and tensioners are manufactured using high performance phenolics. There are a number of benefits, including lower cost, weight savings compared to the metal version, cooler and quieter operation at all engine speeds. Furthermore, they do not require balancing or anticorrosion treatment (Fig. 16.25).

Fig. 16.26 Cog belt pulleys – belt driven camshaft

Cog Belt Pulleys – Belt Driven Camshaft

Replacing sintered metal in this application was a challenge for a polymeric material. High performance phenolics designed with superior dimensional stability provide high reliability in a wide range of temperatures. The compound allows the possibility of producing camshaft pulleys without a metal hub insert. This solution offers cost reduction, substantial weight savings, and eliminates corrosion (Fig. 16.26).

Multi-V Pulleys

High mechanical strength, low creep, and good chemical resistance are the critical properties required to convert from metal to plastic multi-V pulleys in such applications as idlers, alternators, water pumps, power steering, and air conditioners. High performance phenolics provide great advantages as they require no balancing, are corrosion resistant, and have proven to be highly reliable in multi-V pulley applications (Fig. 16.27).

16.6.4.6 Transmission Systems

Torque Converter Stator and Thrust Washers

The principle benefit of a stator molded from high performance phenolics is the fact that they can be assembled into the torque converter with very few secondary

Fig. 16.27 Multi-V pulleys

Fig. 16.28 Torque converter stator and thrust washers

operations after molding. Another benefit is the good molded surface finish of the vanes, which results in improved pumping efficiency (Fig. 16.28).

The principle benefit of the phenolic thrust washer is lower system cost. However, a phenolic thrust washer may have higher “drag torque” over a needle roller bearing. This increased “drag torque” can be marginal depending upon the torque converter and phenolic thrust washer designs. A major advantage is that the phenolic thrust washer can be integrated into the phenolic stator, thus eliminating a needle roller bearing at a minimal incremental cost.

Clutch Actuation Pistons

An integrated magnetic sensor in the clutch actuator precludes the use of steel pistons. High performance phenolic pistons achieve higher efficiency, reduced NVH, weight reduction, and are quite durable (Fig. 16.29).

Fig. 16.29 Clutch actuation pistons

Valve Block for Dual Clutch Transmissions

Dual clutch transmissions (DCTs) offer smooth acceleration by eliminating the shift shock that accompanies gearshifts (up-shifts taking a mere 8 ms) in manual transmissions and even some automatics. It affords drivers the luxury of choosing whether they prefer to control the shifting or let the computer do all of the work. But, the most attractive advantage of a DCT is improved fuel economy. As power flow from the engine to the transmission is not interrupted, fuel efficiency increases dramatically (up to 10% increase in relative fuel efficiency). The hydraulic control system of the DCT is equipped with two valve bodies made from high performance phenolics. Using glass fiber reinforced phenolics provides advantages such as reduced cost, weight savings, and high reliability. These advantages result in better fuel economy and reduced emissions (Fig. 16.30).

16.6.4.7 Automotive DC Motor Systems

Many small DC motors are used in today's vehicles, including the starter motor, blower motor, window shield wiper motor, HVAC motors, and more. Good heat resistance, combined with excellent mechanical and electrical properties of high performance phenolics can result in part consolidation in applications such as brush holders, solenoid covers, and housing applications (Fig. 16.31).

Fig. 16.30 Valve block for dual clutch transmissions

Fig. 16.31 Automotive DC motor systems

16.7 Comparison with Other Materials

16.7.1 Comparison with Engineering Thermoplastics

Table 16.4 compares typical engineering thermoplastics with several phenolic molding compounds. These materials are compared for temperature dependence of flexural strength and modulus (Fig. 16.32), heat resistance (Fig. 16.33), water and engine oil resistance (Figs. 16.34 and 16.35), tensile creep (Fig. 16.36), stress relaxation (Fig. 16.37), tensile fatigue strength (Fig. 16.38), and dimensional accuracy at molding (Fig. 16.39).

As shown in Fig. 16.32, as PPS, PPA, and PBT approach their glass transition temperatures, their flexural strength and modulus change dramatically. Conversely, phenolic molding compounds retain their strength and modulus at temperatures exceeding 150°C due to the three-dimensional cross-linked structure.

Table 16.4 Materials used for evaluation

Typical properties			Phenolic molding compounds			Engineering thermo plastics		
Item	Method	Unit	PM-9640	PM-9615	X655	PPS (40)	PPA (35)	PBT (45)
Glass fiber		wt%	55	65	15	40	35	45
Specific gravity	ISO 1183	–	1.78	1.87	2.08	1.66	1.48	1.68
Rockwell hardness (M scale)	ASTM D-785	–	127	127	117	119	125	120
Flexural strength	ISO 178	MPa	230	230	185	270	285	215
Flexural modulus	ISO 178	GPa	17.6	20.2	25.0	14.2	11.7	13.3
Tensile strength	ISO 527-1,2	MPa	125	140	90	135	165	120
Tensile modulus	ISO 527-1,2	GPa	18.6	21.6	29.4	15.7	13.4	15.1
Compressive strength	ISO 604	MPa	320	345	360	245	315	190
Charpy impact strength notched	ISO 179-1	kJ/m2	2.8	3.2	2.7	9.0	8.9	8.7

Note: The values in parenthesis indicate wt% fiberglass in each material

Note: Injection molded multi-purpose test specimens (MPTS) in accordance with ISO 3167

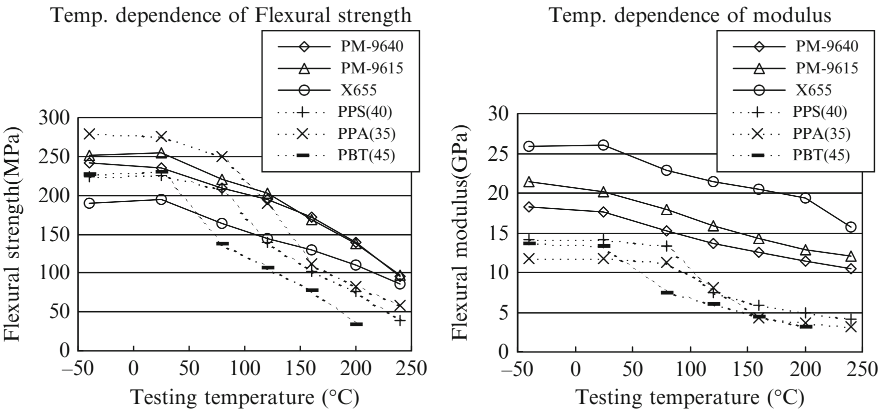


Fig. 16.32 Temperature dependence of flexural strength and modulus

As shown in Figs. 16.33–16.35, phenolic molding compounds perform as well as or better than engineering thermoplastics in heat resistance, water and engine oil resistance.

Figures 16.36 and 16.37 show the superior creep resistance and stress relaxation resistance of phenolic molding compounds, making them well suited for long-term reliability under load.

Also, Fig. 16.38 shows the superior fatigue properties of phenolics in comparison with the engineering thermoplastics.

Lastly, as shown in Fig. 16.39, phenolic molding compounds become quite rigid as the result of the three-dimensional cross-linked structure in the die and the isotropy compares well with engineering thermoplastics. For these reasons, the

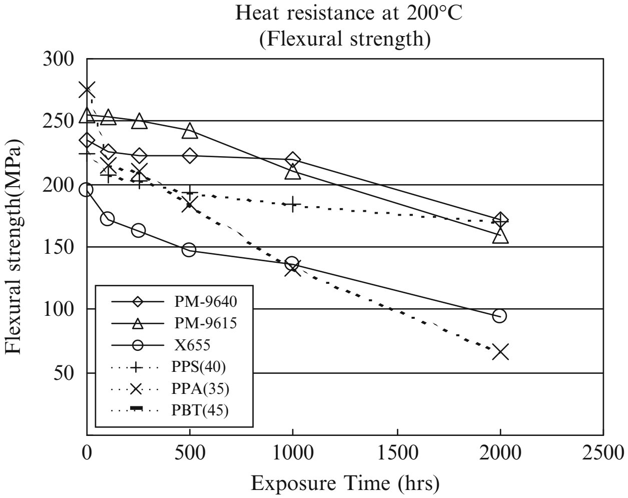


Fig. 16.33 Heat resistance

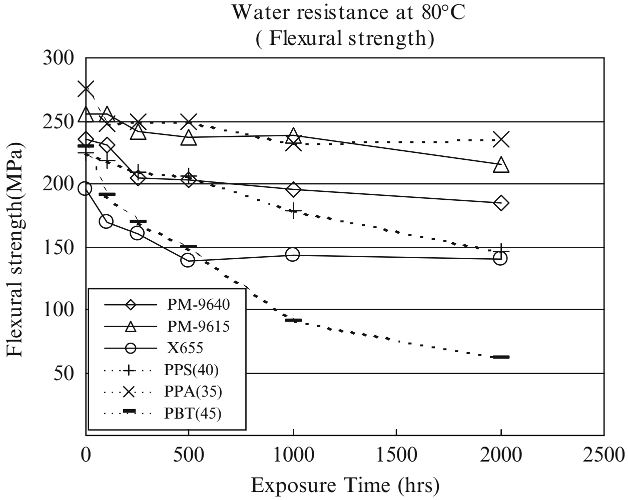


Fig. 16.34 Water resistance

materials have a good transcription to the die. As a result, dimensional accuracy and roundness are typically much better than engineering thermoplastics.

Because of the excellent heat resistance and good long-term reliability of glass-filled phenolic molding compounds, phenolic molding compounds continue to be used in automotive applications where thermoplastics can- not be tolerated.

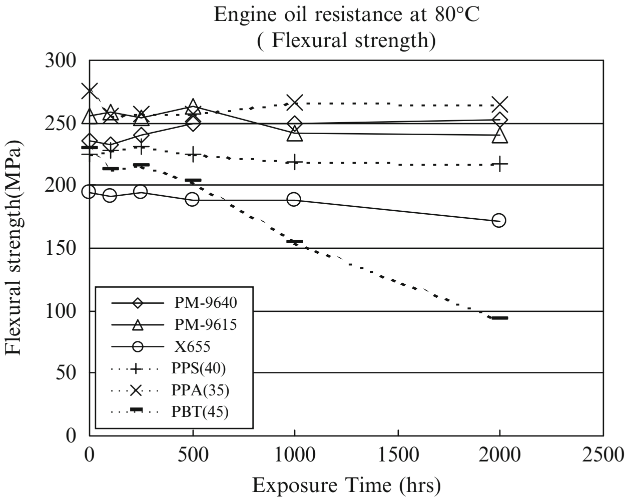


Fig. 16.35 Engine oil resistance

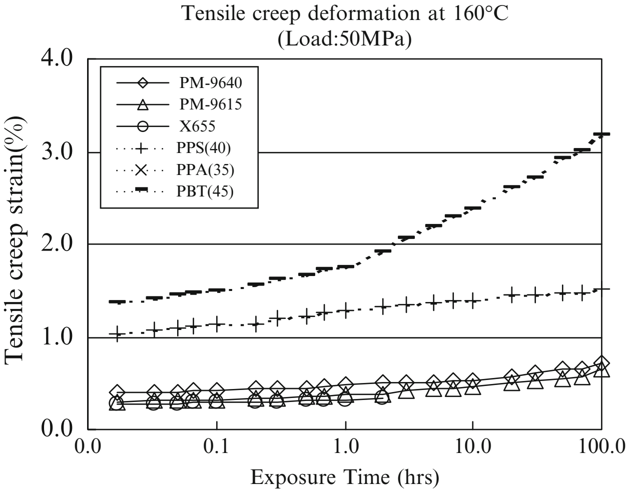


Fig. 16.36 Tensile creep

16.7.2 Comparison with Die Cast Aluminum

Chopped glass phenolic molding compounds and die cast aluminum are popular under-the-hood materials as they can potentially provide both weight and cost savings. Table 16.5 compares the general mechanical properties, and Fig. 16.40 compares the stress-strain curves of a high performance chopped glass-filled phenolic with ADS12 die cast aluminum. The strength of the molding compound is

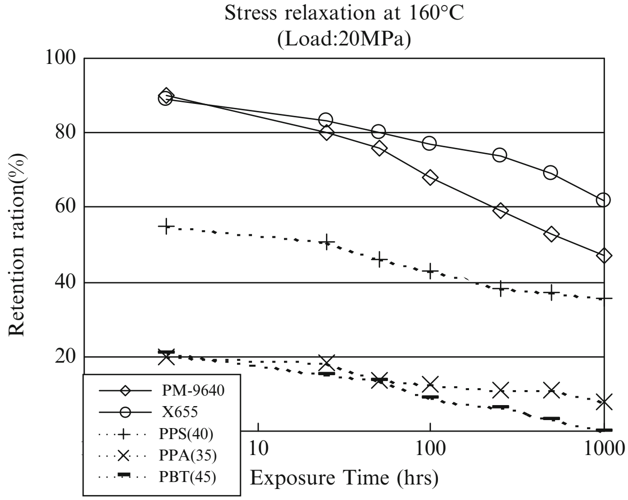


Fig. 16.37 Stress relaxation

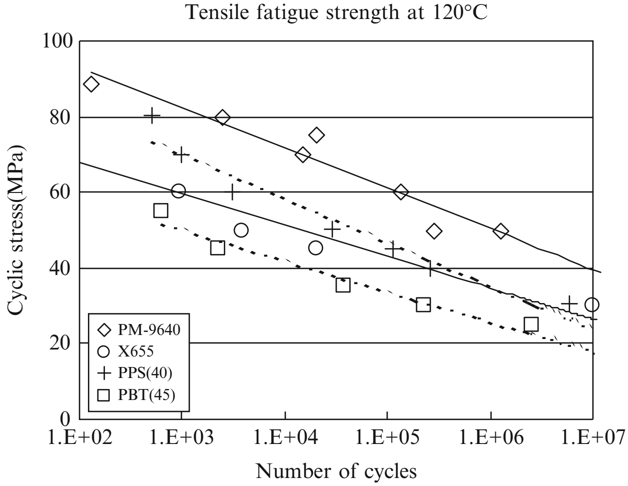


Fig. 16.38 Tensile fatigue strength

inferior to that of ADS12, but specific tensile strength (tensile strength/specific gravity) and tensile yield stress of PM-5210 are similar to those of ADS12.

The Tensile Yield Stress for die cast aluminum is not clear. In this case, a 0.2% strain rate is assumed for a basis of comparison.

Since phenolic molding compounds are a close match to die cast aluminum in specific tensile strength, they make an attractive alternative in under-the-hood applications.

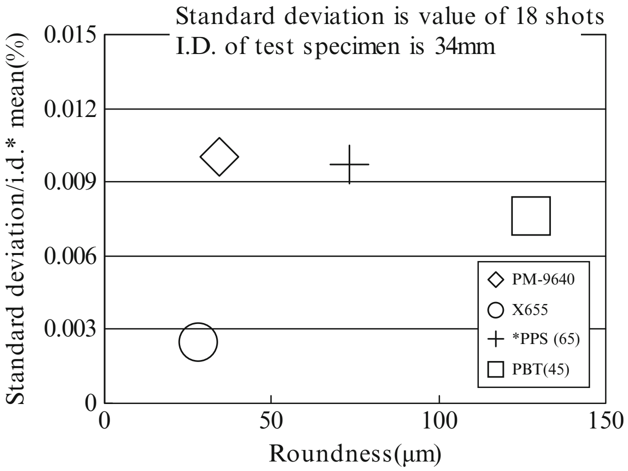


Fig. 16.39 Dimensional accuracy at molding

Table 16.5 Compared with die-casted aluminum

Items	Unit	PM5210	ADC12
Specific gravity		1.79	2.68
Tensile strength	MPa	180	300
Specific tensile strength (tensile strength/specific)	–	100	110
Tensile modulus	GPa	19.0	70.6
Tensile yield stress	MPa	180	180
Flexural strength	MPa	260	525
Flexural modulus	GPa	18.0	63.0

16.8 New Phenolic Molding Compounds

16.8.1 Long Fiber Reinforced Materials

As discussed in the preceding sections, chopped fiberglass reinforced phenolic molding compounds have been widely applied as automotive structural components in recent years. These applications are evidence that the materials' excellent mechanical properties, heat resistance, and other properties are reliable in long-term use. The mechanical strength and high modulus at elevated temperatures make them excellent choices where thermoplastics are subject to failure. On the other hand, their impact resistance is inferior to engineering thermoplastics, despite the excellent static mechanical strengths. Improving the impact resistance of thermoset molding materials has been an industry research objective for many years.

Carbon fiber prepregs, though, have become very popular structural materials for use in such demanding applications as aircraft wings, wing boxes, and fuselages.

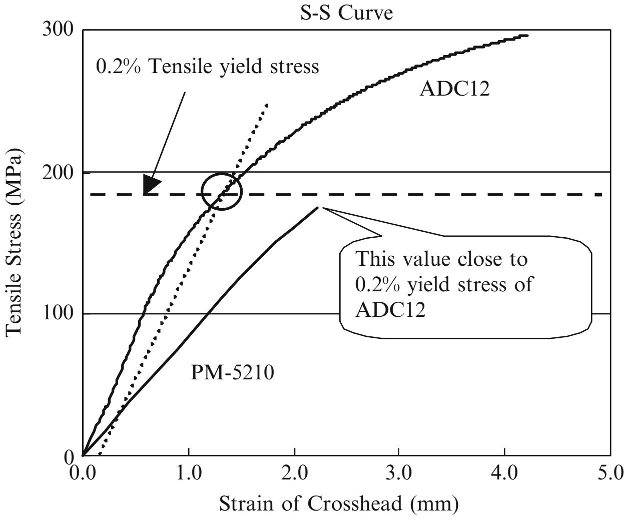


Fig. 16.40 Strain-stress curve of ADC12 and PM-5210

These composites are completely different materials from the shorter chopped glass reinforced molding compounds described in previous sections, comparing mechanical properties, costs, and processability.

A thermosetting resin prepreg composite is usually resin impregnated onto woven fiberglass or carbon cloth, and is assembled in various fiber direction plies. The mechanical strength of these cured prepregs, especially resistance to impact, is vastly superior to the shorter chopped glass forms of phenolic molding compound because of the longer fiber length. The typical fiber length of glass reinforced phenolic molding compounds, after the material has been compounded and molded, is approximately 0.3 mm. In contrast, the typical fiber length of long fiber thermosetting molding compounds is 3–5 mm, and can be 12–50 mm, if higher mechanical properties are required. When reinforced in such a way, these long glass reinforced materials have impact resistance superior to engineering thermoplastics. Typical properties of some long fiber reinforced thermoset materials are shown in Table 16.6 and Fig. 16.41.

These long fiber reinforced thermoset materials have the features of conventional short fiber filled materials like static strength, heat resistance, chemical resistance, etc., but have 10–20 times impact strength of shorter fiber filled materials. Moreover, they have some of the desirable features of the shorter glass-filled materials, such as ease of molding and design flexibility for complex geometries, which prepreg composites do not possess. Long fiber reinforced thermoset materials fill the gap between short fiber filled materials and prepreg composites, and are expected to expand their markets, not only in the direction of these two types of materials, but also to new markets.

Table 16.6 General properties of long fiber reinforced thermoset molding compounds

Matrix resin		Long fiber reinforced materials					Short fiber
		Glass fiber		Carbon fiber		Aramid	Glass
		PF	EP	PF	EP	PF	PF
Fiber length	mm	12	8	12	12	3	—
Specific gravity	—	1.90	1.86	1.51	1.43	1.38	1.78
Mold shrinkage	%	0.09	0.09	−0.01	0.02	0.34	0.24
Tensile strength	MPa	115	119	151	145	185	140
Tensile modulus	GPa	30	24	49	46	14	22
Flexural strength	MPa	283	223	340	363	268	230
Flexural modulus	GPa	25	17	31	32	10	20
Charpy impact str.	KJ/m^2	55	52	60	50	37	3

Molding method: Compression molding (long fiber reinforced materials) and injection molding (short glass fiber filled material)
Test method: based on ISO
PF phenol–formaldehyde resin, *EP* epoxy resin

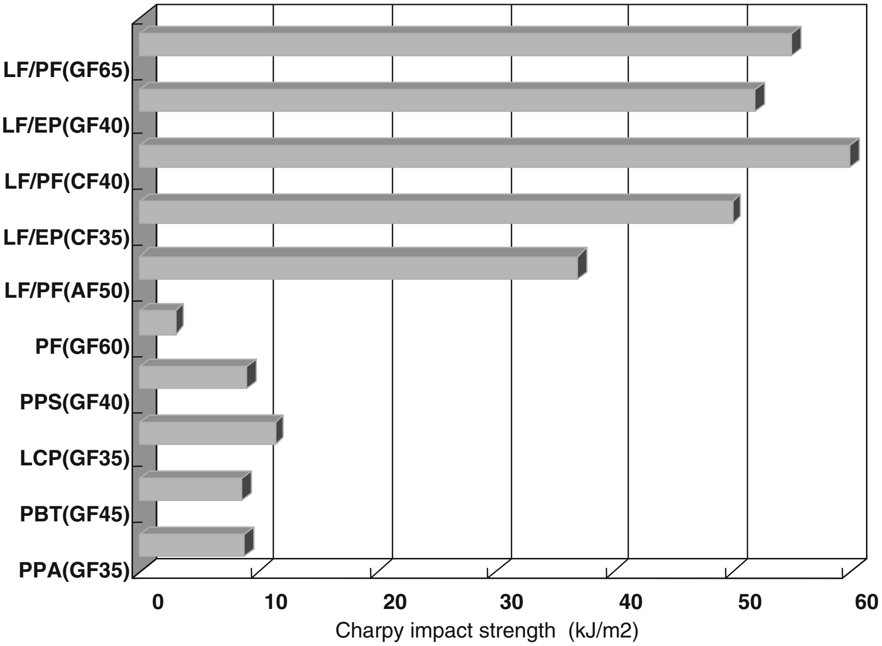


Fig. 16.41 Charpy impact resistance of long fiber reinforced materials, conventional short glass fiber reinforced phenolic molding compound, and short glass fiber reinforced thermoplastics. GF: Glass fiber, CF: Carbon fiber, AF: Aramid fiber. The values following GF, CF, and AF indicate wt% of each fiber

Conventional short fiber filled materials are generally produced by heating and kneading resins, fibers, powder fillers, and additives under comparatively strong shear, generally with extruders and rolls. Under these process conditions, carbon and glass fibers are broken and the resulting fiber length is considerably shorter that at the start of the process, perhaps 0.3 mm. Therefore, some production technologies to improve fiber length have been developed and applied to both thermosets and thermoplastics. Examples of methods developed to improve fiber integrity in thermoset molding compounds include a method to run a fiber bundle through resins in solution and impregnate the resins into the bundle, then dry and cut to a specified length. There is a method to run the fiber bundle through molten resins to impregnate resins into the bundles, then draw the bundle through a die, and a method to impregnate powdered resins into fiber bundles in a fluidized bed or in a suspension. The process resembles pultrusion (Chap. 12) to some extent.

Compression molding is the best molding method for long fiber reinforced thermoset materials to take advantage of their most important features. Appropriate preheating is desirable for compression molding, with radio-frequency and oven preheating leading the list of recommended methods. In case of injection molding, special considerations are required in order to minimize breakage of fibers in each step of the process, including plasticizing, material flow through the nozzle, sprue, runner, gate, and filling the cavity. In the authors' evaluation, using a specialized tool to suppress flow resistance, glass fiber length averaging 3 mm in molded specimens was realized from a 5 mm glass fiber reinforced material by decreasing back pressure and screw RPM.

Carbon and aramid fiber reinforced materials have lower specific gravity values than glass-filled materials, and the resulting effect of weight reduction is expected to increase metal replacement in the automotive and aerospace markets to the benefit of these carbon fiber and aramid containing materials. Growth of these materials and further developments are predicted for the future.

16.8.2 Carbon Fiber Reinforced Phenolic Molding Compounds

Carbon fiber reinforced phenolics represent the next step in composite advancement by breaking old boundaries and establishing a new generation of materials that can outperform metals and specialty engineering thermoplastics (Fig. 16.42).

Developed to provide an easily moldable, cost efficient, lightweight material for demanding applications in aggressive environments, short-carbon fiber reinforced composite delivers an unmatched balance of mechanical and tribological properties.

Carbon fiber reinforced phenolic molding compounds (CFRPMCs) promise benefits due to the nature of carbon fiber and phenolic resin (Table 16.7).

- Low density due to carbon fiber reinforcement
- High mechanical properties at high temperatures
- Excellent tribological properties
- High thermal and chemical resistance
- Dimensional stability

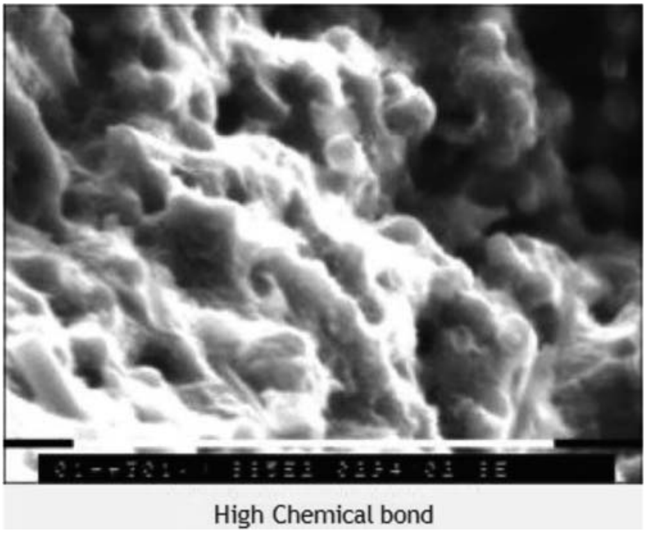


Fig. 16.42 Broken-out surface of CFRPMCs

Table 16.7 General properties of carbon fiber reinforced phenolic molding compounds

Item		Test method	Unit	Glass fiber GF: 55%	Carbon fiber CF: 30%	Poly ether ether ketone CF: 30%
Specific gravity		ISO 1183	–	1.78	1.35	1.4
Water absorption		ISO 62	%	0.05	0.07	0.06
Rockwell hardness	(M Scale)	ASTM D-785	–	127	120	107
Temperature of deflection under load	(1.8 MPa)	ISO 75-2	°C	235	260	315
Coefficient of linear thermal expansion	(Parallel)	–	ppm	17	6	15
	(Perpendicular)			47	55	($T_g < 143°C$)
Flexural strength	(As mold)	ISO 178	MPa	230	270	298
	(Postbaked)			235	280	
Flexural modulus	(As mold)	ISO 178	GPa	17.6	21.0	19
	(Postbaked)			17.9	21.2	
Tensile strength	(As mold)	ISO 527-1,2	MPa	125	110	220
	(Postbaked)			110	120	
Tensile modulus	(As mold)	ISO 527-1,2	GPa	18.6	23.0	22.3
	(Postbaked)			18.8	21.2	
Tensile elongation at break	(As mold)	ISO 527-1,2	%	0.82	0.50	1.8
	(Postbaked)			0.68	0.53	
Compressive strength	(As mold)	ISO604	MPa	320	275	153–240
	(Postbaked)			400	280	–
Charpy impact strength/ notched	(As mold)	ISO 179-1	kJ/m2	2.8	3.1	7.8

Postbaking condtion: 180°C × 4 h

The key is that, unlike some alternative materials (such as polyetherimide or polyether ether ketone), carbon reinforced phenolics can deliver cost savings without any penalty in performance. Comparisons of the properties of CFRPMCs with those of polyether ether ketone can be found in Table 16.7. In fact, tests show that carbon fiber reinforced phenolics performance can not only match that of high cost materials but, in many instances, is superior to them. Carbon fiber reinforced phenolics are characterized by their unsurpassed combination of properties. Through the use of lightweight carbon fibers, carbon fiber reinforced phenolics exhibit low density, giving it a high stiffness/density ratio. Moreover, optimum impregnation of carbon fibers endows the material with high thermo-mechanical properties and chemical resistance at elevated temperatures, as shown in Fig. 16.43. Underpinning its performance profile are its outstanding tribological properties, which provide it with a very high level of resistance to wear, together with a low coefficient of friction at high temperatures, as illustrated in Fig. 16.44. This gives the material an excellent fit in applications where one or more interconnected parts are in motion, of particular value in applications where the lubrication of moving parts is undesirable or impractical. This characteristic opens the way for carbon fiber reinforced phenolics to fulfill the operating criteria of applications such as rotors and impellors in vacuum and fluid pumps, various types of bearings, as well as seals in brake and engine systems. Furthermore, because CFRPMCs consistently maintain their surface properties and mechanical performance at continuous-use temperatures in excess of 150°C, a level at which the performance values of many engineering thermoplastics decline dramatically, its potential use extends to a broad range of harsh environment automotive and industrial applications for which long-term, robust performance is demanded.

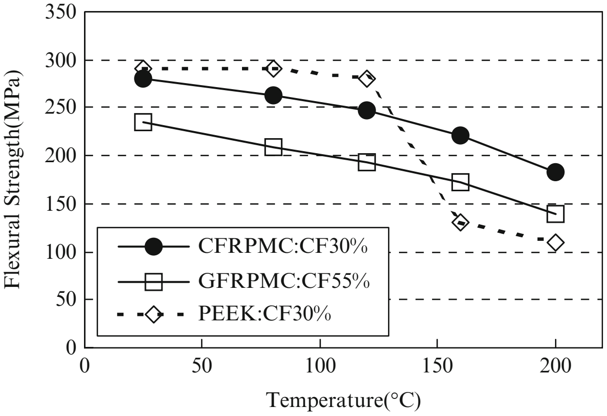


Fig. 16.43 Temperature dependence of Flexural strength. CFRPM: CF30% is carbon fiber (30%) reinforced phenolic molding compounds. GFRPM: CF30% is glass fiber (55%) reinforced phenolic molding compounds. PEEK: CF30% is poly ether ether ketone molding compounds

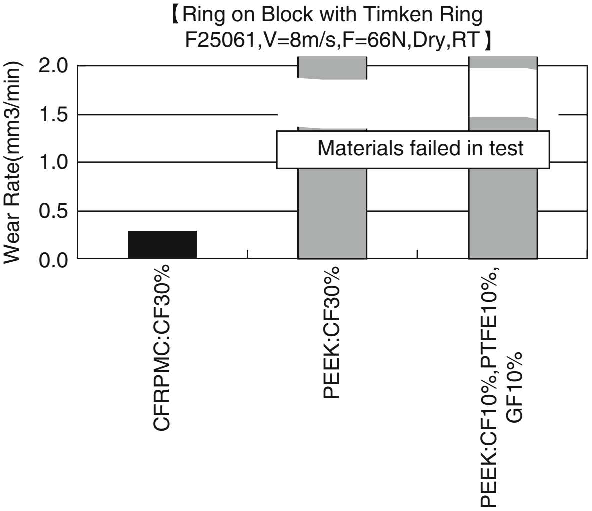


Fig. 16.44 Wear resistance at high loads and speeds. CFRPM: CF30% is carbon fiber (30%) reinforced phenolic molding compounds. GFRPM: CF30% is glass fiber (55%) reinforced phenolic molding compounds. PEEK: CF30% is poly ether ether ketone molding compounds

16.9 New Technical Developments

16.9.1 Finite Element

The best way to determine if an application could use high performance phenolics is by applying finite element analysis. Using FEA offers numerous advantages:

- Adapting the design to the material (properties and processes)
- Predicting deflections and stresses (including heat transfer, vibrations. . .)
- Quick design of components able to support known application constraints

High performance phenolics are creep resistant and dimensionally stable, which are rare qualities. However, this also means that any molded-in stresses that are in the part when it is new and assembled will remain there for the service life of the component. In other words, engineering phenolics have no stress relaxation, as do metals or thermoplastics. This means molded-in stresses need to be lowered to an acceptable level from the start, by modifying the part design. For example: stress peaks at sharp edges will not disappear after time, or be radiated out to the neighboring area. The only way to make sure the stresses of a part are acceptable is by means of an FEA model (Fig. 16.45).

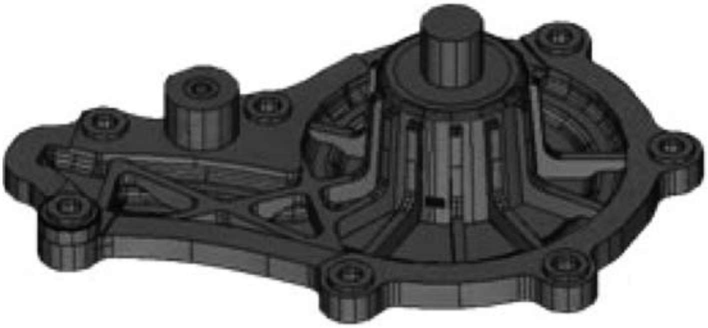


Fig. 16.45 3D-model of original accual part

16.9.1.1 Component Loads and Constraints

Before doing any FEA, engineers must obtain all loads and constraints applied to the proposed component. It makes no sense to use a sophisticated tool like FEA and input approximate load and constraint values. Building a useful FEA model with the proper loads and constraints requires the time and effort to anticipate the precise operating conditions of the part.

Some details require more precision, such as bolts pressing on a bolt eye. Sometimes, it is useful to model these details in full 3D and transfer it into the larger model. Thus, the correct deformation of the bolt eye and the rigidity of the bolt shaft are considered. Further it must be determined whether the part can withstand the loads of the most demanding test conditions beyond those of the normal operating conditions.

It is also important to have a clear understanding of the assembly process. The assembly conditions and mating parts can induce stresses and deformations on the thermoset part, or may restrict deformations. One must consider the molded part deformations!

It should be mentioned that a CAD model is geometrically perfect, while a molded part may be slightly warped (flatness, perpendicularity…). These geometrical imperfections can cause nonnegligible stresses on the assembled part (e.g., flatness tolerance).

16.9.1.2 Models and Methods

CAD models must be identical to the real part. All radii, draft angles, ribs, and holes must be integrated in the CAD model. However, small details that will not affect the strength of the part can be ignored. To reduce the number of elements and calculation time, symmetry of the model and constraints should be used. But keep in mind that this can only be used if model geometry, loads and constraints can be mirrored (all three are necessary if you want to calculate on only a portion of the model).

In some particular cases, just half of the model is analyzed, or a sector of the part, or an axis-symmetrical model (a section rotated around an axis). It is recommended to use quadratic volume elements (tetrahedron) for meshing. The higher the number of elements (in stress areas), the higher the accuracy of the results (at a certain mesh size the results will be very accurate and a further refinement is not necessary). A first quick simulation with a low number of elements can identify the location of the highest stresses, while a second simulation with local finer elements on those places, shows the exact value of the stresses. A noncontact analysis is the best method to use for an isolated part, reserving the contact analysis method for applications using assembled components or inserts (accurate method but time and memory consuming) (Fig. 16.46).

16.9.1.3 Calculation Data

The following material data are typically needed for the simulation:

- E-modulus at temperature.
- Density.
- Poisson’s ratio.
- Coefficient of thermal expansion.
- Other properties of interest in the model.

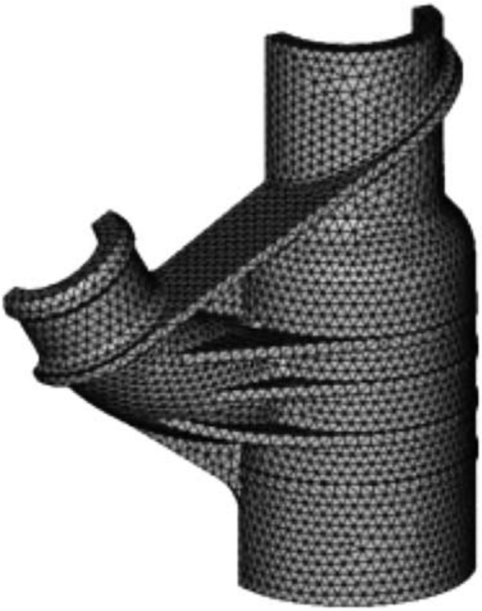


Fig. 16.46 Half of the model

16.9.1.4 Result Interpretation

First, results must be displayed exclusively in:

- Tensile stress (maximum principal), and
- Compressive stress (minimum principal).

Do not use averaged methods like "Von Mises," since those methods will mask stress concentrations for phenolics. Tensile strength is the weak property of all engineering phenolics. A good knowledge of the tensile stresses on a part will lead to an improved probability of success. Part failure occurs when the local stress within the part is higher than the local strength. FEA can predict all local stresses with great detail, but the software does not know the local strength. This local strength depends on fiber orientation, knit lines (weld line), etc. So, the FEA model cannot predict precisely at what tension a part will crack. It can only show you the local tensions. By using filling simulation, one can predict where the knit lines will form and can approximate the fiber orientation. In this way the designer can obtain a better understanding for the local strength, as well. Always take into consideration field and area of stresses.

16.9.2 Flow Simulation

A flow simulation is a kind of finite element analysis. Currently, it must be considered a complementary tool to the classic stress FEA calculation to help the designer plan a mold that will produce useful parts and to aid in approximating the injection parameters. The main targets of any flow simulation should be the predictions of:

- Cavity filling (the filling pattern, weld lines, etc.).
- Temperature profile in the material mass.
- Flow filling speed.
- Degree of cure at each filling step and during curing.

16.9.2.1 3D Flow Simulation Software

3D flow simulation software gives the user the opportunity to take into account thickness variations, local masses, edges, and radii... in other words the real shape of the anticipated part (Fig. 16.47).

16.9.2.2 Model, Sprue, Runners, and Gates

As shown in Fig. 16.48, any flow simulation model should include the injection sprue, runners, and gates. It is extremely important to take into account all detailed

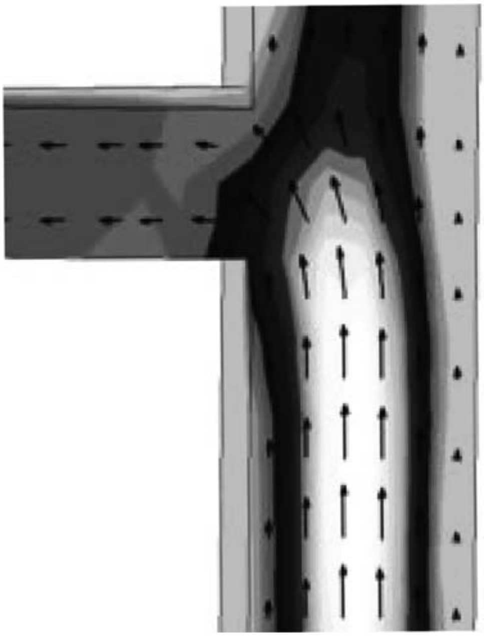


Fig. 16.47 Results of direction flow by 3D flow simulation

Fig. 16.48 Model included the injection sprue, runners, and gates

shapes from the machine nozzle to the part itself. All shapes influence the material rheology.

16.9.2.3 Mold Cavities Orientation

The gravitational forces influence the filling of the cavities. Therefore, it is also important to model all the cavities.

16.9.2.4 Mold and Insert Temperatures

Temperature is an essential factor of fluidity (filling speed) and reactivity (curing speed). All models must include the temperature of each mold element such as cavities, cores, slides, etc. In the same way, any over-molded insert has to be modeled (shapes and material – thermal conductivity) and needs to be given its proper preheated temperature.

16.9.2.5 Air Vents

Any entrapped air may interfere with the cavity filling (back pressure, high temperature around the entrapped air, etc.). Therefore, all mold vents have to be considered in the model.

16.9.2.6 Injection Cycle Profile

The total injection cycle profile must be defined or known. Even if all process steps are essential, two important steps should not be overlooked:

- Degassing; during degassing the material mass temperature increases, degree of cure increases, fluidity decreases, influencing the final filling of the cavity.
- Manipulations; regarding the filling of the cavity, manipulation time may appear negligible. In case of over-molded insert, however, this time becomes an important factor (temperature evolution of the insert).

16.9.2.7 Result Interpretations

Any flow simulation has to be related to the FEA calculation in order to avoid mechanical resistance or process issues (Figs. 16.49 and 16.50).

Mold Filling and Mass Temperature

Mold filling simulation aids in identifying the weld junctions of the flow fronts (weld lines). Design engineers must ensure that no weld line will be located in a high stress area.

Tracer Particles

Tracer particles allow modeling of the speed or “go-stop-go” and “go-back” effects of the filling flow fronts. A well regulated front speed ensures good quality of the molding material. The model can be used to eliminate any stop or back effect, which can cause shear issues, especially as the flow front approaches the cured state.

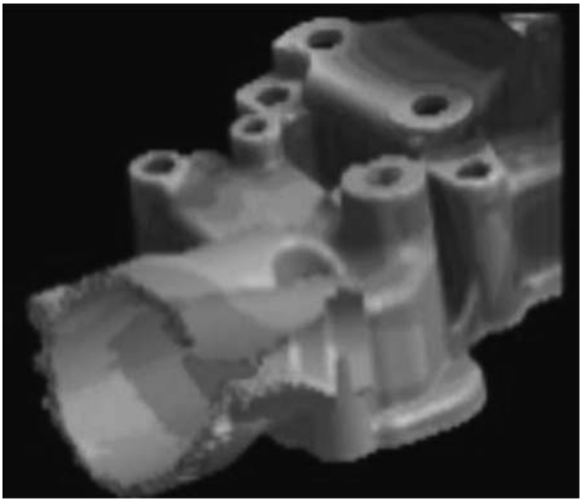


Fig. 16.49 Result of simulation

Fig. 16.50 Result of actual molding

Encapsulated Air

Trapped air must always be avoided. Understanding the conditions that may lead to air entrapment provides the design engineer an opportunity to modify the part design, change the injection gate location, and/or define venting strategies.

Degree of Cure

The degree of cure can be obtained at each step (time) of the filling simulation. These values must be associated with the different events (degassing, flow junctions, front speed, etc.) of the injection cycle in order to identify the most critical variables within the cycle design. It also provides a way for the designer to identify the areas within the part requiring longer cure times (allows shape optimization).

16.9.3 Fatigue Fracture Behavior of Glass-Filled Phenolic Compounds

In order to assure the long-term reliability and durability of GF/Phenolic materials, it is necessary to understand fatigue fracture mechanism at various temperatures.

Fatigue tests were performed at room temperature for the virgin and two kinds of after-cured specimens [7]. Figure 16.51 shows S-N (maximum stress to number of cycles to failure) curves for those specimens. It is proved that the short-term after-cure increases fatigue strength as well as static tensile strength. On the other hand, the long-term after-cure largely decreases the strength. The increase in strength of short-term after-cure is caused by postcure effect while the long-term one decreases the strength because mechanical properties of resin and fiber/resin interface are presumed to be degraded as will be shown later.

Fatigue crack propagation (FCP) tests and in-situ microscopic observation under tensile loading were also conducted using notched specimens. Figure 16.52 shows crack propagation length in the FCP tests for the specimens with fiber weight fraction (Wf) of 30% and 60%. Large amount of the specimens fractured without showing any stable crack growth. However, a crack propagates from the notch tip in some specimens, which shows damage tolerance of this material to some extent.

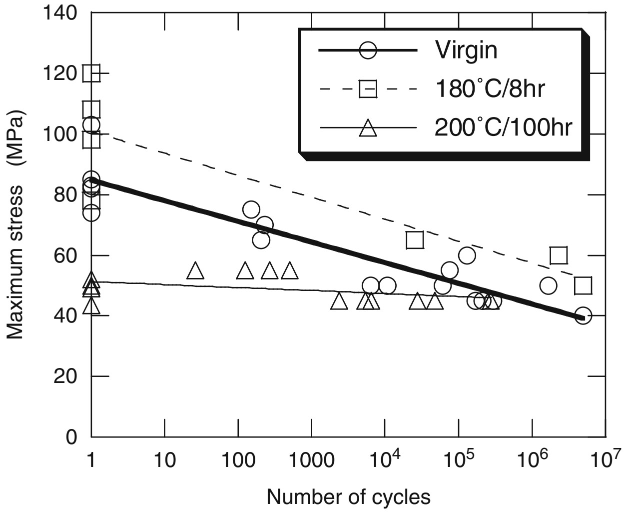


Fig. 16.51 S-N curves for virgin and after-cured GF/phenol specimens

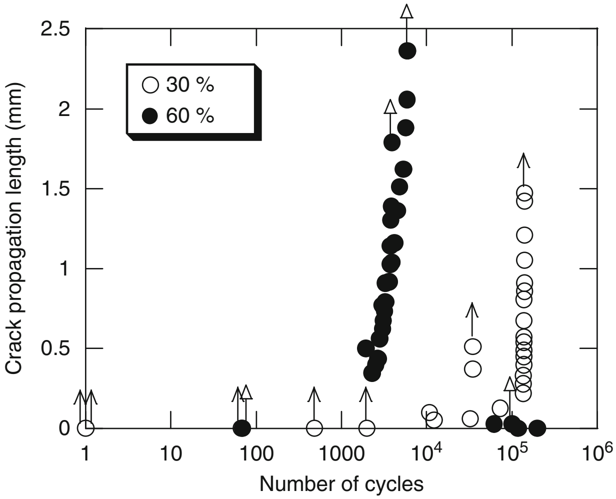


Fig. 16.52 Crack propagation length in the FCP tests. The *arrows* denote final fracture

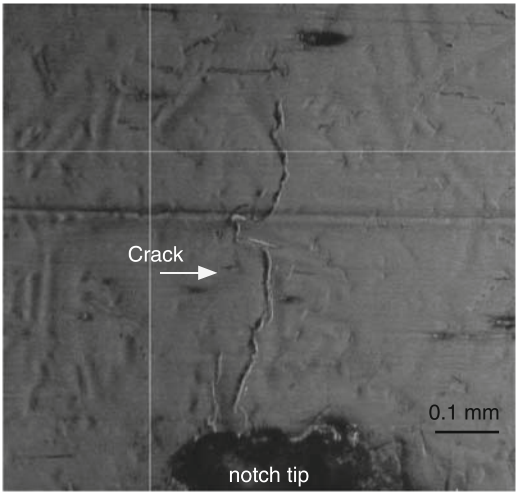


Fig. 16.53 Optical micrograph showing the crack propagating from the notch tip in the FCP test (Wf = 60%)

Figure 16.53 shows the crack propagating from the notch tip in the FCP test (Wf = 60%). The crack path is tortuous due to the presence of fibers.

Fracture surfaces after the tests were observed by means of scanning electron microscopy (SEM). Figure 16.54 shows fracture surfaces of the virgin and long-term after-cured specimens after fatigue tests. It is very difficult to identify a starting point of fatigue fracture of this material because the specimen fractures in a brittle manner without a striation pattern. The resin particles observed in Fig. 16.54.a. are assumed to be generated by friction at the fiber/matrix interface because of relative displacement between fiber and resin after debonding. On the

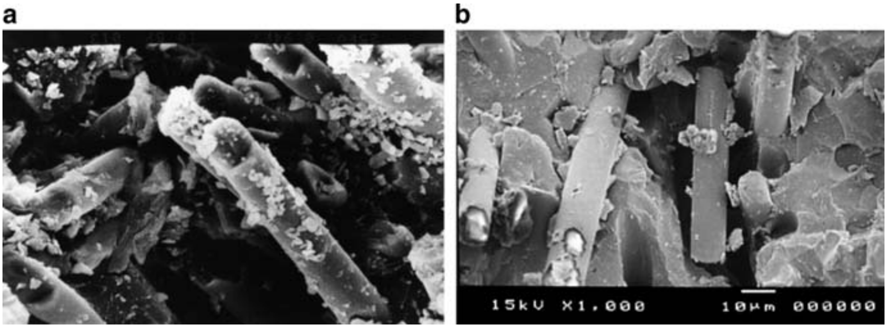


Fig. 16.54 Fracture surfaces of the (**a**) virgin and (**b**) long-term after-cured (200°C/100 h) specimens after fatigue tests

other hand, the resin is detached from the interface in the long-term after-cured specimen (Fig. 16.54b), which leads to degradation of fiber/resin interface and hence the strength of the composite as shown in Fig. 16.51.

16.10 Recycling

Once phenolic molding compounds are molded, they form a three-dimensional, cross-linked matrix which does not dissolve or melt. So, in general, they cannot be recycled in the same fashion as thermoplastics. Phenolic parts can be finely ground and used as a filler in phenolic molding compounds or coarse crushed and used in paving materials. But neither of these methods is widely used because of unattractive logistics and separation costs. Recently, however, technological innovation established a new method; chemical recycling to transform molded compounds into the original phenolic resin and filler components. Mass production using this new method will begin in 2009 at Sumitomo Bakelite, Japan (see Chap. 20).

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Chapter 17
Alkyl Phenol Resins in Adhesive and Rubber Applications

John D. Fisher

Abstract The use of phenolic resins with an elastomer or a rubber often involves phenolic resins based on alkylated phenolic monomers. This chapter discusses the details of the products used and describes the various applications where this practice is commonly found. It also attempts to explain why each choice is made and to compare the choices made to alternate technologies used to accomplish similar goals.

17.1 Introduction

Phenolic resins based on alkylated phenol monomers are used in a variety of applications in conjunction with elastomers. These include their use in the formulation of various rubber based adhesive systems and in the compounding of rubber for the production of rubber articles. The ability to adjust compatibility of phenolic resins with elastomers by means of substitution on the phenolic ring, primarily by means of alkylation with assorted olefins, enables the use of phenolic resins with a wide variety of elastomers and rubbers. The variation of reactivity between resole and novolak type phenolic resins also allows the alkylated phenolic resins to serve a variety of different purposes when used in conjunction with elastomers and rubbers.

17.2 Phenolic Resins in Rubber Based Adhesives

There are a wide variety of adhesives and a somewhat smaller assortment of rubber based adhesives. Rubber based adhesives offer the advantage of resistance to deterioration in applications where substrates are subjected to flex or vibrations in

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use. In the subset of rubber based adhesives, phenolic resins are a common additive in the formulation of these adhesives. Phenolic resins are in practice added to rubber based adhesive formulations to improve the performance of these adhesives. Both resole and novolak type resins are used in rubber based adhesives although the use of the reactive resole type resin is more prevalent. Resole type phenolic resins are typically used to improve the strength or heat resistance of an adhesive. Novolak phenolic resins are also used to increase the tack of the adhesive. Typically, phenolic resins are used in the production of solvent based adhesives although there are some exceptions. Three of the more common rubber based adhesive systems are discussed in this section. These include adhesives based on chloroprene and nitrile butadiene rubbers and rubber based pressure sensitive adhesives which can be on the basis of a variety of different elastomers.

17.2.1 Chloroprene Rubber Based Contact Adhesives

One of the most popular adhesive applications that uses phenolic resins is the production of polychloroprene rubber based adhesives. Polychloroprene adhesives have enjoyed broad popularity because they are easy to use and often do not require clamping after bonding. They also form strong bonds to a wide variety of surfaces and can be bonded over a wide period of time, still forming a strong bond. Polychloroprene rubber based adhesives have been used commercially in many applications ranging from construction to apparel accessory fabrication. They may be applied also in a variety of methods ranging from spray application which requires a very low viscosity version to trowel application which requires a very high viscosity.

A typical polychloroprene rubber adhesive formulation based on 100 parts chloroprene rubber will contain from 45 to 75 parts of a reactive alkyl phenol based resin. Typically, the phenolic resin is prereacted in solution with a metal oxide – most often magnesium oxide – prior to being added to the polychloroprene rubber solution. The polychloroprene rubber must either be fairly low in molecular weight to produce a workable solution or must be processed using mastication to reduce the molecular weight mechanically to allow easy dissolution of the elastomer. The inherent strength of the adhesive produced using a low molecular weight elastomer is enhanced by the addition of the phenolic resin/magnesium oxide complex to the adhesive. The latent reactivity of the phenolic resin will also add to the heat resistance of the resulting adhesive.

The use of a reactive alkyl phenol based resin to improve the performance of polychloroprene adhesives is well documented in the literature and generally indicates the use of resins based on para-tertiary-butyl phenol or modifications of this type of resin [1]. Phenolic novolak resins or terpene modified phenolic resins can also be added to the formulation. The addition of these thermoplastic resins is generally for the purpose of increasing the time during which successful bonding can be achieved or to enhance the instantaneous bond strength achieved when the two substrates are joined.

Changes in governmental legislation related to the release of volatile organic solvents have reduced the demand for solvent based adhesives and hence polychloroprene rubber based adhesives in the more developed regions of the world. The ease of use and good bond strength of polychloroprene rubber based adhesives make them difficult to replace in some applications.

17.2.2 Nitrile Butadiene Rubber Based Adhesives

Adhesives based on nitrile butadiene rubber are often used in applications where other rubber based adhesives cannot be used. This is usually because of the need for either greater chemical resistance or higher heat resistance than can be obtained using the other elastomers typically used in rubber based adhesives. Like other rubber based adhesives, both resole and novolak type phenolic resins are used in combination with the nitrile butadiene rubber to produce this type of adhesive. Novolak type phenolic resins are typically added as tackifiers to enhance the initial tack of the adhesive and are typically on the basis of alkylated phenols. Resole type phenolic resins are typically added to cross-link the adhesive system and are usually from highly branched phenolic resin systems.

17.2.3 Other Adhesives that Use Phenolic Resins

A variety of other types of adhesive based on an assortment of polymers use small amounts of phenolic resins as modifiers to the base chemistry of the system. Phenolic resins are sometimes used to improve the performance of acrylic based adhesives. Novolak type phenolic resins have been used to modify vinyl acetate and polyolefin based hot melt adhesives where the relatively high melting point and low melt viscosity compared to the base polymers can be an advantage. Generally these applications represent a minor use of phenolic resins in adhesive applications.

17.3 Rubber Based Pressure Sensitive Adhesives

Pressure sensitive adhesives are used to produce tapes of many varieties. This form of adhesive has enjoyed a growing market in recent years because of the convenience and ease of use of this form of adhesive. There are two popular types of adhesive used in the production of most tapes. One type is acrylic resin based and the other is rubber based. It is easy to distinguish the two types as acrylic resin based adhesives tend to be optically clear while the rubber based pressure sensitive adhesives are opaque. Like polychloroprene rubber based adhesives most rubber based pressure sensitive adhesives used in the production of tapes are solvent borne.

However, because the adhesive is applied and converted to a finished form in an industrial setting, the solvent may be recovered for reuse as solvent or fuel, thereby avoiding release into the environment.

Rubber based adhesives for pressure sensitive applications have traditionally been on the basis of natural rubber but over time have become more often on the basis of synthetic elastomers such as styrene butadiene rubber or styrene isoprene styrene block copolymer. The other principal component of a pressure sensitive formulation is a tackifier resin which can be used at levels equal to the amount of elastomer. The tackifier resin in a pressure sensitive adhesive formulation can be a phenolic novolak but more typically is either a hydrocarbon resin, or a terpene or rosin based resin. In addition to the elastomer and the tackifier resin, other components of the formulation include a metal oxide and a reactive component intended to crosslink the elastomer. This reactive component is often a resole type phenolic resin.

Curing rubber with resole type phenolic resins is discussed in detail in a subsequent section (see Sect. 17.3.2). The main advantages of using a phenolic resin to cure rubber based adhesives are that the cure once achieved is irreversible and adhesives made from phenolic resin cured rubber tend to have improved removability in applications where this is a desired feature. The resistance to reversion is a particularly important feature because of the process used to produce tape. To produce tapes, rubber based pressure sensitive adhesives are typically applied either to a release liner in solution form or as molten mastic. The adhesive coated release liner is passed through an oven to remove any volatile components and most importantly to cure the rubber which imparts greater strength to the finished adhesive. Because a phenolic resin cured elastomer will not exhibit reversion, there is little to fear from over-curing a phenolic resin cured pressure sensitive adhesive. Following the cure, the adhesive coated release liner is passed through a transfer or nip roller where the adhesive is transferred to the desired face stock. A variety of face stock types can be used including paper, polymer film, cloth, and foil depending on the application where the finished tape will be used. Figure 17.1 is a pictorial representation of this process.

17.4 Phenolic Resins in Rubber Compounding

Phenolic resins can be used for several different applications in rubber compounding. Phenolic tackifier resins are blended with rubber to increase the tack of a rubber compound to aid in building rubber articles. Rubber curing resins are used to cross-link rubber. Rubber reinforcing resins are blended with rubber and cross-linked during the rubber cure process to strengthen and harden the rubber. Adhesion promoting resins are added to rubber compounds to improve the adhesion of rubber to nonrubber portions of a rubber article.

Phenolic resins are typically added to the rubber compound during the milling process. In addition to the other features that the phenolic resins add to a rubber

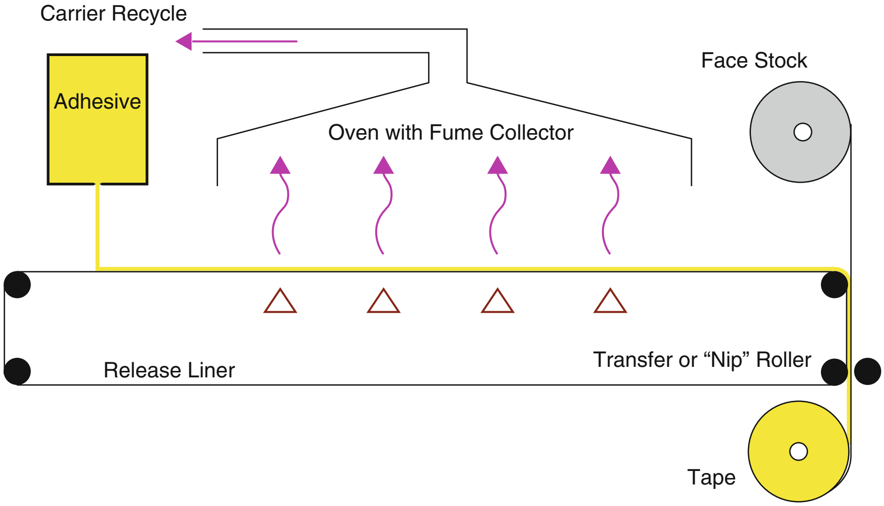

Fig. 17.1 Rubber based pressure sensitive adhesive production schematic

compound, they also act as process aids during the mixing process. The phenolic resins are much lower in molecular weight and viscosity than the elastomers and the immediate effect of adding the phenolic resin to a rubber compound is to reduce the torque required to mix the elastomer. The other effects of addition of a phenolic resin to a rubber compound are to reduce the milling time and energy and to reduce the mastication of the rubber during the milling process.

17.4.1 Rubber Tackifier Resins

The use of tackifier resins in rubber compounding is driven by the need to bond different parts of a rubber article together during construction and to maintain temporary bonding between adjacent parts until vulcanization. The principal application that consumes rubber tackifier resins is tire building. Various parts of the tire require different properties and hence the rubber compounds they are made of have dissimilar compositions. These different parts must adhere to each other until the tire is vulcanized and permanent chemical bonds are formed across the boundaries between the different rubber compounds. Other articles that are made from more than one rubber compound such as belts and hoses have similar requirements. The addition of a rubber tackifier resin to a rubber compound promotes the formation of the temporary bond.

Historically, several diverse paths have been taken to satisfy this bonding need encountered during rubber article construction. Natural rubber contains some resinous impurities that help tackify rubber compounds. These natural rubber based compounds typically require less or no tackifier resin be added to produce a suitably tacky compound. Synthetic elastomers do not contain these impurities and so require the addition of a tackifier resin to achieve the desired level of building tack in a rubber compound. The increasing use of synthetic rubber has resulted in an increase in the use of tackifier resins. Besides phenolic resins, several other types of resin have been used to tackify rubber compounds. These include coumarone/indene resins, hydrocarbon resins, wood and gum rosin, and rosin based resins. All of these products have the ability to plasticize the rubber compound and by doing so, increase the fraction of the surface area that is contacted when two rubber parts are joined. This improvement in contact area enhances the ability of the adjoining parts to form temporary bonds as a result of polymer chain entanglement and van der Waals forces. Use of phenolic resins enables these bonding strategies to occur as with the other tackifier resins but in addition offers the ability to form multiple hydrogen bonds through the aromatic hydroxyl present on each repeat group of the phenolic resin polymer chain.

The unique ability of phenolic resins to form multiple hydrogen bonds results in improved performance when compared to the other types of resins used for this application. One effect of this improved performance is that less tackifier resin is required to achieve the desired level of tack. Use of lower levels of tackifier resin in a rubber compound has been demonstrated to be of value in applications where heat build-up due to flexing is a concern as the various tackifier resins tend to be much less flexible than the elastomers they are blended with. Another benefit that is realized by using phenolic resin tackifiers is that the hydrogen bonds they form are much less affected by age and the environment than in the case of the other tackifier resin types.

The typical chemical structure of alkylated phenolic novolak resins is pictured in Fig. 17.2. R is typically a tertiary octyl group although resins with tertiary butyl substitution are used as well. The octyl substituted polymer is preferred because the resulting rubber compound is more resistant to scorch during compounding and curing. It is generally believed that the aliphatic portion of the phenolic resin molecule, because it is compatible with the elastomer, intimately mixes with the elastomer. Conversely, the aromatic hydroxyl group is not as compatible with the

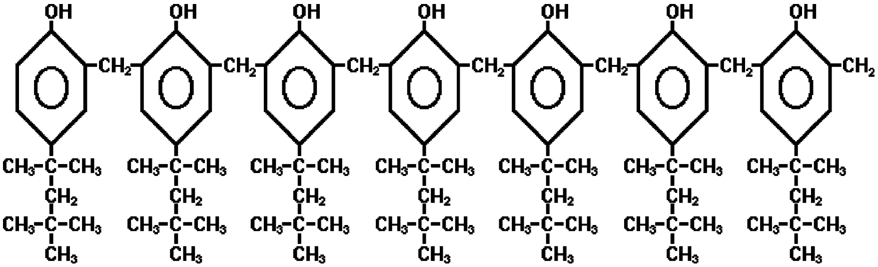

Fig. 17.2 Alkylated phenolic novolak resin structure

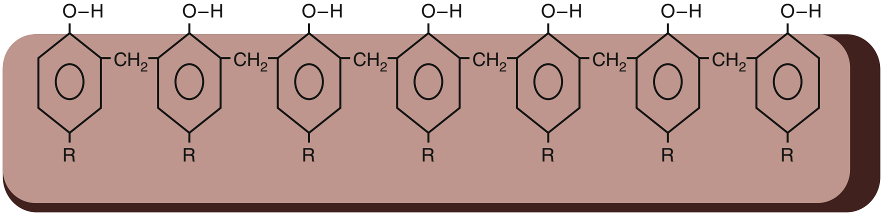

Fig. 17.3 Alkylated phenolic novolak in a rubber matrix

elastomer and tends to "bloom" on the surface of the rubber compound. This tendency makes the aromatic hydroxyl more readily available for hydrogen bonding as is pictured in Fig. 17.3.

The level of use of phenolic tackifier resins in rubber compounds generally is left to the discretion of the rubber compounder. Typically, three to five parts of phenolic resin tackifier are used per 100 parts elastomer, but the level depends on many factors including the type of elastomers being used, the geometry of the parts being assembled, the relative humidity, and more. Recent patent literature indicates that modification to the standard alkyl phenolic novolak resin can be used to enhance tack in special needs applications [2].

Although some of the other tackifier resins are still used in rubber compounds for tire applications in developing countries, use of alkyl phenolic novolak resins as tackifiers is the dominant technology used for production of rubber compounds for tire applications.

17.4.2 Rubber Curing Resins

Curing or vulcanizing of rubber involves reaction at the points of unsaturation in the backbone of the elastomer to cross-link or partially cross-link the elastomer. The vulcanization process reduces the plasticity and increases the elasticity of a rubber compound by the formation of cross-linking bridges between the long elastomer polymer chains. By curing rubber, improvements in abrasion resistance, tensile strength, and chemical resistance are achieved in a rubber compound. The most prevalent technology for curing or vulcanizing rubber is the use of sulfur based compounds. Sulfur curing is also the oldest and typically the least expensive technology used to cure rubber. Other technologies used to cure rubber include peroxide based curing agents and phenolic resins.

Use of phenolic resins as vulcanizing agents for rubber compounds offers several advantages over the other technologies. Rubber curing using sulfur compounds produces a carbon–sulfur bond while a phenolic resin cure relies on formation of a carbon–carbon bond. The carbon–sulfur bond is more subject to hydrolysis upon exposure to moisture particularly at elevated temperatures than is the carbon–carbon bond. A typical rubber cure using sulfur technology will exhibit reversal after a peak in crosslink density is achieved due to the decomposition of the carbon–sulfur bonds. Phenolic resin cured elastomers exhibit reversal at a much slower rate than sulfur cured elastomers and because of this feature offer value in some specific applications. Peroxide based rubber curing has limitations because of the free-radical mechanism employed. This mechanism limits the types of rubber that can be cured using peroxides and some common types of rubber such as butyl rubber cannot be effectively cured using peroxides. In addition, the fragments of the peroxide created by the dissociation required to initiate the curing process may be hazardous and may also remain fugitive in the finished rubber compound.

Phenolic curing resins are typically resole type resins based on alkylated monomers. The typical structure appears in Fig. 17.4. R is typically a tertiary octyl group, but other alkyl groups may also be used. Between adjacent phenols in the polymer chain can be either a methylene or a dibenzyl ether bridge. Phenolic resins of this type are typically difunctional and during the cure process will react at both ends to form bridges between adjacent elastomer molecules. The generally accepted mechanism for phenolic curing of unsaturated elastomers is by the formation of a chroman ring [3] as illustrated in Fig. 17.5.

One of two common applications of phenolic resins in rubber curing is in the production of butyl rubber bladders used in tire manufacturing. Butyl bladders are used in the vulcanization process in tire manufacturing. When tires are completely assembled, they are put into tire molds. Butyl bladders are placed inside the tires and the molds are closed. Steam is forced into the butyl bladders under pressure and while the pressure from the steam forces the tire into the mold, the heat from the steam initiates the curing process. Because the phenolic resin cure forms a carbon–carbon bond, the stability of phenolic resin cured butyl bladders is much longer than that of sulfur cured butyl bladders. Phenolic resin cured butyl bladders are the dominant technology used in most regions of the world today. The other popular application that uses phenolic curing resins is the formulation of thermoplastic vulcanizates (TPVs) [4]. TPVs are typically a blend of a thermoplastic polyolefin and an unsaturated elastomer. The technology used to produce TPVs involves

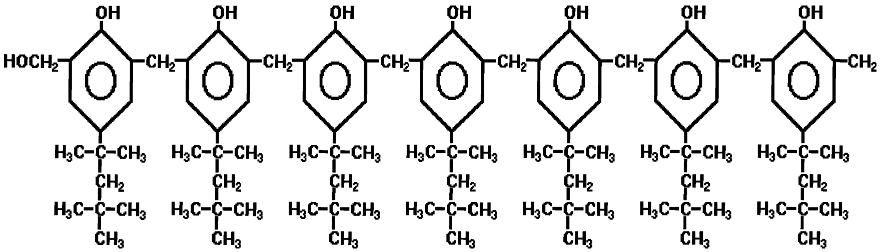

Fig. 17.4 Alkylated phenolic resin with reactive end groups

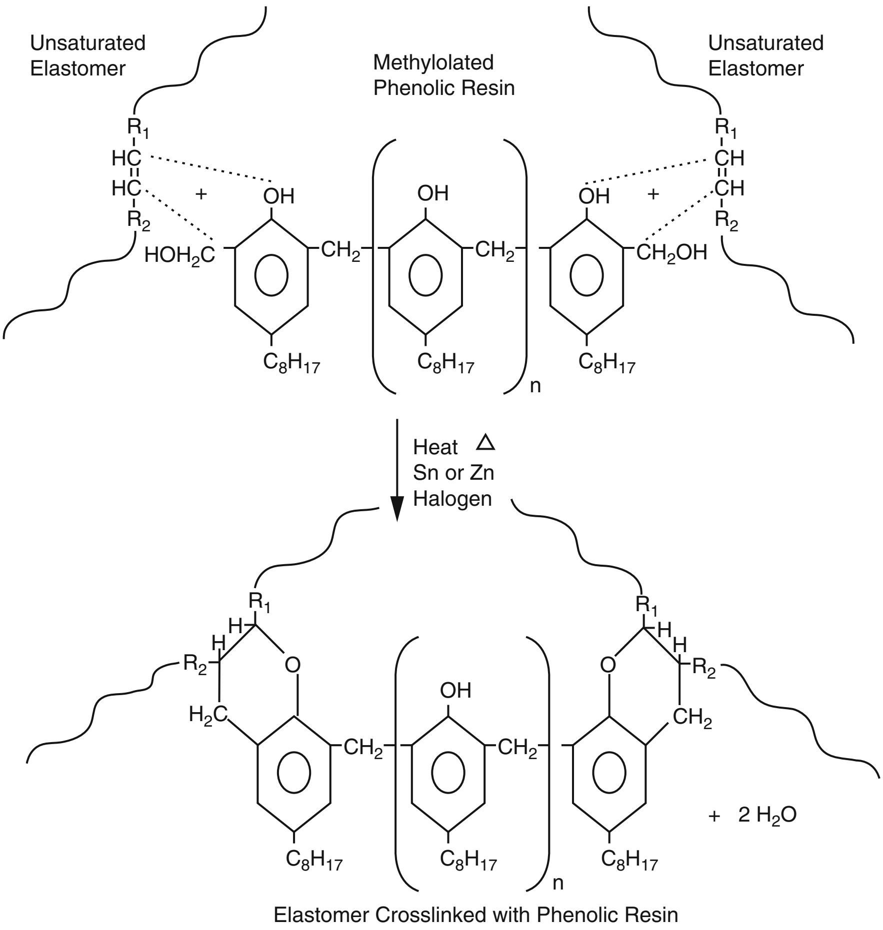

Fig. 17.5 Reaction of phenolic resin with unsaturated elastomer

mechanically blending the elastomer, the polyolefin, and the curing agent. The elastomer is "cured", but because of the high polyolefin level the material remains thermoplastic and has elastic characteristics. As such, the resulting product can be injection molded and does not require a postcure to achieve elastic characteristics.

Phenolic curing resins are typically used at a level of 8–12 parts per 100 parts rubber. The level of cure can be increased or decreased depending on the intended application. To catalyze a phenolic resin cure, it is required that a halogen be present in the rubber compound. Typically the addition of a halogen source is accomplished by use of a small amount of a halogenated elastomer such as polychloroprene or bromobutyl rubber, but other options also can be considered. Halogenated phenolic resins are commercially available [5] and valued for their fast reaction and offer another option for introducing halogen into a rubber compound. It is also typical to add a metal compound into a phenolic resin cured system to accelerate the curing. Usually this is a tin or zinc based compound and some of the common materials used include zinc oxide or zinc modified wood or gum rosin. An option that is popular and accomplishes both these desired tasks is the addition of tin chloride. Phenolic resin induced rubber cure is typically achieved at temperatures around 175–200°C.

The formation of carbon–carbon bonds, as well as the stability of these bonds, is what differentiates phenolic resin cure from sulfur cure. Critical applications where exposure to heat and humidity will occur demand the value of a phenolic resin cure.

17.4.3 Rubber Reinforcing Resins

Phenolic reinforcing resins are added to rubber compounds to adjust the physical properties of the rubber article after it has been fully cured. The physical properties influenced by the addition of rubber reinforcing resins include hardness, toughness, stiffness, abrasion resistance, and tear resistance.

Alternate technology for reinforcing rubber compounds is the addition of fillers such as carbon black or other mineral based fillers. The use of fillers alone to reinforce rubber compounds creates problems for the rubber mixing process. As more filler is added to the rubber compound, it becomes more difficult to process and requires more energy to make the physical mix. The use of phenolic resins in a rubber compound reduces the energy required to mix rubber compounds because of the low melt viscosity they exhibit during mixing. When used in conjunction with fillers, there is a synergistic effect [6] such that both the phenolic resin and the filler will increase the reinforcing of the rubber compound and the addition of the phenolic resin will compensate for the increase in mixing energy needed to mix the increased filler loads.

Phenolic reinforcing resins are typically highly branched phenolic novolak resins that have been modified to improve compatibility with various elastomers. Commercially, the modification is typically with cashew nut shell liquid, tall oil rosin, or alkylated phenols. The reinforcing resins are used in conjunction with a methylene donor, commonly hexamethylene tetraamine, although other methylene donors are sometimes used. When the rubber compound is subjected to heat for the purpose of vulcanization, a parallel reaction between the phenolic novolak and the methylene donor occurs. The reaction of the phenolic resin and methylene donor forms an interpenetrating polymer network within the rubber compound matrix. The formation of the cross-linked phenolic polymer within the cured rubber polymer serves to reinforce the finished rubber article.

Phenolic reinforcing resins can be used at different levels depending on the properties desired in the finished product. Table 17.1 depicts the effect on hardness of the use of various levels of a phenolic reinforcing resin in different rubber compounds and at constant filler loading [7]. More significant differences may be obtained by implementing reinforcing resin level changes in conjunction with filler

Table 17.1 Shore A hardness at different reinforcing resin levels in different rubber compounds

P-87[a]	0 phr*	10 phr	20 phr	30 phr
NBR*	55	60	70	82
CR*	58	71	80	89
EPDM*	55	64	68	73
SBR*	60	74	81	86
P-55[a]	**0 phr**	**10 phr**	**20 phr**	**30 phr**
NBR	55	61	65	74
CR	58	75	82	84
EPDM	55	62	65	66
SBR	60	68	71	76

[a] P-87 and P-55 are products of Akrochem Corp
* *Phr* parts per hundred parts of rubber
NBR nitrile butadiene rubber
CR chloroprene rubber
EPDM ethylene propylene diene monomer rubber
SBR styrene butadiene rubber

loading changes. Phenolic resin reinforced rubber compounds are used in many different applications where a harder rubber compound is needed. Some examples include the teeth on drive belts, the surface layer of conveyor belts and rollers, and in various parts of a tire where higher hardness is required.

17.4.4 Adhesion Promoters for Rubber Compounds

Many rubber articles when fabricated contain materials other than rubber as an integral part of the design and function of the article. Some examples of nonrubber materials that can be part of a rubber article include steel, polyester or aramid fiber belting and bead materials in tires, fabric or cable strengthening in belting, and fiber or fabric reinforcing of hoses. To be an effective part of these composite articles, the nonrubber portion must form a strong and permanent bond with the rubber portion of the article. It must also prevent the nonrubber material from moving independently of the rubber. Adhesion promoting resins aid in promoting formation of a bond between the rubber and nonrubber materials and also toughen the rubber adjacent to the nonrubber materials.

The bonding of the nonrubber portion of an article to the rubber portion is accomplished by two technologies. One strategy is to pretreat the nonrubber portion of the article with liquid adhesion promoting system often called “latex dip.” The pretreatment dips are typically water-borne and are based on either natural or synthetic elastomer latex. The dip also contains vinyl pyridine, a phenolic novolak, and a methylene donor. Typically the phenolic portion of the dip is a novolak made using resorcinol as the principal monomer and the methylene donor is a methylolated melamine oligomer. In practice, the fabric or fiber being treated is submerged in the liquid dip, drained, and dried but not fully cured. The second adhesion promoting strategy is to encapsulate the nonrubber portion of the article in a special rubber compound especially formulated to form a strong bond to nonrubber materials and often called a “skim compound.” This skim compound is designed to bridge the boundary between the nonrubber and rubber portions of the article. The skim compound must form a strong bond with the nonrubber portion of the article and must also form a strong bond with the other rubber compound adjacent to it. The skim compound should also be tough enough to prevent the nonrubber portion of the article from moving independently from the rubber portion of the article. A typical skim compound formulation is primarily elastomer based but also contains adhesion promoters. Like the latex dip, the adhesion promoters used in a skim compound formulation are typically on the basis of a novolak type phenolic resin and are used in conjunction with a methylene donor. The methylene donor can be either a methylolated melamine oligomer or hexamethylene tetraamine. The phenolic resin can also be resorcinol based although phenol and alkylated phenol based products are also used.

Either of the latex dip or skim compound strategies can be used alone, but most commonly and most effectively they are used together. In typical practice, the pretreated nonrubber portion of an article is encapsulated in the skim compound and fabricated with the other rubber compounds into the form of the desired article. The use of adhesion promoting phenolic resins ensures that a permanent bond between the rubber and nonrubber portions of the article is formed during the vulcanization of the finished article. A competitive technology used to form a strong bond between rubber and nonrubber portions of an article is the use of cobalt based adhesion promoters. Use of cobalt based materials is often in addition to the resin based technologies discussed above.

17.5 Summary

Use of phenolic resins in conjunction with elastomeric and rubber materials often involves the use of alkylated phenolic monomers. This choice of starting materials is driven by the compatibility of the resins made from these monomers with elastomers and rubbers of various types. Generally, the choice of using a resole or novolak type resin is driven by the desired functionality. Resoles are the choice if latent reactivity is desired and novolaks are the choice if a thermoplastic product is desired.

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Chapter 18
Foundry

Douglas M. Trinowski

Abstract This chapter reprises the authors' original work and covers the ubiquitous uses of phenolic resins as sand mold and core binders in the metalcasting (foundry) industry. An overview of the economic and technical significance of metalcasting is provided along with a simplified description of the process of casting. A description of all synthetic organic resins used as foundry binders is provided with an overview of the chemistry and coremaking process. Where appropriate, significant advancements made in each process are described. A new section on emissions from phenolic resins used as foundry binders is provided. Finally, comments on the future of phenolic resins in this field are described.

18.1 Introduction (Economic and Technical Survey)

Shaped metal parts (Fig. 18.1) of iron, steel, and nonferrous metals (bronze, brass, aluminum, magnesium, etc.) may be produced by various methods. The most important method is by casting. The final product is directly produced from molten metal as compared to forming, staking (staking is a method of fastening by squeezing a protrusion formed in one part inside a hole in the second part, and then deforming the protrusion – the act of deformation causes radial expansion of the inner part and locks it in the hole), and sintering methods. Nearly all metals are castable through a variety of methods.

The global metalcasting industry nearly topped the 95 million-ton production mark in 2007, reaching 94.9 million metric tons – a 3.9% increase over 2006. About 75% of this production originates in countries mentioned in Table 18.1. The data reported in Table 18.1 are production numbers provided by each nation's metalcasting association for 2007. This list is led by China, the United States, Russia,

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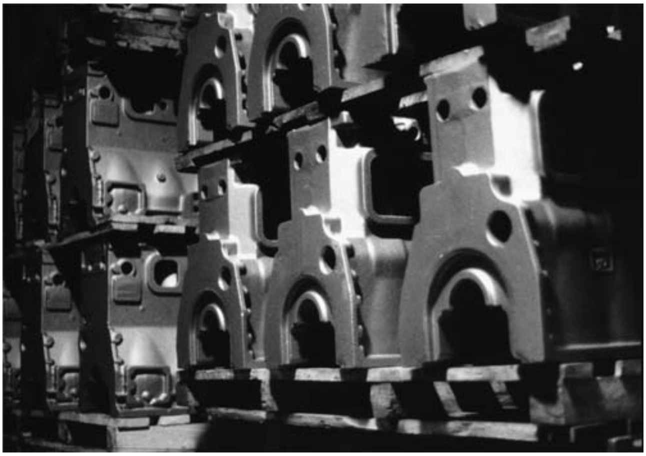


Fig. 18.1 Gray iron engine blocks
Source: Eisengiesserie Fritz Winter, Stadtallendorf, Germany

Table 18.1 Castings produced in various countries and worldwide in metric tons

Top 10 casting producers						
Rank	Country	Gray iron	Ductile iron	Steel	Nonferrous	Total
1	China	15,460,176	7,698,396	4,047,505	3,528,237	31,269,630
2	U.S.	3,889,000	3,890,000	1,248,000	2,592,000	11,686,000
3	Russia	3,320,000	1,800,000	1,300,000	1,200,000	7,800,000
4	India	5,332,000	802,000	964,000	608,000	7,771,100
5	Japan	2,856,064	2,044,055	292,908	1,714,444	6,960,765
6	Germany	2,717,100	1,796,300	211,200	1,056,522	5,840,022
7	Brazil	2,690,000	*Included in gray iron*	303,200	233,900	3,227,100
8	Italy	966,014	600,200	89,600	1,087,100	2,742,914
9	France	940,900	1,060,900	114,600	355,300	2,471,700
10	Korea	1,002,500	586,900	151,200	236,800	2,023,900

Source: Modern Casting, December 2008

India, Japan, Germany, and Brazil. Germany produces about 5.8 million metric tons of castings annually and leads the list of Western European countries.

Table 18.1 breaks down casting production into the following categories: gray and ductile irons, steel, and nonferrous castings. The ferrous casting industry is composed of foundries producing gray, ductile, malleable, compacted graphite iron and carbon low alloy, corrosion resistant, heat resistant, manganese, and other steel cast products. Nonferrous includes copper-based alloys, aluminum, magnesium, zinc, and other nonferrous metals.

The global annual total of 94.92 million tons is composed of approximately 83.4% ferrous metals and 16.6% nonferrous. Of ferrous metals, gray iron accounts for 56.8% of the total, ductile iron for 28.9%, steel for 12.97%, and malleable iron for 1.4%. Among the nonferrous metals, aluminum dominates with 81% of the total, copper alloys account for 10.25% of the total, followed by zinc at 6%, and magnesium at 1.8%.

Once metal is molten, it is a liquid, and its fluidity provides potential for its transformation into usable articles. As with other liquids, molten metal must be contained or confined and will conform to the shape of its container. It will seek its own level and will displace other lighter materials, such as air and other gases. To confine molten metal and provide shape to the cast item, molds and cores must be prepared.

Casting is performed using disposable (nonpermanent) or reusable (permanent) molds. In nonpermanent or disposable molding, the mold is destroyed when the metalcasting is removed from the mold. The opposite is true for permanent molds. In this case, the mold is reused after the casting is removed.

The finished mold [1] may consist of one or more parts (mold sections), such as the cope (top), drag (bottom), and cores, which form internal passages or cavities in the metal casting (Fig. 18.2). Molds and cores are generally produced from similar

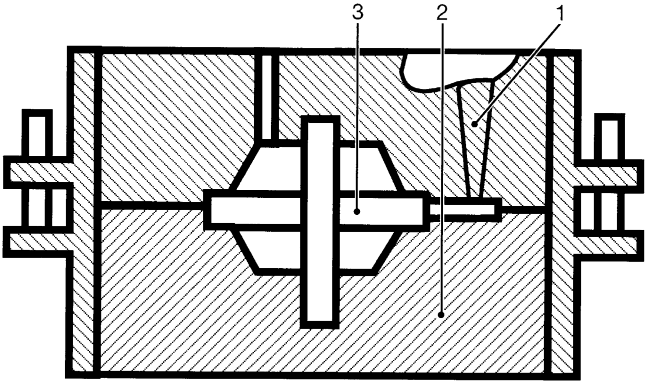


Fig. 18.2 Corebox system (1 = cope, 2 = drag, 3 = core) from [1])

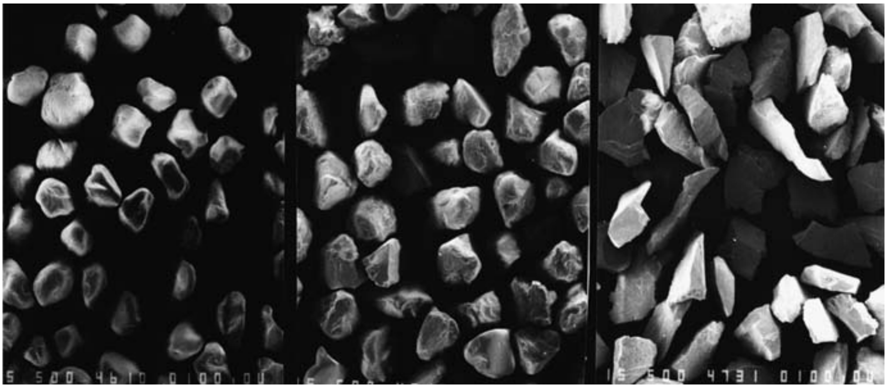


Fig. 18.3 Grain structure of silica (quartz) sand, magnification ×50, from *left to right*: round, subangular, angular (photo: Quartzwerke, Frechen)

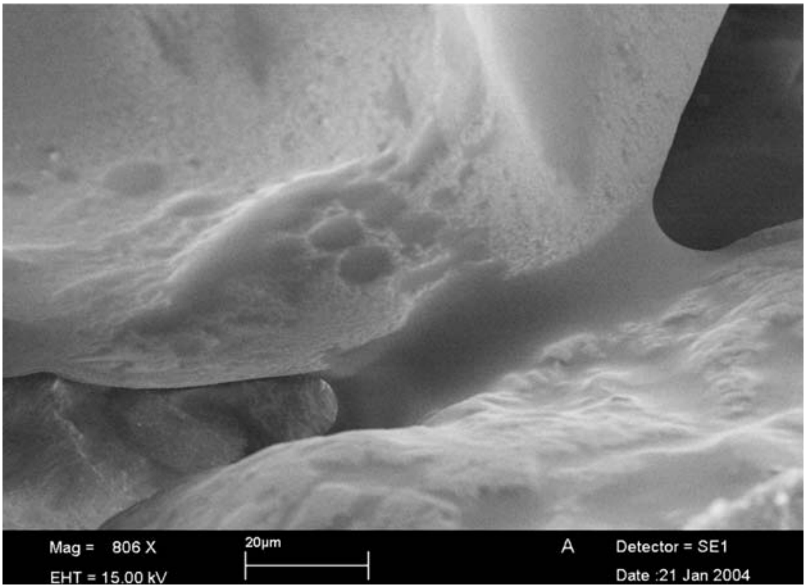


Fig. 18.4 Scanning electro micrograph of a silica-resin "bridge" between sand grains, illustrating the importance of the binder
Source: Hüttenes-Albertus, Düsseldorf, Germany. Pictures were recorded in 2004 at Münster University, Germany

molding materials. In most cases, the main component of these is silica (quartz) sand (Fig. 18.3) shaped with inorganic or organic binders (Fig. 18.4).

In high production foundries, molds are produced on molding lines with cores produced using "core shooters" or "blowers" (Fig. 18.5) that use compressed air to facilitate filling of the core box with the sand/binder mix prior to hardening.

The most important raw material for disposable molds is quartz sand [2, 3]. Quartz (α-modification) is the most common modification of silica (SiO_2). When heated, α-quartz undergoes a transition to the "β-quartz" modification at temperatures above 573°C (1,063°F). This reversible transition is accompanied by the expansion of the crystalline lattice leading to a drop in the density from 2.65 to 2.50 g/cm^3. Because of this quartz transition, "heat cracks" leading to casting defects such as "veining" may arise when the resin-bonded molds and cores are poured, depending on the degree of compaction of the molding material, the weight and temperature of the melt, and the cross-linking density of the cured binder.

Besides silica sand, minerals such as chromite, olivine, and zircon sands may be used in special cases. These types of substrates can be used to prevent expansion defects in molding materials exposed to particularly stringent thermal stresses. New substrates are being introduced as certain mineral sands that increase in cost and/or become scarce. It is beyond the scope of this chapter, but synthetic ceramic mullites, graphite sands, and kerphalites, to name a few, can also be used as substrates for foundry applications.

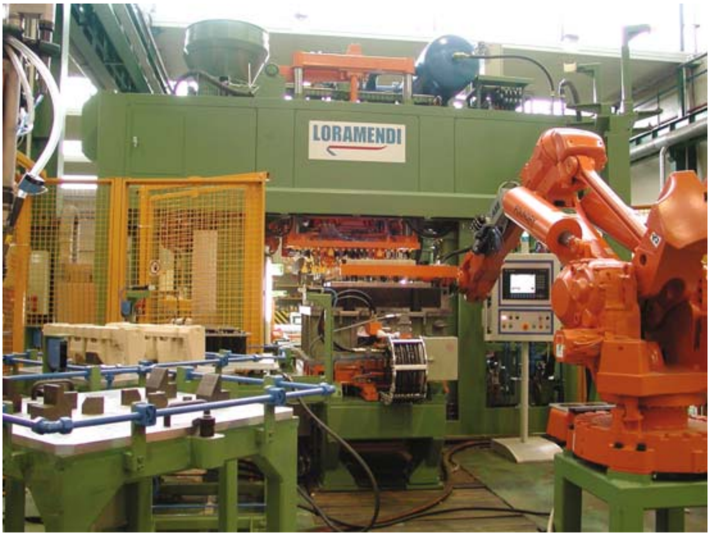


Fig. 18.5 Core shooter, encapsulated to capture and reduce emissions and permit use of gas curing processes requiring sealed systems; production of urethane cold-box cores (photo: Loramendi, Fenton, MI and Vittoria, Spain)

Different binder systems are generally used for specific molding processes. Molds for ferrous casting traditionally have mainly been produced using inorganic binders such as clay and in a very few remaining cases, cement or waterglass. The use of bentonite clay, water, and a carbon-producing substance such as seacoal (a traditional name for powered coal) is referred to as "green sand" molding, due to the fact that the binder never hardens or cures and remains moist. It remains "green."

Traditionally, this process required skilled laborers, known as molders. Mechanization in the foundry industry has seen a shift away from skilled labor involved in preparing molds by hand to highly automated production equipment that can form a mold using hydraulic or pneumatic pressure to squeeze and/or blow the green sand into the desired shape.

The advent of organic chemical binders has initiated a change in the foundry industry toward the replacement of green sand molding with organic binders for certain types of castings. Cores are prepared using processes involving organic binders, prominent members of which are coremaking grades of phenolic resins.

In many cases, the advances [4] that have been achieved in molding technology by the use of new core/mold binders and production methods have resulted in the efficient and economical production employing a high degree of mechanization possible in modern foundries. This is illustrated by the rise in productivity at German foundries during the period of 1950–2000 (Fig. 18.6). The production per employee nearly quadrupled over these 50 years. Germany continues to lead most industrial countries in metalcasting productivity, producing close to 10,000 tons of casting per metalcasting facility. Austria, with 357,000 tons

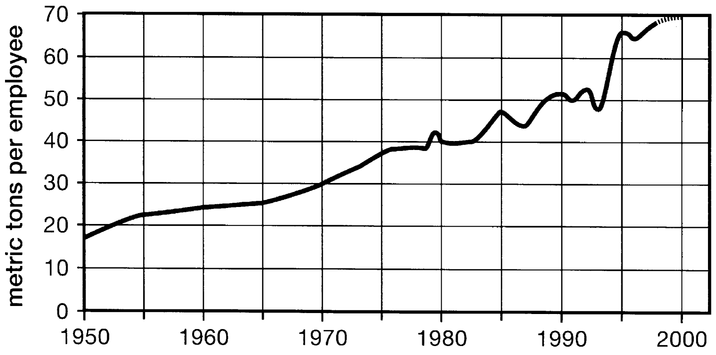


Fig. 18.6 Productivity increase in the German foundry. Industry from 1950 to 1997, in tons of production per employee
Source: Verein Deutscher Giessereifachleute, Düsseldorf, Germany

Table 18.2 Forecast of aluminum usage in motor vehicles produced in the U.S. as a percent of total vehicles produced

Component	2010	2012
Engine block	80%	85%
Cylinder head	99%	99%
Suspension castings	70%	80%
Differential carrier	55%	60%
Intake manifold	15%	12%
Wheel	70%	70%
Transmission case	97%	97%

Source: American Foundry Society Metalcasting Forecast and Trends, Unpublished 2009

produced, makes 7,000 tons per metalcasting facility. U.S. productivity continues to be one of the highest of all the nations at 5,434 tons per plant [5].

One of the driving forces for this increase has been the meteoric rise in capacity of the automotive industry. According to the American Foundry Society [6], new proposed fuel economy standards will continue to spur the conversion of iron engine blocks, cylinder heads, and differential and suspension castings to aluminum in passenger cars and light trucks and increase the growth of light metals (Table 18.2).

This trend toward aluminum for motor blocks and cylinder heads has led to conversion away from green sand molding with phenolic urethane cold-box and hot-box cores. For aluminum blocks, a "precision sand" mold is prepared. Precision sand refers to a molding process to produce castings with low dimensional variation in a bonded molding media (usually sand). Numerous cores are held together in a flaskless package, and the internal passages and external geometry of castings are produced without the use of a traditional mold or pattern plate. All cast features produced through precision sand processes achieve about ±0.04 in. (±1 mm) tolerances [7]) and are made entirely using the phenolic urethane cold-box process. This process is rapidly becoming the accepted production method for larger displacement motor blocks (along with other light metal semi-permanent molding and die casting methods for smaller displacement engines).

These technological and material changes will continue to affect metalcasting facilities and cause significant change in the global supply and demand of castings. The change to light metals in automotive applications has caused the closing of many operations and reduction in production capacity in iron casting operations, while aluminum demand and supply numbers rise to new peak levels in both die casting and permanent mold operations (Table 18.3) [6].

In an assessment of coremaking processes, the demands of which have reached a high level in recent years for ecological and economical reasons, attention must be directed not only to the production process itself, but also to disposal of exhaust gases at the work station, minimization of emissions, and recovery of used core and mold sands. The later is particularly prudent, since it avoids dumping and is desirable for economical and ecological reasons.

Many technical developments in foundries have only become possible because of the fact that the "art of casting" has developed into the foundry industry in its present modern form [8]. Many new core and mold production processes have been developed since the end of World War II (Table 18.4). The variety of coremaking processes is in turn basically related to six potential binder functions, which may also be analogously correlated with foundry binders. The greater the extent to which a system provides a balanced mix of these (permanent, temporary, intermediate, complementary, carbon-forming and chemically reactive binding) functions, the better the system ranks in comparison to other processes.

Thus, cores should exhibit "permanent" dimensional stability prior to pouring operations, and feature high strength levels during intermediate handling – in transportation, storage, and insertion into the mold. The molding material should then temporarily withstand high temperatures during pouring. Its hot tensile strength over time (Fig. 18.7) should be as high as possible during the initial period following pouring, but should fall precipitously thereafter to provide good collapsibility. The complementary binding function indicates the capacity for modification and adaptation of the binder systems and the carbon-forming function has the effect

Table 18.3 Forecast of casting consumption in light vehicles in the U.S.

Year	Shipments of castings for use in light vehicles (tons)		
	Gray iron	Ductile iron	Aluminum
2005	995,000	981,000	1,359,000
2006	894,000	880,000	1,171,000
2007	836,000	830,000	1,104,000
2008	675,000	663,000	900,000
2009	480,000	470,000	630,000
2010	550,000	550,000	730,000
2011	660,000	660,000	880,000
2012	668,000	750,000	1,102,000
2013	684,000	770,000	1,166,000
2015	692,000	811,000	1,315,000
2015	729,000	850,000	1,391,000
2016	756,000	880,000	1,459,000
2017	774,000	890,000	1,490,000

Source: American Foundry Society Metalcasting Forecast and Trends, Unpublished 2009

Table 18.4 History of core and mold processes using synthetic resins as binders

Year	Process	Resin
1950	Use of shell molding	Phenolic novolaks
1958	Furan no-bake	Furan resins (straight and modified)
1962	Hot-box	Urea, furan, and phenolic resins
1965	Alkyd oil urethanes	Alkyd drying oils
1965	Phenolic hot-box	Phenolic resoles
1968	Phenolic urethane cold-box	*Ortho*-condensed resoles
1971	Furan SO_2	Condensed furan resins
1978	Warm-box	Modified furan resins
1981	Warm-box-vacuum	Furan or phenolic resoles
1982	Ester-cured no-bake	Alkaline phenolic resoles
1983	MF-cold-box	Alkaline phenolic resoles
1983	Cold-box plus	*o*-condensed resoles
1984	Acrylic-epoxy SO_2	Acrylic and epoxy resins
1987	Hot-box plus	Modified phenol resins
1988	Acetal (methylal)	Resorcinol resins
1990	CO_2-resole cold-box	Alkaline resoles (boron modified)
1995	Biodiesel-based UCB	*o*-condensed resoles with methyl ester solvents
2001	TEOS UCB	*o*-condensed resoles with tetraethyl silicate solvents

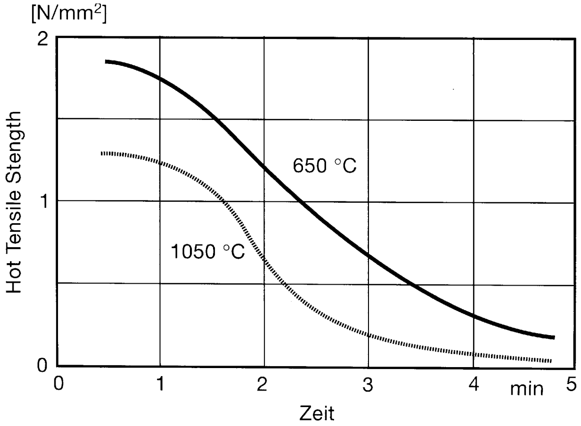


Fig. 18.7 Hot tensile strength levels of resin-bonded molding materials after 1–4 min at 650 or 1,050°C. Zeit is German for Time

that resins produce a compatible level of carbon under pyrolysis conditions. “Compatible” means that such levels exert a positive effect on the surface of the castings, but do not contribute to undesirable “glossy” or “lustrous” carbon defects that can considerably detract for the processing quality and integrity of the castings.

The variety of coremaking processes is also related to the wide range of chemical reactivity of the resins, citing phenolics (Table 18.5) as an example. Thus, phenolic novolaks may be reacted with hexamethylene tetramine (HMTA or hexamine, “hexa” for short) at elevated temperatures. Free flowing, storable phenolic resin coated sands are produced with hexa in the shell molding process. Phenolic resoles can react with acids at ambient or high temperatures (no-bake and hot-box processes), undergo polyurethane reactions with diisocyanates in the presence of tertiary amine catalysts (polyurethane cold-box and no-bake processes), and be used with methyl formate (MF) or carbon dioxide for precipitation and solidification processes (MF or CO_2 “resole” method).

The above comments of phenolic resins apply analogously to furan, urea, epoxy, and acrylate resins (Table 18.6). A representative process is the epoxy or furan gas curing method [9], in which the reactive resins are cured in closed systems by

Table 18.5 Varieties of possible phenolic resin reactions and use of these in phenolic and furan resins

Phenolic resin	Reactivity	Process
Novolak	Hexa (HMTA)	Shell molding (Croning)
Resole, neutral	Acid	No-bake phenolic resin
	Acid, heat	Hot-box phenolic resin
Resole, *ortho*-condensed	Polyisocyanate	Phenolic urethane cold-box Phenolic urethane no bake
Resole, alkaline	Ester, liquid	Phenolic ester no-bake
	Ester, vaporized	MF-resole
	Carbon dioxide	CO_2-resole

Table 18.6 Reactivity of furan, urea, epoxy, and acrylic resins and their use in core and mold making processes

Binder type	Reactivity	Process
Furan resins	Acid	No-bake furan resins
	Acid (in situ from SO_2)	Furan SO_2 cold-box
	Acid, heat	Furan warm-box
Urea resins	Acid	No-bake[a]
	Acid, heat	Hot-box[a]
Epoxy resins	Acid (in situ from SO_2)	Epoxy-SO_2 cold-box
Acrylic resins	Polymerizable	Free radical cure (FRC)[b]

[a] Generally in combination with furan or phenolic resins
[b] Gassing with diluted SO_2 gas

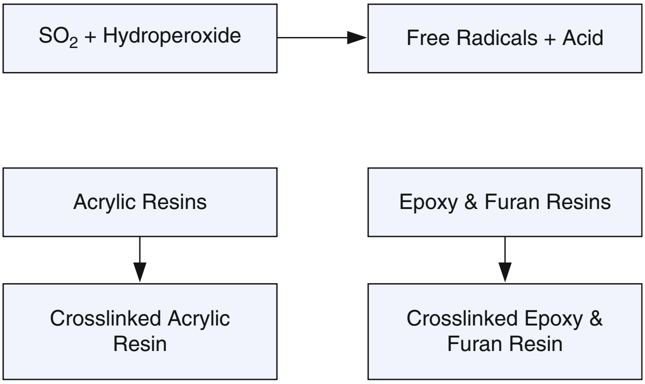


Fig. 18.8 Principle of the SO_2 process for coremaking

Table 18.7 Classes of core and molding process by type of cure

1.	Hot (180–280°C) and Warm (100–160°C) curing
2.	Cold curing (ambient temperature)
3.	Gas curing[a] (ambient and warm (40–60°C) temperature

[a] One component is in gaseous form and is used as a catalyst, coreactant, curing agent, and/or solidification/hardening agent

Table 18.8 2007 Annual binder requirements for core and mold fabrication with chemical (synthetic) binders in metric tons in the U.S. and Germany

Type of Cure	Process	US	Germany
Gas curing (cold-box)	PUCB	43,963	48,012
	PECB (MF & CO_2)	2,545	2,737
	Epoxy–acrylic SO_2	1,588	–
Room temperature (no-bake)	PUNB	27,862	–
	FNB	15,878	27,957
	PNB	2,561	4,564
	PENB	7,211	1,037
	Silicate (CO_2 and ester)	1,512	–
	Other	460	–
Heat curing	Shell resin	7,063	2,838
	Hot/warm-box	2,921	6,454
	Resin coated sand[a]	11,579	9,701

[a] As novolak resin at average of 3% based on sand

Source: estimated from various statistics

gassing with SO_2, which together with oxygen (in the form of an organic peroxide) and water forms sulfuric acid in situ (Fig. 18.8). The process is carried out in sealed systems. The SO_2-containing exhaust is conveyed to a wet scrubber containing sodium hydroxide solution for treatment.

The different reactive properties of synthetic resins result in three groups of core-making – or mold fabrication – processes (Table 18.7) as given below:

1. Warm and hot curing at temperatures ranging from 150 to 280°C (302–536°F) depending upon the type of process.
2. Cold curing with direct addition of a curing agent at the ambient temperature prevailing in the plant during summer and winter, with possible adaptation of the resin systems or substrate temperature for summer or winter conditions.
3. Gas curing, initiated by gaseous substances or vapors and possibly involving formation of reaction products requiring additional attention in exhaust gas disposal or neutralization (scrubbing). Some gas curing processes may be operated at temperatures of 40–60°C (104–140°F) for process operations and productivity concerns, and are thus no longer "cold" processes in a strict sense.

Accurate statistics on binders and mold/core binders are difficult to determine; however, estimates for 2007/2008 indicate that more than 125,000 metric tons of synthetic binders (mainly phenolic and furan resins) are used to produce sand for

Table 18.9 Percentages for core and mold fabrication with chemical (synthetic) binders in metric tons in the US for 2007

Type of cure	Process	Usage (mt)	% of total	% within type
Gas cured	PUCB	43,963		91.4%
	PECB (MF & CO_2)	2,545		5.35%
	Epoxy–acrylic SO_2	1,588		3.3%
Total gas cured:		48,096	38.4%	–
Room temperature	PUNB	27,862		50.2%
	FNB	15,878		28.6%
	PNB	2,561		4.6%
	PENB	7,211		13.0%
	Silicate	1,512		2.7%
	Other	460		0.8%
Total room temperature:		55,484	44.3%	–
Heat cured	Shell	9,785		32.8%
	Hot/warm-box	2,921		13.5%
	Resin coated sand[a]	21,563		53.7%
Total heat cured:		12,706	17.2%	–
Total (all systems):		125,143	100.0%	–

[a] As novolak resin at average of 3% based on sand

Source: estimated from various statistics

fabrication of molds and cores in the U.S. and more than 103,000 tons in Germany (Table 18.8).

On the basis of these statistics, phenolic urethane cold-box (PUR) system accounts for more than 90% of cold curing systems used in both the U.S. and Germany (Table 18.9). For room temperature cured (no-bake) systems, in the U.S. the phenolic urethane no-bake system predominates with over 50%, followed by furan and phenolic acid-cured system at 33%. In Germany, furan and phenolic acid-cured systems amount to nearly 97% of all no-bake systems, as the phenolic urethane no-bake process is little used in Germany.

Resin coated sands and novolak resins for so-called "captive" coating (foundries that coat their own resin coated sands) account for 86.5% of all heat curing process in the U.S. In Germany, resin coated sands and novolak resins account for some 66% of all heat-cured processes. In the U.S., the use of hot-box continues to decline with the aforementioned change from iron engine blocks and heads to aluminum castings.

Figure 18.9 represents an alternative way of looking at the ubiquitous nature of phenolic resins in foundry binder. PF resins are used exclusively as novolaks in the resin coated sand process (although some of the newer technologies combine a resole with the novolak), and in every other process, no-bake and cold-box, except for SO_2-cured processes. It is worthwhile to note that even in that process, phenolic resin may be added as a modifier and/or makes its way into epoxy resins as Bisphenol A and F or other higher functional novolak resins used in the system. In total, phenolic resins make up the majority of the synthetic resins used in foundry applications.

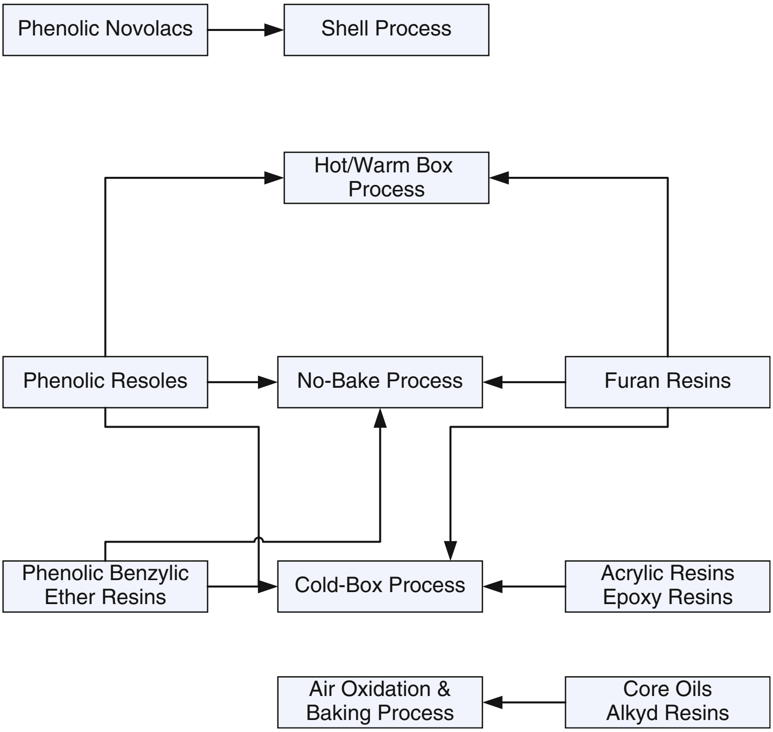


Fig. 18.9 Polymer types used in foundry binders

18.2 Hot Curing Processes

The shell molding and hot-box processes, the warm-box method, and the warm-box vacuum technique represent hot curing processes [10–12]. Considering only phenolics, the resin systems used in the processes are phenolic novolak-hexa blends as well as various modified and unmodified resoles in which the modifier can represent urea resins, furan resins, and monomeric and polymeric furfuryl alcohol.

18.2.1 The Shell Molding Process

The Croning method [13–15], termed the shell molding, shell process, or resin coated sand process in English-language foundry literature, has been applied to series production since around 1948. In this process, silica sand is coated with a phenolic novolak-hexamine film at elevated temperatures and the coated sand cured on hot pattern plates or in coreboxes to form shells or cores. Shells represent a special type of mold, and are produced nearly exclusively by the shell molding process.

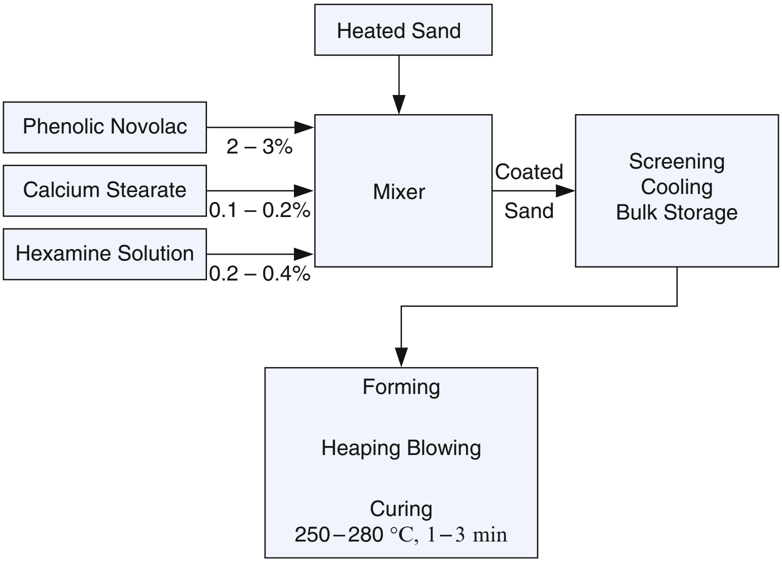


Fig. 18.10 Croning (also known as shell molding or resin coated sand) process for making cores and molds (schematic description)

The shell molding method (Fig. 18.10) may be differentiated into two basic process stages:

1. Sand coating (or conditioning); that is, production of free-flowing storable phenolic resin coated sand by a) hot coating or b) warm coating.
2. Production of shells, and hollow and solid cores on hot pattern plates or in heated coreboxes.

18.2.1.1 Sand Coating (Conditioning)

Hot Coating

The washed and dried silica sand is heated to 120–150°C (248–302°F). The granulated phenolic novolak resin (Fig. 18.11), with a melting point of around 80–100°C (176–212°F), is added to the mixer at 1–5% resin (based on sand and depending upon application). It melts and coats the grains of sand. The quantity of HMTA (or hexamine, "hexa" for short – see Fig. 18.12) required for later curing of the resin is then added as an aqueous solution (25–40% solids). Sufficient hexa solution to both cool the sand and deliver the correct amount of curative is added. The hexa level is 15–20% on the basis of resin, depending upon the desired properties. The cooling effect produced by the addition of the water solution prevents premature curing of the binder, although it is possible that some degree of cure occurs. Additives such as calcium stearate are incorporated during this stage

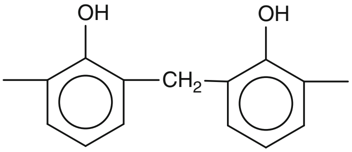


Fig. 18.11 Phenolic novolak general structure

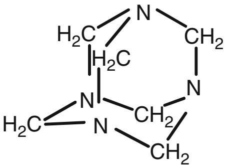


Fig. 18.12 Hexamethylenetetramine (HMTA, hexamine, or "hexa")

of the coating operation. The added calcium stearate promotes collapse of the sand aggregates in the mixer and serves as a parting agent in final mold production. The water is driven off by the heat in the sand during subsequent screening and cooling operations in the coating process. After these processes, the dry, free-flowing sand is stored and/or packaged.

Warm Coating

In this process, the phenolic novolak resin is used in the form of a solution in methanol and water. Powdered hexa is first added to sand heated to 60–90°C (140–194°F) in mixing equipment. After a brief mixing period, the alcohol solution of resin is metered in and the sand thus coated. At the same time, hot air is blown through the mixer to drive out solvents and water. Calcium stearate is added shortly before the end of the mixing period. The coating process is concluded by cooling and storing the dry, free-flowing resin coated sand.

18.2.1.2 Fabrication of Cores and Shells

The resin coated sand is capable of lengthy storage. It is converted into shells (Fig. 18.13) and cores by dumping it on heated pattern plates (dump method) or by shaping it under air pressure in heated coreboxes on single-stage, transfer, and multi-stage rotary shooting or blowing machines. Depending on the thickness and shape of the cores and shells, the curing periods range from 0.5 to 3 min at about 250°C (482°F). In foundry practice, curing is performed at temperatures ranging from 180–350°C (356–662°F).

Shells, molds, and cores produced in this manner are not hydroscopic and provide the casting with a high level of dimensional accuracy and surface smoothness. Steel, light metals, and copper alloys, in addition to the various types of cast

Fig. 18.13 Production of camshafts by the shell molding process

iron, are cast in "shell mold packets" (an assembly of shell mold and cores). The shell molding process is mainly used to produce castings for automotive, truck, and machine construction and cast ductile iron pipe.

The possible workplace emissions of ammonia and phenol experienced during production of cores and/or shells by the shell molding process have been reduced by development of binder systems that are low in free phenol and hexa, and thus afford a reduction in the phenol and ammonia levels to well below the threshold limit values (TLVs). Free phenol levels less than 1% are now common by using new production techniques.

It is furthermore possible to replace hexa-containing novolak systems partially or completely by combinations of novolaks and resoles. As approximately 50% of the nitrogen in hexa is released as ammonia during curing, reduction in the hexa level can significantly reduce odor at core and mold making.

Plant trials have demonstrated that a significant reduction in pollutant emissions during the coating process is in fact achieved when resins exhibiting low levels of free phenol are used. In these trials, an 80% reduction in the exhaust gas levels of phenols corresponded to a decrease in the level of free phenol in the binder from around 5% to less than 1%.

Table 18.10 shows a comparison of traditional resin coated sand emissions to a new generation low-odor system at core/mold sand mixing, making, and storage tests conducted at CERP (see Sect. 18.7 later). Significantly lower hazardous air pollutant (HAP) emissions were achieved, primarily through reductions in phenol and formaldehyde emissions. Two target analytes comprised 97% of the emissions. Ammonia had the highest contribution at 78% followed by phenol at 19%.

Table 18.10 Comparison of traditional resin coated sand emissions to a new generation low-odor system at core/mold sand mixing, making, and storage tests

	Total HAPs (lb emission/lb resin)	TGOC (as propane)	CO	CO_2	Sum VOCs
Traditional RCS	0.0022	0.009	0.027	0.002	0.01
Low emission RCS	0.0007	0.016	0.026	0.002	0.025

Source: CERP Test Report Nos. HN and HO

While phenol and formaldehyde are HAPs, ammonia is not. But, its dramatic reduction contributes to the lower odor of these systems.

18.3 The Hot-Box Process

The hot-box process [11, 12, 16–18] was the method of choice for mass production of cores for gray iron, light metal, and heavy metal casting. With the transition from iron to aluminum cylinder heads and blocks, the usage of hot-box resins has declined. Additional concerns over worker exposure to free formaldehyde have also hastened the decline of this process.

In iron casting, unmodified and modified phenolic resoles are mainly used as binders. In light metals casting, such as aluminum, urea-modified furan resins are the binders of choice. For heavy metals casting (copper, bronze), straight furan resins are the binders of choice. In this specific coremaking technique, a wet sand mix is first prepared using a liquid resin and curing agent (Fig. 18.14 – in the schematic, BOS refers to the binder weight as a percentage based on the weight of sand; BOR refers to the catalyst weight as a percentage based on the weight of the resin). The wet sand mix is then cured at 180–250°C (356–482°F) in heated coreboxes.

The hot curing with simultaneous acid catalysis employed in the hot-box process affords particularly short curing cycles in series production. Complete curing of the molding sand mix in the hot coreboxes is furthermore unnecessary as the material may be removed from the coreboxes after it has formed a solid outer shell. Final, complete curing takes place outside the coreboxes. Rapid curing at elevated temperature is achieved by use of "latent" curing agents or catalysts. These generally represent salts of strong inorganic and organic acids, such as ammonium nitrate coupled with specific additives, dissolved in water. The coremaking sand mix is prepared by wetting alkali-free silica sand and then coating it with the liquid phenolic resin and the latent catalyst. While high-purity silica sands are recommended, the U.S. automotive foundry industry made use of local "lake" sands available in deposits in the southern peninsula of Michigan. These lake sands have a higher amount of alkaline impurities and lower silica content than high-purity silica. The term "Acid Demand Value" or ADV, became important to define these sands based on their acid soluble impurities.

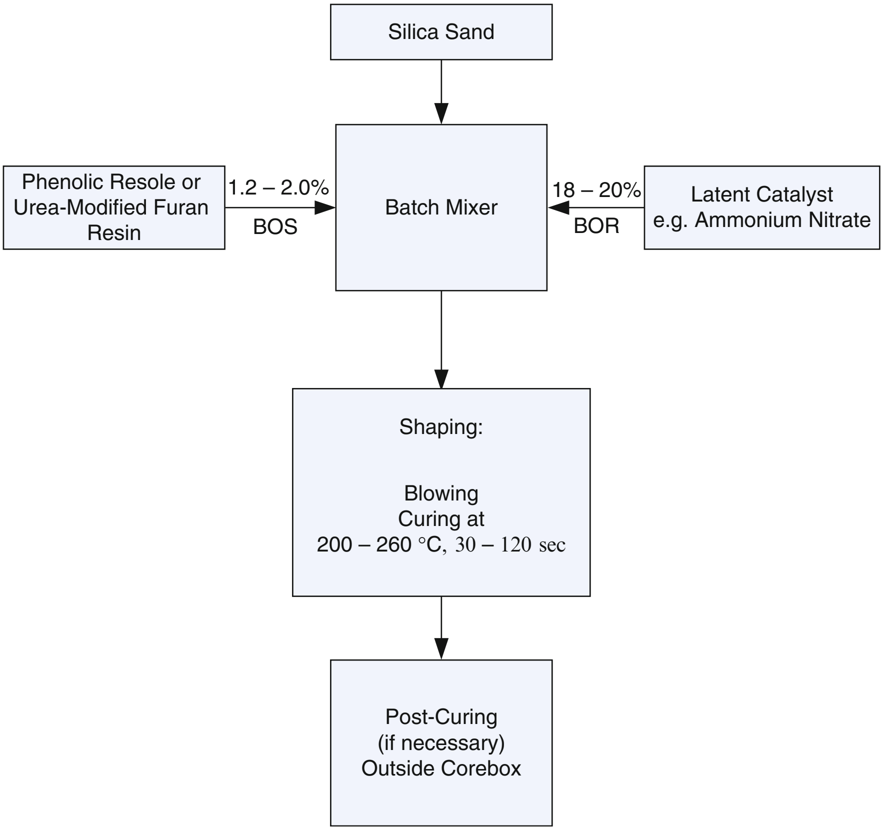


Fig. 18.14 Hot-box process for making cores (schematic description)

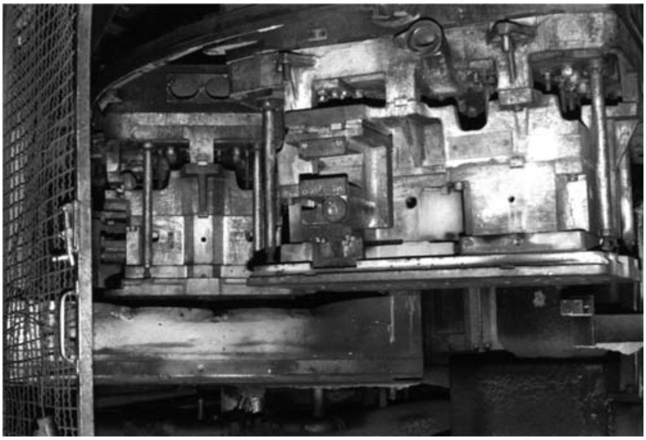


Fig. 18.15 View of a rotary shooting machine used to increase the productivity of hot curing coremaking process, for example, the hot-box method

The moist prepared core sand mix with a resin level of 1.2–2.0% depending upon sand type and core geometry, may be used for a period of 30–120 min depending upon the type of resin, catalyst type and level, sand type and ADV, and the sand and ambient temperatures. The mix is converted into cured cores on single-stage, transfer, or multi-stage shooting or core blowing machines (Fig. 18.15). The cores are poured off in both sand molds, and (in aluminum casting) semi-permanent metal molds. As these hot-box cores exhibit very good dimensional stability, the nominal casting wall thicknesses may be more precisely achieved than by other methods. In addition, the higher hot strength of phenolic resole resins allowed this system to be preferred for certain core applications. The main fields of use are in engine casting, particularly for delicate water jacket cores, other automotive applications, and in the fabrication of copper-based fittings. Because of workplace environmental concerns, primarily with free formaldehyde, the use of hot-box resins as a whole continues to decline.

A newer version of the hot-box method is the hot-box plus process [19]. In this method, a moist sand mix is prepared with a phenolic resole and curing agent as in the standard process, but the blended curing agent additionally includes HTMA. The moist sand mix is then cured in the standard manner at 180–250°C (356–482°F). The core sand properties – that is, rapid curing, high strength levels, and good thermal properties of the cores when poured off – are comparable to those in the hot-box process. However, the extremely long bench life compared to that in the conventional hot-box process is a great advantage. This method can mainly be used in iron casting, but is little practiced today.

18.4 The Warm-Box Process

The "warm-box" method [11, 12, 20], in which the curing temperatures range from 130 to 180°C (266–356°F) and are thus lower than in the hot-box process, represents a variant of the latter technique. The curing periods are generally shorter than those in the hot-box process. Highly modified furan resins are used as binders. Phenolic resoles and novolaks are used as modifiers. Specific sulfonic acids and/or copper and aluminum salts of these [11, 21] are used as latent catalysts. The added binder levels are lower than in the hot-box process, and generally amount to 0.9–1.4% on the basis of sand; the level of curing agent (catalyst) is 18–30% on the basis of binder.

The three major advantages of this coremaking process over the hot-box method are the lower energy demand, increased productivity, and decreased pyrolytic potential, that is, the reduction in gas evolution during casting (Fig. 18.16). A reduction in emissions is possible because of both lower resin levels required and the unique structure of these binder systems. In iron casting in the U.S., this method is particularly useful for the production of ventilated disk brake rotor cores and for boiler cores. However, cores from warm-box process are slightly higher in moisture sensitivity than those from the hot-box process. For this reason, organosilanes are typically added either to the binder during manufacture or directly to the sand mix to improve resistance to humidity degradation of the cured cores.

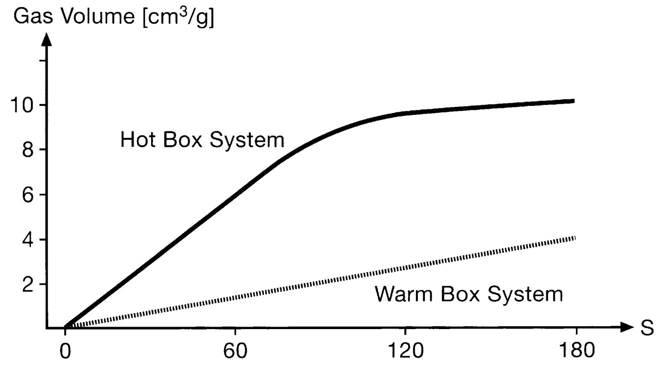


Fig. 18.16 Comparison of gas evolution from hot-box and warm-box cores at 800°C

Also, especially when compared to phenolic hot-box resins, warm-box binders have considerably different thermal expansion characteristics. For this reason, substitution for phenolic hot-box binders needs to be carefully considered and the finished casting dimensions evaluated before full production conversion.

As noted in the earlier Pizzi reference, tannin particularly that condensed from quebracho wood has been used as a modifier in warm-box binders, especially for rotor core production. The benefits to such addition are a reduction in free formaldehyde generated during curing (a worker exposure concern), fast curing (as compared to nonmodified resins), and higher "hot" tensile strength (the strength of the core upon removal from the core box).

A process variant of the warm-box technique is known as the "vacuum warm-box process." This process allows cores to be produced at temperatures as low as 70–100°C (158–212°F) [22]. Core boxes in which a reduced pressure can develop when a vacuum is applied are used in this method. This reduced pressure differential allows pollutants to be removed directly from the corebox and treated by conventional methods. Phenolic resoles and furan resins may be used as binders in combination with specialty curing agents. These specialty curing agents may contain materials including copper chloride. When a vacuum is applied, diluents and water immediately vaporize, causing a reduction in the pH and initiating the cure even at relatively low temperatures.

Because of the cost and difficulty of establishing and maintaining a vacuum at the core box, this process is little used today.

18.5 Cold Curing with Direct Addition of a Curing Agent (No Bake Process)

In the no bake process, involving "cold" or room temperature curing with direct addition of a curing agent (usually as a liquid), cores and molds are produced from self-setting sands in cold (ambient temperature of the foundry) or molding flasks or patterns. The most common method involves the use of acid-catalyzed (phenolic and furan) resin systems that cure without application of heat. Another option consists of the use of highly alkaline binder systems – aqueous phenolic resoles containing a high level of potassium or sodium hydroxide – which are cured by addition of specific acetate esters. A third possibility, the phenolic urethane no-bake (also known as PUR no-bake) method, involves curing *ortho*-condensed resoles with polyisocyanates in the presence of tertiary amine catalysts.

18.5.1 Acid Curing

The binders are furan resin systems (based on furfuryl alcohol, not *furan* as commonly noted), and also straight or modified phenolic resoles in the acid curing no bake process [11, 12, 23], in which the cure is brought about by addition of acids. In Europe, special emphasis is placed on those phenolic resoles exhibiting the lowest possible levels of free phenol (less than 4.5%). In the U.S., emphasis is placed on phenolic (and furan) resins with the lowest possible levels of free formaldehyde, that is, <0.1%. Free formaldehyde is a workplace exposure issue. Solutions containing less than 0.1% free formaldehyde are considered so-called "nonreportable" whereby formaldehyde does not appear (not reported) on the Material Safety Data Sheet.

In the acid-catalyzed no bake process, alkali-free sand is coated with a binder system consisting of an acid-sensitive resin and a curing agent (Fig. 18.17), and is capable of undergoing cure at ambient temperatures; the types of resin and curing agent are selected to match the specific production conditions as well as the requirements of special molds or cores. Blending (or mixing of the acid catalyst, resin, and sand) is generally performed in continuous throughput mixers (Fig. 18.18). With all heat-cured, no-bake, and cold-box binder systems, as sand makes up at least 98–99+% of the mixture from which molds and cores are to be made, the mixing and metering of the various binder ingredients (resins, coreactants, hardeners, and catalysts) is critical to making high quality castings. Over the last 20 years or so, equipment manufacturers have made considerable progress in the design of both the mixers (both batch and continuous) and the pumping and metering systems used to deliver the chemicals. Figure 18.19 shows a recent design metering system using mass flowmeters to accurately deliver a three-part chemical binder independent of the viscosity of the materials.

The molding sand possesses a limited bench life, referred to in the U.S. as "work time" (to distinguish it from bench life of cold curing systems), and gradually cures after being charged and evenly distributed into the mold and compacted to a uniform density. The level of free formaldehyde, which typically does not exceed 0.5% (typically <0.1% in the U.S.), is presently an important factor in selection of the phenolic or furfuryl alcohol-containing binders. Furan resins, which make up the majority (about 70–85%) of the resins used in this segment of foundry binders,

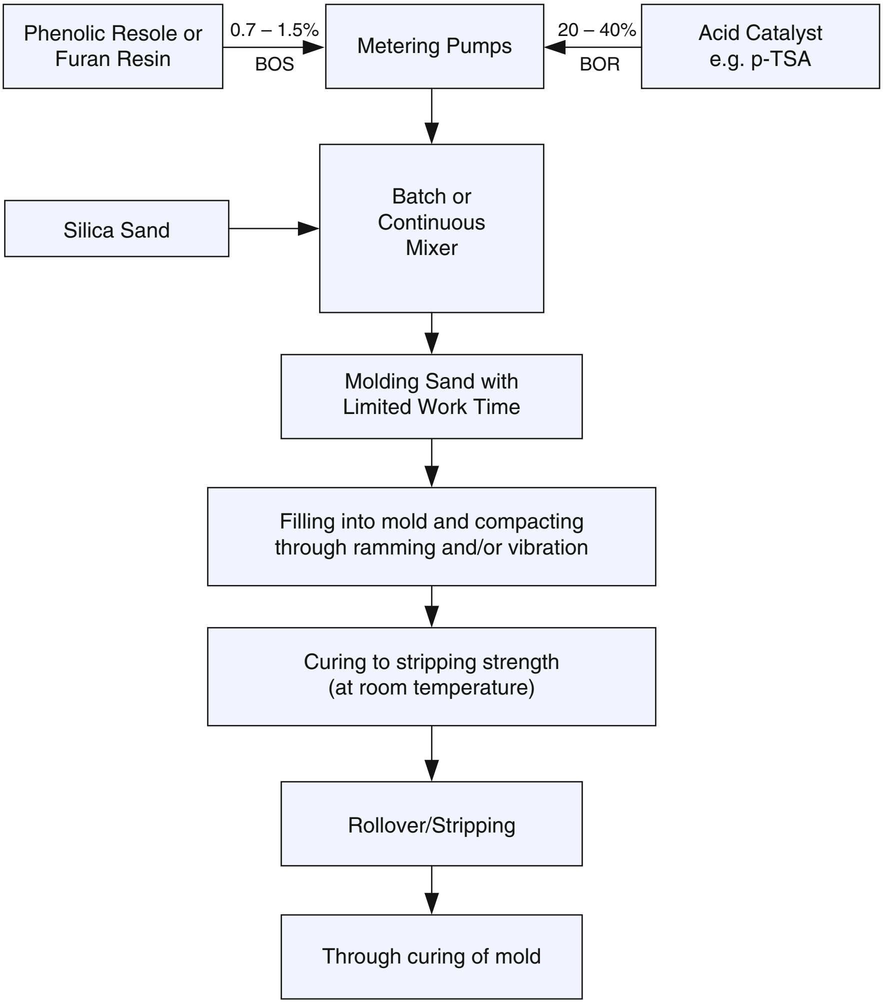


Fig. 18.17 No-bake acid curing process scheme

have frequently undergone dramatic price fluctuations because of limited availability and the sometimes volatile pricing of furfuryl alcohol.

Furfuryl alcohol, unlike phenolic resins being discussed here, is derived from agricultural by-products, such as corn cobs, rice hulls, and sugar cane bagasse. Thus, its price is dependent upon the availability of these raw materials, which can fluctuate depending upon the timing of the harvest and the yield of the various crops.

As a result of this volatility, phenolic resoles were used as early as 1975. From the very beginning, demands to hold the levels of free phenol and formaldehyde as low as possible were proposed for these products. These demands have in fact been met by special developments by various manufacturers.

Fig. 18.18 Modern continuous mixer for no-bake sand
Source: IMF Luino, Italy and Indianapolis, IN, USA

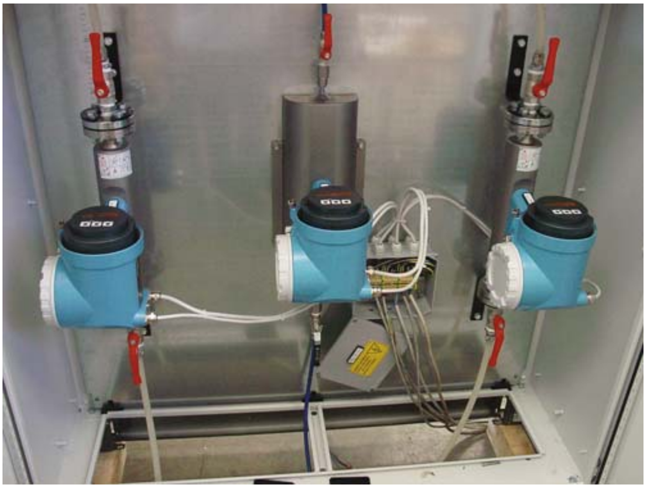


Fig. 18.19 Modern mass flow metering system for a continuous mixer for no-bake sand
Source: IMF Luino, Italy and Indianapolis, IN, USA

The molding sands are generally prepared using the following formulation as a guideline (PBW = Parts by weight):

- 100 PBW silica (quartz) sand
- 0.7–1.5 PBW resin
- 0.2–0.6 PBW acid catalyst

The dry, alkali-free (high pH or ADV sand can adversely affect the curing rate by consuming some of the acidic catalyst to neutralize alkaline impurities on or in the sand) silica sand is wetted with the acid in a mixer and then coated with the liquid resin. The liquid coated molding sand is slightly moist and possesses certain flowability. It can only be worked for a limited period, which is dependent upon several variables:

- Temperature of the sand
- Temperature of the liquid components (binder and catalyst)
- Amount and type of acid catalyst used

The length of the limited molding sand bench life or working time, the subsequent stripping or "demolding" time of molds and cores, and the time required until the maximum mechanical strength is reached depend upon the level and type of acid used, and particularly on the temperature of the mix, in addition to the type of resin. The curing times are shortened by increased temperatures and higher acid levels, as well as by the use of stronger acids. In general, all chemical curing systems obey the "10°C/18°F Rule" (a simple rule of thumb more exactly defined by the Arrhenius equation): reaction rate doubles or halves as temperature increases or decreases by this amount, and is incrementally affected as temperature changes.

The most commonly used curing agents include organic sulfonic acids (mainly *p*-toluenesulfonic acid (Fig. 18.20) with sulfuric acid levels of 0.5–2%) and phosphoric acid, which is now seldom used. In Europe, these sulfonic acids are commonly referred to as "*p*-TSA" and just TSA in the U.S. Benzene- and xylenesulfonic acids are also used when faster curing is required, although more so in the U.S. and Canada, respectively.

The phenolic resoles used in this case generally possess the following properties: low levels of free phenol and formaldehyde, low water levels and desirable viscosity range, fast curing rates upon addition of acid and good plasticity following curing. These properties ensure good handling, uniform sand coating, ease of compaction, low odor, and a long period during which the molds or cores can be "stripped" (i.e., removed or demolded from the pattern or core box), coupled with desirable curing times. The high strength levels of the cured molding sand permit low resin addition levels and subsequent reuse of up to 90–95% reclaimed sand.

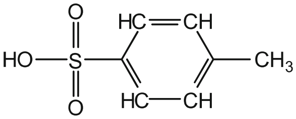


Fig. 18.20 *p*-Toluenesulfonic acid

“Reclaimed sand” is generally considered to be the silica (quartz) sand from a used mold or core that has been thermally or mechanically regenerated for reuse. The rich carbon supply and very low nitrogen level of the residual phenolic resin binders afford castings of high surface quality.

A general comparison of the use of phenolic and furan resins in this process affords the following summary. The viscosity of furan resins is generally lower than that of phenolics, and furan is generally considered to be less temperature dependent, especially when lower ambient temperatures retard curing. Reclaimed sand from used furan resin-bonded molds or cores is also generally easier to reuse, presumably due to the brittle nature of the cross-linked furfuryl alcohol polymer. This brittleness of the cured resin makes it easier to remove from the sand grains by attrition methods. In addition, the higher hot strength of phenolic resole and its more elastic nature when cured (as compared to furan) make it more difficult to mechanically remove from bonded sand exposed to the casting process.

If these two points are considered when using phenolic resins (reduction of the base viscosity and thermal regeneration of reclaimed sand), significant economical advantages are definitely apparent in phenolic resins.

18.5.2 No Bake Curing with Added Esters

The procedure of the ester-cured alkaline phenolic [11, 12, 24] no bake process (known widely as the ALpHASET process) is similar to that of the acid-catalyzed no bake method with respect to the mixing and other processing operations, but the resin is very different. The resin is a highly alkaline, water soluble phenolic resole salt that can be on the basis of potassium hydroxide, sodium hydroxide, or a hybrid of the two. Potassium-based resoles generally work best on new and thermally reclaimed sands; sodium-based on mechanically reclaimed sands and hybrids on both sands.

The coreactants are organic esters and their blends, typically triacetin and butyrolactone. Dibasic esters can also be used as coreactants. Because these materials are coreactants and not catalysts, and the esters become chemically combined with the resin, they must be added at a fixed rate to the sand mix on the basis of the weight of the resin used. In terms of speed, dibasic esters cure the slowest, followed by triacetin, with butyrolactone the fastest.

In sand preparation, 1.0–1.75% of the highly alkaline phenolic resole (based on sand) is first blended into the sand, followed by 20–30% (based on resin) of the ester, or ester blend. The reaction between the specific esters or mixtures of these with the alkaline resin leads to curing/setting and solidification. Depending on the type of ester or the ester blend used, stripping times may be adjusted from 3 to 60 min and longer. The throughcure allows these binders to be used for automated molding applications. As the binders are almost free of nitrogen and sulfur, they afford foundry engineering advantages for steel, nodular iron, and aluminum casting. However, handling strengths are lower relative to competing organic binder systems.

The unique feature of ester-cured alkaline phenolic is its "two-stage" cure: upon curing with an ester an unstable intermediate is formed that provides sufficient handling strength. But, during the casting process, the unstable intermediate dissociates, and the phenolic resole heat cures. It is speculated that this reaction occurs during the maximum silica sand expansion. As a result, ester-cured alkaline phenolic no-bakes have very little tendency toward veining defects in gray and ductile iron and hot tearing defects in steel casting.

18.5.2.1 Effect of Alkali Metals on Mechanical Reclamation

In reclaiming ester-cured alkaline phenolic systems [25, 26], it is important to note that alkali metals can react with the sand surface during casting forming silicates. The alkali salts can change the sand surface chemistry, and remain in the sand. This can interfere with reclaimed sand re-bonding. It can also make the reclaimed sand appear "dry" by absorbing water from resin. In general, for mechanical reclamation, sodium salts show less effect than potassium; therefore, use of sodium-based resins on mechanically reclaimed sand is preferred. Also, water additions of 0.2–0.3% based on sand during re-bonding can improve performance.

18.5.2.2 Effect of Alkali Metals on Thermal Reclamation

The effect of alkali salts on thermally regenerated sands is even more dramatic [27, 28]. The salts can and will react with silica sand forming silicate glass. These sintered silicates can foul the reclaimer. In addition, sodium or potassium salts can build-up in reclaimed sand and reduce re-bonding strengths. To prevent this from occurring, a patented additive was developed that is added to the shakeout sand just prior to its entry into a thermal reclaimer.

The proprietary mineral additive, which is added to the sand at a level of 0.6–1.0%, minimizes sintering at all temperatures. The additive complexes with alkali metals and removes them as fines. As with mechanically reclaimed sand, water additions may be helpful in improving re-bonding strengths. In contrast to mechanically reclaimed sand, potassium-based resins may provide better performance on higher quality thermal reclaim sands.

As mentioned earlier, the alkaline shakeout or spent sand can be successfully reclaimed with the advent of new binders and additives. Foundries are able to reuse reclaimed sand from this process anywhere from 60% to 80% using a mechanical process, depending on handling requirements. The sand from a thermal reclamation process is nearly a 100% replacement for new sand, but only when the special additive is used to pretreat the sand prior to thermal treatment. The ester-cured alkaline phenolic system offers environmental advantages over the acid and amine cured phenolic resins (see Sect. 18.7).

18.5.3 No Bake Process with Isocyanate Curing

The urethane no-bake (called UNB in the U.S. and PUR in the EU) method [11, 12], a no-bake process using polyisocyanates as curing agents [29] is chemically related to the urethane cold-box process (see Sect. 18.6.1). In contrast to the urethane cold-box process, which is a gas curing process, a liquid catalyst (or curing accelerator) is used. Thus, the UNB system is a three-part system:

- Part 1 (Part I or A resin) *o*-condensed phenolic resin in solution
- Part 2 (Part II or B resin) polymeric MDI in solution
- Part 3 (Part III or catalyst/activator) tertiary amine in solution

One reaction component is an *o*-condensed phenolic resole diluted with solvents, and the other is a diphenylmethane-4,4′-diisocyanate-based polyisocyanate (also known commonly as polymeric MDI or just MDI) dissolved in similar solvents. A tertiary amine is added as a liquid catalyst to the sand mixture to accelerate and control the curing speed. When the p-MDI comes into contact with the phenolic resin, the catalytic action of the amine initiates the actual reaction leading to urethane formation after a brief initial delay. The latency is unique in foundry binders, and gives phenolic urethane no-bake a considerable advantage. Figure 18.21 illustrates this process on the basis of the compression strength relative to that in an acid-catalyst process with furan resin as the binder. In the case of the acid curing sand,

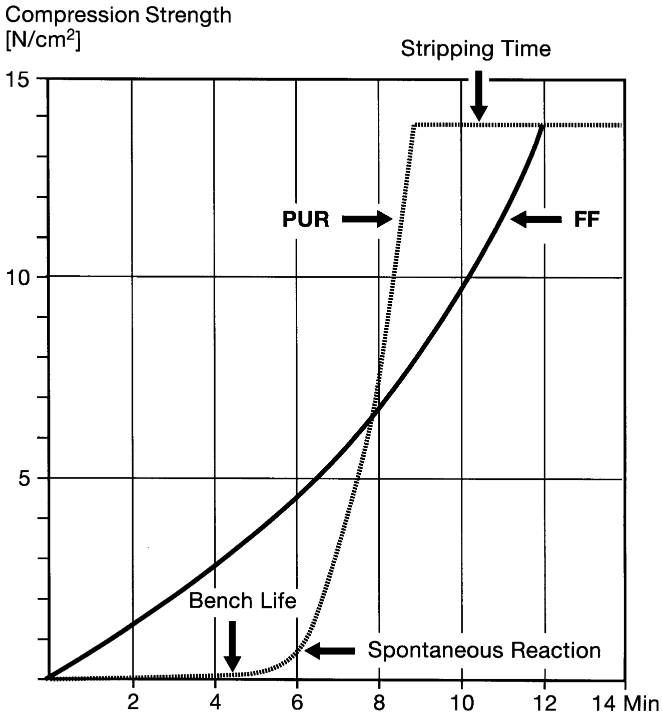


Fig. 18.21 Curing curves in the polyurethane (PUR/UNB) and furan no bake processes

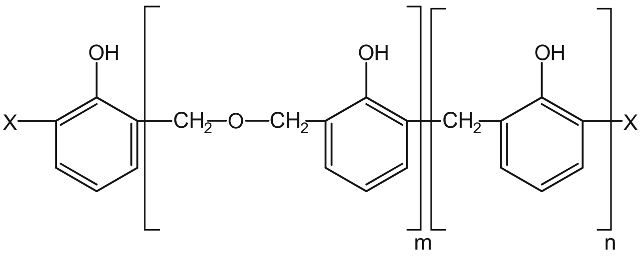


Fig. 18.22 Benzylic ether structure (also known as *ortho*-condensed phenolic resole). The sum of *m* and *n* is at least 2 and the ratio of *m*-to-*n* is at least 1, and X is an end-group from the group consisting of hydrogen and methylol, the molar ratio of methylol-to-hydrogen end groups being at least 1. The most preferred benzylic ether resins are those in which any phenolic ring substitution in the meta position is hydrogen as shown here

the reaction begins immediately as indicated by the compressive strength level; whereas the urethane no-bake reaction only proceeds spontaneously after a certain "open" time, which provides for an extended shaping time.

In North America, particularly in the U.S., the "open" or working time of a particularly no-bake process binder is called the work time. In similar fashion, the strip time is the time that a mold or core can safely be removed from its pattern or core box without deformation. As measured in laboratory situations, it is common practice to refer to the ratio of the work time to the strip time. For urethane no-bakes, this ratio is typically >60% compared to <30% for acid curing systems.

The key innovation in this technology, the *o*-condensed phenolic resin, was the development of Dr. Janis Robins [30–32]. It is also referred to as benzylic ether, or polyether polyol resin. The key structure is shown in Fig. 18.22.

The phenols employed in the formation of the benzylic ether resins are generally all phenols which have been employed in the formation of phenolic resins; however, for no-bake applications straight phenol is used. The aldehyde typically reacted with the phenol is formaldehyde, usually in the paraformaldehyde form, but also as a formalin solution of varying concentrations.

One of the unique features of this benzylic ether resin is that during the condensation reaction between phenol and formaldehyde, the by-product water is removed under vacuum distillation to a low level (<0.5%). The low level of water is important in the subsequent compatibility and room temperature curing with the isocyanate component. Because of the very low water solubility of this type of benzylic ether structure phenolic resin, the resin is typically dissolved in nonaqueous systems, preferably a mixture of polar and nonpolar solvents.

Part 1 resins may be viewed in their simplest terms as being comprised of three components:

- Phenol–formaldehyde resin (benzylic ether structure)
- Solvents
  - Polar
  - Nonpolar
- Additives

The benzylic ether PF resin typically comprises 50–60% of a part 1 resin and varies in molecular weight according to manufacturing conditions, and to the relative amounts of phenol and formaldehyde used (mole ratio). Manufacturing conditions are critical to the performance characteristics of the phenolic urethane system and are precisely controlled. The "time–temperature profile" carefully specifies manufacturing conditions used to produce a benzylic ether resin. By changing the production conditions and also the molar ratio of phenol to formaldehyde, the manufacturer can give the resin drastically different properties. These resin properties are typically the molecular weight distribution, viscosity, and amount of free formaldehyde remaining in the resin. Table 18.11 shows the typical viscosity, average molecular weight, and hydroxyl number for benzylic ether base resins.

Equally important to the polyurethane process is the isocyanate used in the process. It was known at the time that isocyanates react with phenolic resins to result in cross-linked materials, but heating was always required to obtain acceptable material properties. While many different types of aliphatic and aromatic isocyanates can be used, the preferred isocyanate for both the urethane no-bake and cold-box processes are aromatic isocyanates, usually diphenylmethane-4,4′-diisocyanate-based polyisocyanate (also known commonly as polymeric MDI or just MDI). MDI is available in several forms based on two types of products, purified monomeric MDI and polymeric MDI. Pure MDI is primarily the 4,4′ isomer, but contains a small amount of the 2,4′ isomer (see Fig. 18.23). Most commercial polymeric MDI compositions are available with effective functionalities from about 2.0 to 3.0. Polymeric MDI compositions are characterized by their viscosity and their content of reactive isocyanate groups. Viscosity increases with increasing molecular weight and polymeric isocyanate content.

All forms of MDI are very reactive with water [33]. The reaction of isocyanate and water yields a substituted urea and carbon dioxide. The initial product of the reaction with water is a substituted carbamic acid, which breaks down into an amine

Table 18.11 Typical base UNB resin properties

Viscosity, cps at 65°C	Molecular weight (avg)	Hydroxyl number
800–3,500	350–500	450–500

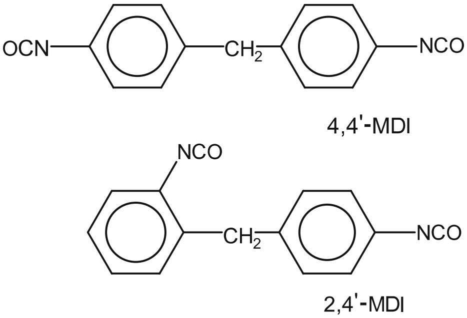


Fig. 18.23 Pure MDI isomers

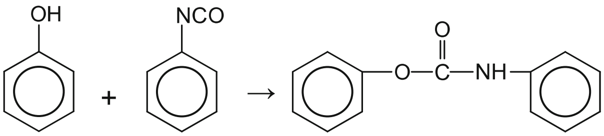


Fig. 18.24 Polyurethane no-bake or cold-box process – general reaction equation

and carbon dioxide. The amine then reacts with further isocyanate to yield the substituted urea. One mole of water reacts with 2 moles of isocyanate. Because of the large difference in molecular weight, a small quantity of water, even that from atmospheric humidity, will react with isocyanate in part 2 resins. For example, one fluid ounce (ca. 30 mL) of water can release as much as 40 L of carbon dioxide [34]. It is extremely important that users protect part 2 isocyanates from inadvertent exposure to moisture. Large consumers with bulk storage tanks will typically utilize a dry (–40°C, –40°F dew point) inert nitrogen gas to "pad" the tank and prevent moisture from entering temporary (day) and permanent storage tanks. For drum and tote containers, special tubes containing a desiccant drier are available to attach to the vent to remove moisture from the air venting the container.

While foundry binder manufacturers all use polymeric MDI, there are many choices available. In general, for urethane no-bake, two types are used for formulation of part 2 resins: high functionality (3.0+), high viscosity (ca. 2,000 cps) and mid-functionality (2.7), medium viscosity (ca. 200 cps).

The chemical reaction between the part 1 resin and part 2 isocyanate to form a urethane bond (Fig. 18.24) is an addition reaction; no by-products are produced. Urethane no-bake systems cure and develop strength at a uniform rate throughout the core or mold, independent of section thickness. In systems such as acid-cured furan and phenolic resins, throughcure depends upon removal of by-products (in this case water by evaporation) for the reaction to continue to completeness.

The rate of cure can be adjusted by way of the catalyst level and type and amount of tertiary amine used in the catalyst. Three liquid tertiary amines are used commercially as catalysts, or activators (Fig. 18.25):

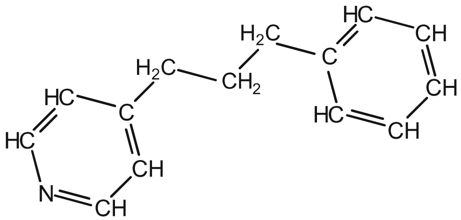
- 4-Phenylpropylpyridine
- 1-Methylimidazole
- 1-Vinylimidazole

18.5.4 Polyol Urethane No Bake

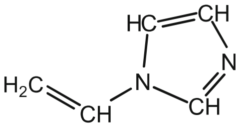
This system [11, 12] is a variation of the phenolic urethane no-bake process. It is a low hot strength binder first introduced in 1978. It is useful for aluminum, magnesium, and other light metal applications where shakeout of the molds or cores from the casting is needed.

In this application, amine-based polyether polyols are substituted for PF resin in the part 1. One type of polyol used is the Mannich polyols [35], an important group

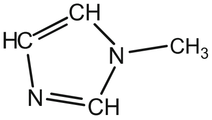
Fig. 18.25 Liquid tertiary amines used as catalysts in the urethane no-bake process



4-phenylpropylpyridine



1-vinylimidazole



1-methylimidazole

of aromatic polyols. They are obtained by the alkoxylation with propylene oxide and/or ethylene oxide of the Mannich bases obtained by classical Mannich reaction between phenols (typically phenol or *p*-nonylphenol), formaldehyde, and alkanolamines (diethanolamine, diisopropanolamine, monoethanolamine, monoisopropanolamine, etc.).

The most useful polyol resins will have molecular weights ranging from 400 to 2,000, hydroxyl numbers from 50 to 300, functionalities from 2.9 to 4, and viscosities from 73 to 14,000 cps at 25°C. Because of the high polyol viscosities, an aromatic solvent is also added to the part 1 resin to improve handling and mixing on sand. Part 1 formulations will use blends of these polyols at different ratios with aromatic solvent and are usually autocatalytic. The blend ratio will determine the useful work and strip time ranges. The part 2 isocyanate composition is similar to that in phenolic urethane no-bake applications. An optional activator can be added to speed the cure.

Because of the more linear nature of the polyether polyol resins, the urethane bond once formed has less resistance to heat than a straight phenolic-isocyanate urethane. With lower hot strength, shakeout in light metals, particularly aluminum is enhanced.

The latest innovations in this area are solvent-free polyol urethanes [11, 36], one of which cures using an additional trimerization catalyst for the isocyanate. The solvent-free systems use a combination of lower viscosity polyether polyols and reactive diluents to reduce VOC content, smoke, and odor on pouring.

18.5.5 Alkyd Oil No Bake Process with Isocyanate Curing

It is appropriate to mention the alkyd oil no bake process with isocyanate curing as the precursor system to urethane no-bake [11, 12]. Introduced in 1965, the system utilized an alkyd oil resin that was reacted with polymeric isocyanate for a condensed "first-stage" cure that facilitated very easy removal from the pattern or core box. Then the oil resin would completely cure on the basis of air oxidation of the alkyd resin ("second-stage" cure).

The part A alkyd resins used in this process are of the drying type and are produced from anhydrides such as phthalic anhydride, polyols such as pentaerythritol, and polyunsaturated fatty acids derived from vegetable oils such as linseed or soybean oil. In the drying or second-stage cure, the alkene groups react with oxygen from the air and cross-link. The drying speed depends upon the type of drying oil employed (more unsaturated oil means faster reaction with oxygen from the air) and the use of organic metal salts or "driers" that catalyze the cross-linking of the unsaturated oil. Most driers used today are on the basis of carboxylates of cobalt, zinc, and iron.

This system is little used today, except for certain applications in the U.S., where extended work times are needed for large cores and molds and ease of release from old patterns is required.

18.6 Gas Curing Processes Using Phenolic Resin Binders

In "gas curing" processes, one reaction component is introduced into the sand mix in the form of a gas or vapor and can produce various effects and reactions (Fig. 18.26). The gas or vapor, the additional component in these processes, can act as a precipitating agent (to cure and solidify the product), and as a catalyst (such as the amines used in the polyurethane process with *o*-condensed phenolic resoles). The gas or vapor can be transformed into or can develop various reactive materials such as formaldehyde from methylal or formic acid from MF, or – in the case of the SO_2 process – can aid in forming sulfuric acid, which in turn acts as the curing agent. In the "resole process" involving the use of highly alkaline potassium hydroxide containing phenolic resoles, which also include boron compounds (boric anhydride or borates), CO_2 similarly functions to initiate precipitation

Gas	Effect	Reaction	Process
CO_2	Precipitation	Setting	CO_2-Resole
Amine	Catalysis	PUR-Reaction	PUR Cold-Box
Methyl Formate	Precipitation	Setting	MF-Cold-Box
Methylal	Formaldehyde	Reaction	Acetal Process
SO_2	Sulfuric Acid	Reaction	SO_2-Cold Box
SO_2	Free Radical	Catalysis	SO_2-Cold Box

Fig. 18.26 Overview and principle of gas curing processes

reactions. Gas cured processes are now typically carried out in sealed, enclosed systems to permit direct removal of the resulting exhaust streams (catalysts, after cure excess coreactants, or by-products generated during cure).

The CO_2-silicate method [11, 12], which involves the use of an inorganic sodium silicate binder, is noteworthy from a historical viewpoint. This process is very environmentally friendly and exhibits relatively low costs. On the other hand, the poor collapse of cores after casting, the moisture sensitivity of the CO_2-hardened cores, the low strength levels, and the high alkalinity of the resultant spent sand represent serious disadvantages. However, keen interest in reducing emissions during the casting process has resulted in renewed interest in this process and recent advances have been made to improve the apparent disadvantages (see Sect. 18.7.1).

As a group, the gas curing processes have gained considerable significance over the past few years due to efforts to save energy and cost in both short and long production runs of cores. Not only are the binder levels and thus energy requirements expended in these processes reduced, but the productivity is increased because of much shorter cycle times.

18.6.1 The Polyurethane Cold-Box Process

Since the introduction of phenolic urethanes in the late 1960s, phenolic urethane binder systems have improved in performance and increased in complexity and sophistication of design. This has led, in part, to the increased usage of these systems in both the U.S. and Europe and in other parts of the world [11, 37, 38].

Phenolic urethane cold-box (called PUCB in the U.S. and PUR cold-box in the EU) systems have become the most widely used process for a number of reasons. PUCB is a known system, first introduced in 1968. The foundry industry has had the benefit of 40 years of improvements to the system. The system provides good tensile strength development needed for delicate cores, such as water jackets in cylinder head and block manufacture, and is relatively insensitive to sand type.

In the polyurethane cold-box or amine gassing process (also known commercially in the U.S. as Isocure, the tradename of the Ashland Chemical Company, inventor of the process), the amine used to gas the cores (general reaction scheme is shown in Fig. 18.24) acts as a catalyst to accelerate the polyurethane reaction of the *o*-condensed phenolic resole (benzylic ether PF resin) with the polyisocyanate. The resin/binder (see notes above in Sect. 18.5.3 on benzylic ether resin structure) used is produced using catalysts favoring ortho orientation, for example those based on lead, cobalt, or zinc, and is adjusted to a specific viscosity with 30–45% of high-boiling solvents such as aromatic and aliphatic hydrocarbons, esters, and ketones, such as isophorone. The polyisocyanates used in the process represent linear or oligomeric diphenylmethane-4-4′-diisocyanate (commonly referred to as MDI, or polymeric MDI), and are similarly diluted with primarily aromatic hydrocarbon solvents.

It is worthwhile to spend some time discussing the solvents used in the formulation of urethane cold-box systems, for in addition to the unique structure of benzylic ether polyols, the choice of the solvents to dissolve both the resin and isocyanate plays a particular role in the performance of the system. As mentioned earlier, both the phenolic resin and the polymeric isocyanate are traditionally dissolved in organic solvents, in part because of the very high viscosity of the phenolic resin.

The difference in polarity of the polyisocyanate and phenolic resin limits the choice of appropriate solvents that are compatible with both components. This compatibility is necessary to achieve complete reaction and curing of the binder, as well as improve the speed of cure.

Polar solvents like dibasic esters (Fig. 18.27) and dioctyl adipate are, for example, very appropriate for phenolic resins, but less so for isocyanate. The situation is almost exactly the reverse when nonpolar solvents are used. The preferred nonpolar solvents are high boiling aromatic hydrocarbons (generally in the form of mixtures) exhibiting boiling ranges between 100 and 200°C (ca. 200–400°F) at atmospheric pressure.

UCB systems are formulated entirely different from UNB systems, primarily because of the nature in which the catalyst is introduced: as a gas. The benzylic ether PF resin may be different from the one used for no-bake applications, or it may be the same. Solvent "packages" are typically different and are designed to aid in the cure of the resin by helping to physically diffuse the amine vapor throughout the core, often referred to by resin designers as "bulk cure." The choice of polymeric MDI type is usually limited to lower viscosity, lower functionality types, and the type used may affect humidity resistance, strength development, hot strength of the cured cores, and bench life of the mixed sand.

Additives are used more extensively in cold-box formulations and may help increase moisture resistance and bench life, and release of the cured core from the

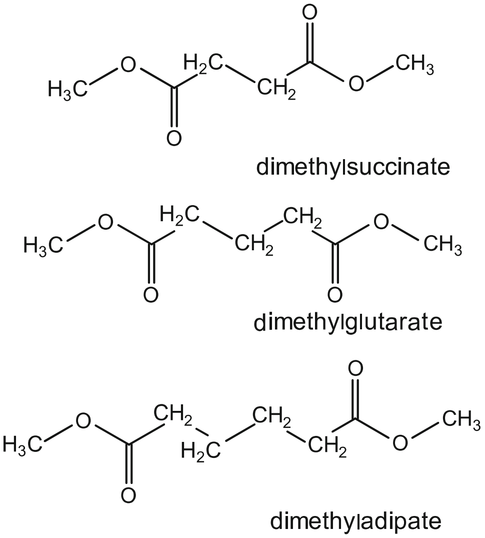


Fig. 18.27 Dibasic esters (dimethyl succinate, dimethyl glutarte, dimethyl adipate)

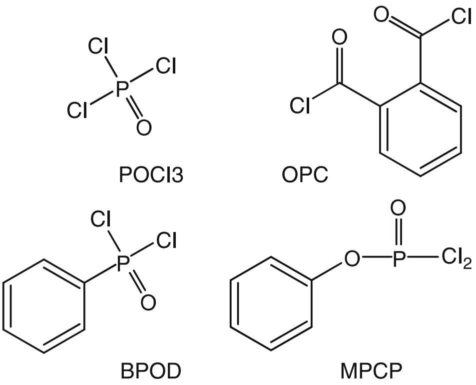


Fig. 18.28 Bench life extenders (inhibitors)

core box. Of particular importance are the bench life additives [39, 40], referred to as inhibitors or "extenders." In general, four organic acid chlorides are used to inhibit urethane formation of the mixed sand (which, in addition to the sand, includes the part 1 phenolic resin and the part 2 isocyanate resin) and "extend" the bench life, or usable time of the sand mix. These four inhibitors (Fig. 18.28) are the following:

- Phosphorus oxychloride: $POCl_3$
- Phthaloyl chloride: OPC
- Benzene phosphorus oxydichloride: BPOD
- Monophenyldichlorophosphate: MPCP

The inhibitor is always added to part 2 and the amount of the extender used in the process is typically from 0.01 to <1.0 weight percent on the basis of the weight of the part 2 binder. These organic acid chlorides are also very moisture sensitive and easily hydrolyzed to form hydrochloric acid. As mentioned in Sect. 18.5.3, it is of great importance to prevent atmospheric moisture from coming in contact with the part 2 resin. Reaction of the isocyanate with moisture can cause a solid polyurea to form. These solids can cause contamination in storage containers, and problems in pumping, metering, and mixing the binder on sand. Ultimately, this can lead to problems with coremaking and casting properties.

The overall process (Fig. 18.29) involves first introducing the prepared sand mix, previously prepared by mixing silica sand, phenolic resin and polymeric MDI solutions, into the corebox by blowing under air pressure or "shooting." The amine catalysts are any of the following four tertiary amines (Fig. 18.30):

- Triethyl amine (TEA)
- Dimethylethyl amine (DMEA)
- Dimethylisopropylamine (DMIPA)
- Dimethylpropyl amine (DMPA)

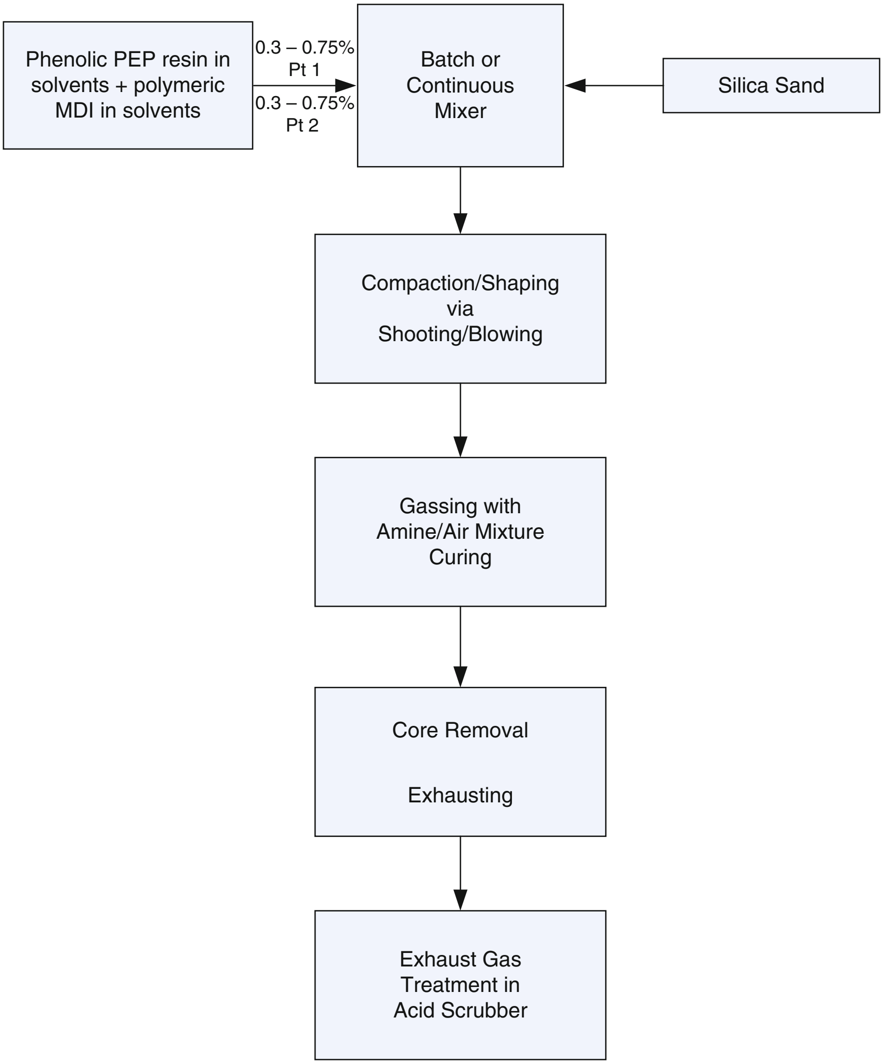


Fig. 18.29 Polyurethane cold-box process (or UCB process) – schematic description

All four are used commercially worldwide, but because of restrictions under the Toxic Substance Control Act (TSCA), DMPA is not used in the U.S. All of these amines are liquids at room temperature and must be vaporized using heat. Figure 18.31 shows a general schematic of a vaporizing system for tertiary amine. Figure 18.32 shows a modern amine gas generator. Once it has been vaporized, the amine gas is sprayed or injected into the corebox at levels of 0.2–1 mL/kg core weight (0.09–0.45 cc/lb core weight) at a pressure of 0.2–2 bar (3–29 psi). Residual amine is then purged out of the core using heated air and subsequently treated in a scrubber containing dilute sulfuric acid. In most cases,

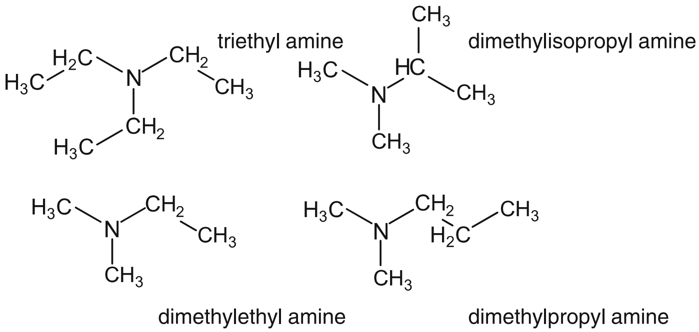


Fig. 18.30 Tertiary amines used in urethane cold-box process

spent scrubber solution is recycled to recover and reuse the amine back into the process.

The polyurethane cold-box method [38] has achieved considerable importance as a cold gassing method in Europe during the past 20 years. The process has been criticized because of the odor nuisance caused by the amine gassing component during the production and storage of cores. Certain technical disadvantages such as the tendency to form glossy (lustrous) carbon due to the high solvent levels are offset by the particularly short cycle times, good coremaking sand flowability, and relatively wide range of application, which represent marked advantages of the process. Thus, this process can be used both for fabrication of cores by shooting or blowing sand under air pressure into core boxes made from wood, plastic, or metal, and for the production of mold components in so-called “boxless” or “flaskless” casting. Figure 18.33 shows the range of mold components used for short series production of a cylinder head for racing cars.

The cold-box plus process, described originally by Boenish, in which the corebox is heated to 50–70°C (122–158°F) [41, 42], represented an improvement over the standard method. The purpose of the elevated corebox temperature is to evaporate solvents in the surface layers of the core and to increase the cross-linking density and strength of the polyurethane. This affords advantages including a significant reduction in the process-specific defects inherent in the cold-box method. As mentioned earlier, most foundries practice some form of “cold-box plus” by using heated purge air to accelerate solvent evaporation, and increase cross-linking density and out-of-box immediate strengths. Other foundries also use heated sand to accomplish the same thing, but this has the disadvantage of reducing the bench life of the mixed sand.

New binders feature low levels of free phenol, “nonreportable” levels of free formaldehyde, and binders designed for improved collapsibility in aluminum casting [43]. In some cases, phenol is partially replaced with *o*-cresol, which provides a polyol with similar coremaking strengths, but lower hot strength, presumably because of steric hindrance in the benzylic ether structure.

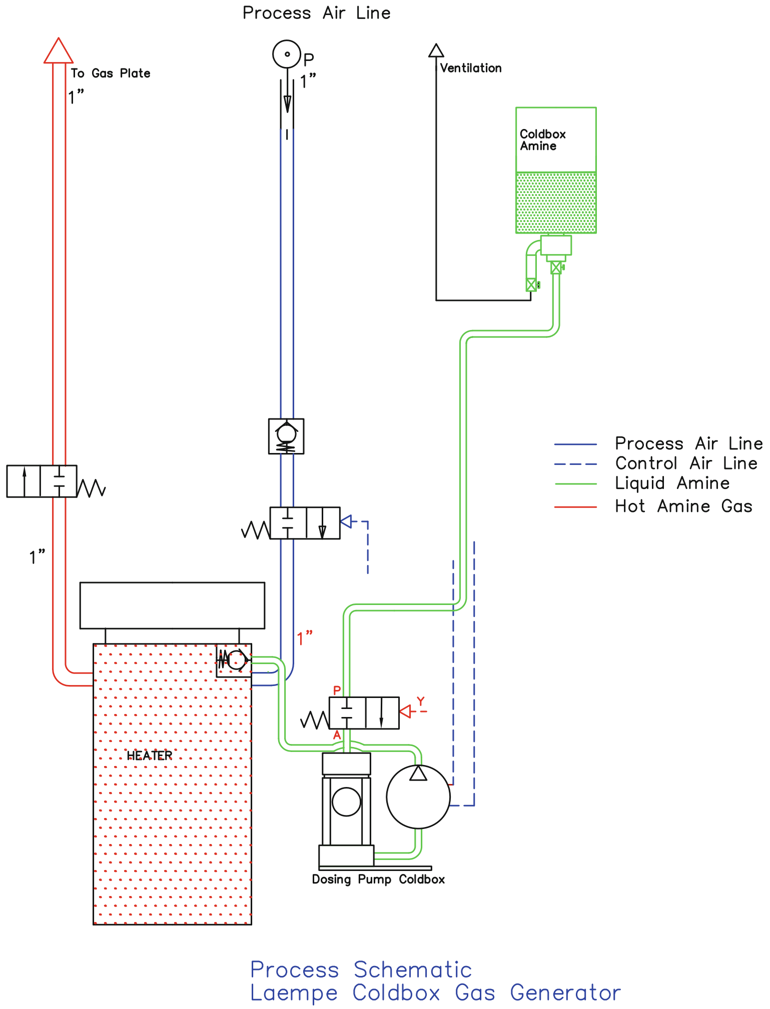


Fig. 18.31 General schematic of an amine gas generating (vaporizing) system
Source: Laempe and Mössner GmbH, Schopfheim, Germany and Laempe + Reich, Trussville, AL, USA

18.6.2 Biodiesel UCB

Introduced in Europe in 1998, and the U.S. soon after [37, 44], a relatively new innovation in urethane cold-box binders has been substitution of methyl esters of vegetable oils (such as the methyl ester of oil from the rapeseed plant) for aromatic solvents in both the part 1 and part 2 resins (The term, "biodiesel" comes from the fact that these methyl esters are used as an oxygenate in diesel fuels to make them burn cleaner). The methyl esters are high boiling, sufficiently low in viscosity,

Fig. 18.32 Close-up of amine gas generator
Source: Laempe and Mössner GmbH, Schopfheim, Germany and Laempe + Reich, Trussville, AL, USA

odorless, and nonflammable. Table 18.12 lists typical properties. As will be discussed later in this section, one deficiency in UCB systems is that they are solvent-based. In traditional systems, the use of aromatic solvents as the nonpolar solvent of choice leads to relatively high volatile organic compound (VOC) content. Typical VOC content for traditional systems ranges from 40% to 50% in part 1 and from 20% to 30% in part 2. With methyl esters, VOC content is roughly 50% less for both parts. Reduction in benzene, toluene, xylene (BTX), and naphthalene emissions at pouring, cooling, and shakeout operations is in the range of 20–30%, depending upon the system used and has been documented in CERP testing (Table 18.13, shown later).

But the advantages of biodiesel solvent are not limited to just environmental opportunities. Productivity advantages in terms of curing efficiency are particularly important to high production foundries. Methyl ester based UCB systems cure

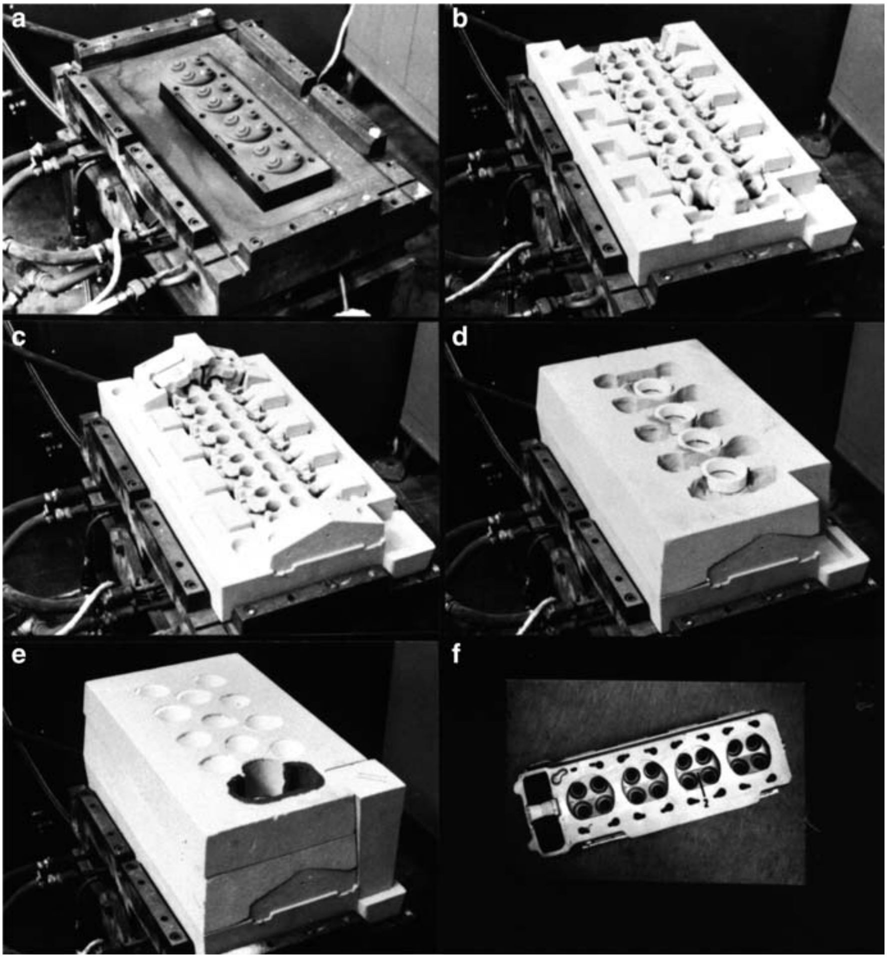


Fig. 18.33 Technical assembly of a boxless (flaskless) mold (*from left to right starting at the top*): (**a**) baseplate, (**b**) primary core with water jacket core, (**c**) oil gallery core, (**d**) cover core, (**e**) finished mold ready for pouring, (**f**) aluminum cylinder head (photo: BMW AG, Munich)

Table 18.12 Methyl ester physical properties

Characteristic	Typical value
Appearance	Yellow liquid
Moisture (%)	0.1 maximum
Viscosity at 40°C, cSt	4.6
Flash point (°C)	190
Density	7.30

Table 18.13 CERP core pouring, cooling, and shakeout tests for cold-box, PHB, WB, RCS in iron

Process	Emission factors[a]	Emission factors[b]	CERP test report
PUCB[c]	0.397	0.0424	FB
PUCB[d]	0.187	n/a	AW
CO_2 PECB[e]	0.122	0.0127	GE
EA SO_2[f]	0.2098–0.306	0.037–0.054	GX, GW
Phenolic hot-box[g]	0.061	0.0064	GH
Warm-box[h]	0.058	0.0039	GJ
RCS[i]	0.295	0.028	FU

Source: CERP

[a] Emission factor expressed as total pounds HAPs per ton

[b] Emission factor expressed as total pounds HAPs per pound binder

[c] High emitting UCB baseline at 1.75%

[d] Biodiesel low-emitting UCB with low-emitting seacoal additive at 1.75%

[e] CO_2 cured PECB at 1.2%

[f] Epoxy–acrylic SO_2 cured at 1.4%

[g] Phenolic hot-box at 1.2%

[h] Warm-box at 1.4%

[i] RCS at 3.5% resin

faster than traditional aromatic solvent based ones. Speculation is that the methyl esters are particularly effective in allowing the tertiary amine to diffuse more quickly through the sand mix (a phenomenon referred to as bulk cure) and that phase separation and subsequent reaction between the PF benzylic ether resin and the isocyanate occur more rapidly.

In general, out-of-box strength development of biodiesel-based systems is similar to traditional aromatic systems, with the exception of immediate and early strengths. However, the somewhat lower initial strengths developed with methyl ester systems are compensated for by easier release from the tooling. Consequently, higher handling strength is not required. Improvement in resistance to strength degradation as a result of high ambient humidity is also a feature of the methyl esters. In addition, when aqueous core coatings are used to coat methyl ester system cores and subsequently dried in heated forced air ovens, the cores gain strength upon drying. Conversely, most traditional aromatic-based UCB systems loose strength during this process.

During the mixing operation, the sand grains are coated with a film of binder consisting of the part 1 PF resin and the part 2 isocyanate. During the blow cycle, when the corebox is filled, some of the sand grains strike the surface of the corebox at high speed. This impingement against the surface of the corebox causes some of the binder-solvent layers to be removed off the grains and simultaneously deposit on the surface of the corebox, an effect termed “resin wipe-off.” Vegetable methyl esters have inherent lubricity and act as internal release agents that provide excellent release from the tooling and minimize the build-up of cured resin on the surface of the core box. This results in less core breakage, lower usage of external release agents, and less downtime for core box cleaning.

Another benefit with biodiesel systems is higher thermal strength, as vegetable methyl esters polymerize and help to stabilize the polyurethane binder linkages.

Gas generation during pouring is different than traditional aromatic solvent based UCB systems. Because of the higher boiling point ranges of methyl esters, gas generation occurs later in time, although the total volume is similar and mainly controlled by total resin content.

Biodiesel or vegetable methyl ester based cold-box systems are not suitable for nonferrous casting applications.

18.6.3 TEOS UCB

The newest innovation [44, 45] in urethane cold-box replaces aromatic solvents in parts 1 and 2 with tetraethyl *o*-silicate (Fig. 18.34). This silicate-based solvent combines organic and inorganic characteristics (silicon bonds are present) that provide very unique features to the cold-box process not easily achieved by any other means. Its primary performance advantages over traditional aromatic hydrocarbon or even biodiesel-based urethane cold-box are reduced condensate formation, and reduced smoke and odor at pouring, cooling, and shakeout.

As mentioned earlier in this section, the shift toward aluminum castings for automotive applications has led to an increase in the use of phenolic urethane cold-box cores in what is referred to as "semi-permanent" molding. This process, which uses steel "semi-permanent" tooling to form the outside surface of the casting, can be used to cast both aluminum cylinder heads and blocks. The lower pouring temperature of aluminum (around 660–760°C or 1,220–1,400°F depending upon the alloy) means that urethane cores burn more slowly than in ferrous castings. This in turn creates excessive smoke and condensate (tar) formation in the die during the casting process. TEOS-based systems reduce condensate formation. Thermal decomposition of TEOS liberates gaseous silicon oxide under reducing conditions; this immediately reacts with oxygen at the exterior surface of the die, forming amorphous silica.

TEOS-based urethane systems can also be used in ferrous castings, where the TEOS solvent decomposes quickly and has the potential to reduce gas defects. In either ferrous or nonferrous applications, the solvent can be used in either part 1 or part 2, or both.

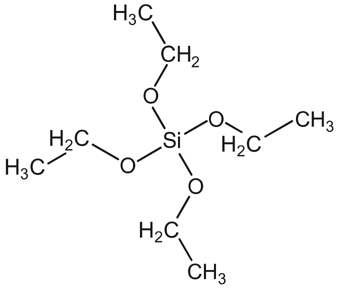


Fig. 18.34 Tetraethyl orthosilicate, $Si(OC_2H_5)_4$

TEOS is flammable with a flash point 118°F. It is sensitive to moisture, and will slowly hydrolyze to silica and ethanol if left unprotected. Therefore, resins containing TEOS must also be protected from moisture. This is generally not an issue with part 2 chemicals, which are already sensitive to moisture, but part 1 resins may need more restrictive handling measures to prevent contact with moisture. TEOS is somewhat more volatile than many aromatic solvents. Systems using the solvent typically have VOC emissions similar to traditional aromatic-based ones, but are higher than biodiesel-based ones.

During the development of TEOS based systems, it became apparent that reduction of odors from foundries is becoming of increasing importance [44]. Foundries have dealt with this issue primarily through the use of abatement and/or treatment systems, such as scrubbers and regenerative thermal oxidizers to destroy not only HAPs, but also odor-causing substances. Extensive research in this area has lead to the conclusion that while odors from the resin itself cannot be eliminated, it is the solvent and its subsequent decomposition that leads to a large part of the odors during pouring, cooling, and shakeout operations (Fig. 18.35). Compared to conventional aromatic-based solvents, TEOS-based systems offer the potential to dramatically reduce odor, particularly in aluminum applications (Fig. 18.36).

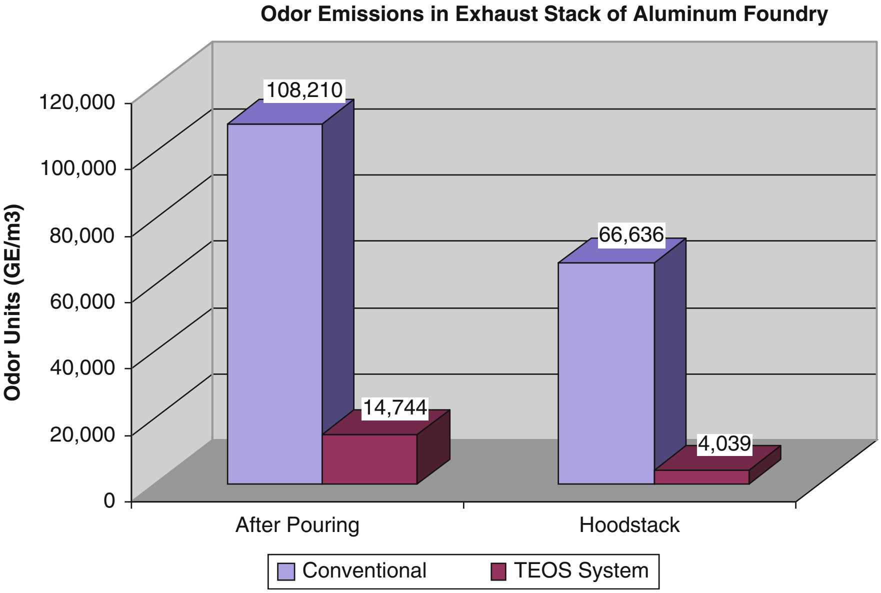


Fig. 18.35 A comparison of urethane cold-box odor emissions as measured in the exhaust stack of an aluminum foundry. Both systems were run at equivalent binder levels
Source: Hüttenes-Albertus GmbH, Düsseldorf, Germany

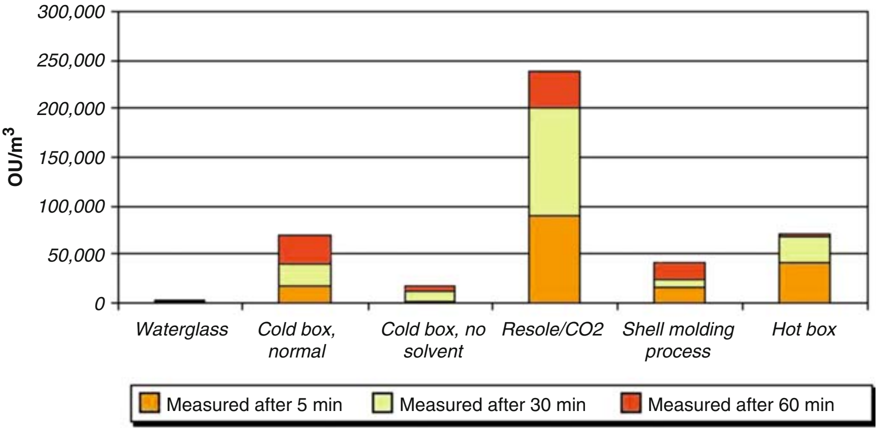


Fig. 18.36 Specific odor emissions of test pieces made using various coremaking processes *Source*: Hüttenes-Albertus GmbH, Düsseldorf, Germany

18.6.4 The Methyl Formate Process

Aqueous alkaline resoles are used as binders (Fig. 18.37) and methyl formate as the gassing agent in the MF (known as the MF cold-box, or BETASET) process [11, 12, 46, 47], which is related to the ester no bake method. The highly alkaline phenolic resole contains up to 15% of a base, generally potassium hydroxide. When gassing occurs, the ester saponifies, leading to reactions that liberate intermediate formic acid used to cure and neutralize the binder and methanol as a by-product. The curing and setting process is relatively complex. It is believed that the resin first transesterifies with MF, then forms quinone methide (Fig. 18.38) and potassium formate, finally undergoing a Michael reaction to form methanol as a by-product.

As with the ester-cured alkaline phenolic no-bake process, MF must be added to the mix in a stoichiometric amount (ca. 25% of resin weight)

A scrubber is utilized to capture excess MF and methanol to minimize release to the atmosphere. The strength development with this binder is generally lower than with the amine cured urethane cold-box binder, but higher than those of the CO_2 cured alkaline resole and CO_2 cured silicate processes.

This process possesses the advantage that the core shooters generally need not be completely enclosed, as would be required for the competing SO_2 and amine cured processes. This is due to the much higher permissible exposure limit of MF, as compared to the SO_2 and tertiary amines. However, effective control of unreacted MF emissions and methanol can be difficult. Usually, emissions are controlled by the use of a caustic scrubber. Emissions of methanol can be a regulatory problem, as methanol is classified in the U.S. as a HAP. Thus, the disadvantage of the process is that methanol cannot be fully captured or abated without using expensive means

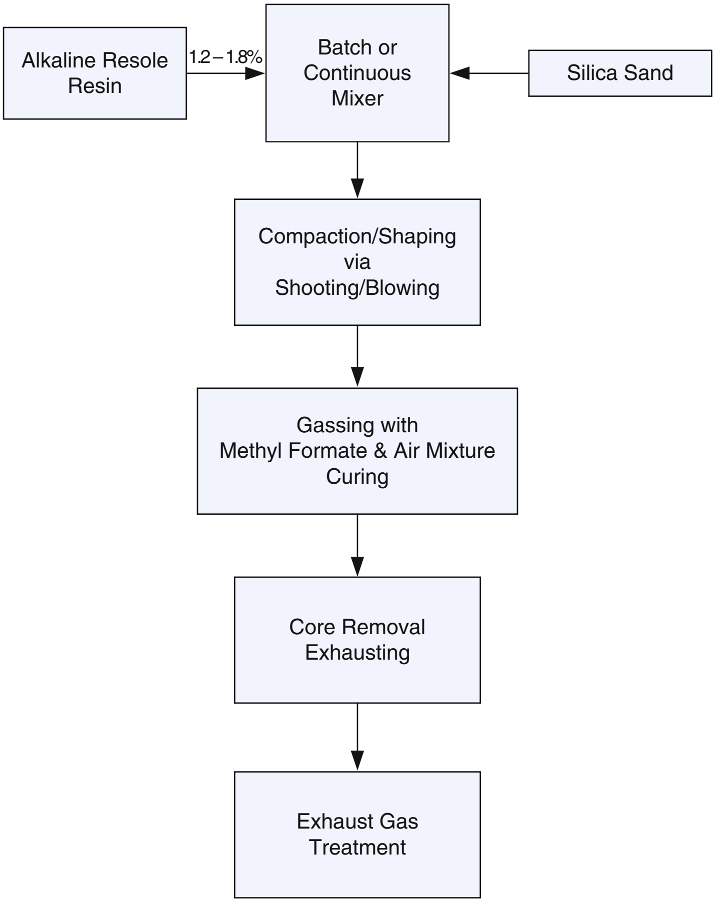


Fig. 18.37 Methyl formate (MF) process scheme

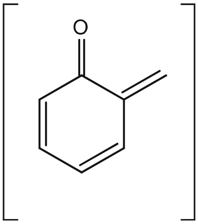


Fig. 18.38 Quinone methide

such as catalytic combustion, permeable membrane, and cryogenic technologies, although water scrubbers are effective to some degree. The alkaline sands can be reclaimed using both mechanical and thermal processes; therefore, dumping of sand can be minimized.

18.6.5 The CO_2-Resole Process

As in the MF process, this method (also known as Ecolotec or Carbophen) makes use of a sodium or potassium hydroxide containing resole [11, 48]. The binder differs from that used in the MF process in that it contains boric acid, borates, and other additives. Carbon dioxide (CO_2) is used as the gassing agent. As in the MF process, carbon dioxide also represents a true reaction component, not just a catalyst.

When gassed, the coremaking sand mix sets due to various solidification reactions. However, the strength levels of the cores fabricated in this manner are about 20–30% lower than those of the MF process. The major advantage of this process lies in the fact that no special treatment of the exhaust gas is required. The high process alkalinity again represents a disadvantage in reclamation of the spent sand.

18.6.6 The Acetal Process

The acetal process was an intrinsically interesting coremaking method, although it is now more of theoretical than practical utility. In this method, the binder is a resorcinol resin (polyphenol) solution and a strong acid (mixture of sulfuric and p-toluenesulfonic acids) is added to the sand mix. The corebox must be held at a temperature of 35–40°C (95–104°F) [49]. Gassing is performed with the dimethylacetal of formaldehyde (Fig. 18.39) also called methylal or dimethyl formal. When gassing occurs, the methylal decomposes into formaldehyde and methyl alcohol in the highly acidic medium. The formaldehyde reacts spontaneously with the resorcinol binder. This leads to a red coloration of the cores.

This process is quite interesting in theory, and in limited field trials conducted in the early 1990s, produced cores that had excellent shakeout and no veining. But serious problems resulted in practice as selective heating of the corebox and the entire sand mix making up the core within it is difficult. At this time, the process is not used commercially.

18.6.7 Other Gassing Processes

It should be mentioned that the epoxy/acrylic or furan gas curing process uses sulfur dioxide as the gassing agent. The binders used in this case are either acrylate-modified epoxies or low-monomer (condensed) furfuryl alcohol resins [50].

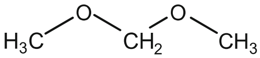


Fig. 18.39 Methyal, the dimethylacetal of formaldehyde

The methods are also known by the tradenames Isoset, Rutapox (epoxy–acrylic), and Hardox (furan) processes [51, 52].

Peroxide, such as methyl ethyl ketone peroxide, in the case of furan resins, is added to the molding sand as an oxidizer. The sulfur dioxide and peroxide react to form sulfuric acid, which initiates polymerization of the furan resin.

With the epoxy/acrylic process, cumene hydroperoxide is added to the "A" resin as an oxidizer. When the core is gassed with sulfur dioxide, it reacts with the hydroperoxide to form sulfuric acid and free radicals, which initiate spontaneous curing of the acrylic binder components. The sulfuric acid then catalyzes the slower polymerization of the epoxy binder components.

New systems use a blend of epoxy and acrylic resins. Epoxy resins improve core release and erosion resistance of the cured cores. Epoxy resins by themselves can be cured with a hydroperoxide and sulfur dioxide, but cure much too slowly for practical use as a cold-box system. It is the extremely rapid cure of the acrylic components that makes the use of the epoxy–acrylic system feasible for foundry core applications.

Furan-SO_2 systems are little used today in the U.S. but may be more widely used in other parts of the world, including Europe.

18.6.7.1 Hybrid UCB

Introduced in the United States in 1998 [53], a relatively new variation to the phenolic urethane cold-box process combines traditional phenolic urethane chemistry with both acrylic initiators and resins to yield a hybrid (Fig.. 18.40). A special phenolic resin mixed with an acrylic initiator forms the part 1 binder. Polymeric MDI mixed with acrylic resins typical of those used in the Epoxy–Acrylic process forms the part 2.

The stated advantages to this process are threefold: significant improvements in bench life and shakeout in aluminum are reported along with greater dimensional stability of the cores.

The process cures with the tertiary amines used in the phenolic urethane process; however, unlike urethane cold-box process, amine vapor diluted in nitrogen is recommended. This improves the out-of-box strengths and shakeout. The use of air (oxygen) reduces strengths and increases shakeout time.

While there is some commercial use of this system today, its use is not widespread.

[Phenolic Resin and Acrylic Initiator] + [p-MDI Isocyanate and Acrylic Resins]
(Part 1) (Part 2)
↓
Cured Resin

Fig. 18.40 Hybrid phenolic urethane acrylic system

18.7 Emissions from Phenolic Binder Systems

While the focus of this chapter examines energy efficiency and productivity as being the key driving forces in the development and use of phenolic resins as foundry binders, environmental regulations and issues are also considered. What are the environmental concerns in using phenolic resins as foundry binders? There are two primary sources of emissions from phenolic-based (and other synthetic resin-based binders) binders: [66]

- Evaporation (due to solvent, by-product, or chemical constituent evaporation – these occur at mixing, at coremaking/mold making, and during core/mold storage prior to pouring.)
- Thermal decomposition (during pouring, cooling, and shakeout operations)

Under the Clean Air Act (CAA) Amendments of 1990, the U.S. Environmental Protection Agency (EPA) is required to regulate the emissions of HAPs from “major sources” within specific industrial source categories, which included iron foundries and steel foundries. Since 2004, HAPs have been subject to Maximum Achievable Control Technology (MACT) standards for iron and steel foundries.

Because of these more restrictive regulations, it became apparent that there was a need for more accurate information on the types and quantities of organic HAPs emitted from the various operations in iron foundries including the use of chemical binders. To address this need, the Casting Emissions Reduction Program (CERP) was created in 1994 to evaluate the HAP emission potential of various mold and coremaking processes and systems [54, 55]. During its 14 year program, CERP performed hundreds of tests on materials and processes supplied by casting industry suppliers. This culminated in the most comprehensive air emissions profile ever compiled for metal casting, including all foundry binder systems using phenolic resins. From these test data, the American Foundry Society published new HAP emission factors.

Emission factors as determined by CERP testing and believed current at this present time are as follows in Table 18.13 for pouring, cooling, and shakeout tests for various cold-box systems, phenolic hot-box, furan warm-box, and resin coated sand in iron. Table 18.14 shows emission factors for pouring, cooling, and shakeout tests for various no-bake systems, including phenolic urethane no-bake, furan no-bake, and ester-cured alkaline phenolic systems.

Of note is that the systems most associated with high productivity, namely phenolic urethane no-bake and cold-box (PUR no-bake and cold-box) have the highest emissions. Of course, this is largely due to the solvent-based nature of both systems. As mentioned in the section on biodiesel-based UCB, some reduction in emissions can be effected by changing solvent. It should be clear that the lowest emissions, especially for phenolic-based systems, are those that do not contain solvent, such as phenolic hot-box, or use water as a solvent, such as ester-cured phenolics. Resin coated sands are higher in emissions than some others because of their higher average resin content.

Table 18.14 CERP no-bake baseline pouring, cooling and shakeout tests in iron

Process	Emission factors[a]	Emission factors[b]	CERP test report
PUNB[c]	2.000	n/a	DG
PUNB[d]	1.521	0.0254	FP
PUNB[e]	1.60	n/a	DP
FNB[f]	0.789	0.0138	GI
PENB[g]	0.803	n/a	DZ

Source: CERP

[a] Emission factor expressed as total pounds HAPs per ton

[b] Emission factor expressed as total pounds HAPs per pound binder

[c] High emitting UNB at 1.1%

[d] Average emitting UNB at 1.1%

[e] Low emitting UNB at 1.1%

[f] FNB at 1.2%

[g] PENB at 1.1%

18.7.1 Low Emission Binders

Clearly, one challenge that threatens the continued widespread use of phenolic resins in foundry applications is lower emission systems, in particular inorganic binders. Improvements to inorganic systems such as sodium silicates, both ester-cured no-bakes and CO_2-cured cold-box varieties are being made and new systems are being introduced. Two examples are a heat-cured blown sodium silicate system called Cordis for aluminum applications and an ester-cured no-bake sodium silicate called Geopol for ferrous applications. The one similarity all newer silicate systems have in common is the use of an inorganic additive (for example, clays or silica fume) that strengthens the silicate bond and improves both the handling strength and the resistance to degradation from exposure to high humidity.

Emission factors for inorganic systems are in the 0.0006–0.0014 lb HAP/lb binder (0.03 lb HAP per ton) range for ester-cured no-bake silicates (as these contain some organic content) to 0.0003 lb HAP/lb binder (0.0073 lb HAP per ton) for heat-cured completely inorganic binders.

One other system that should be mentioned is the protein-based binder, called GM Bond [56]. This system first introduced in 1996, was developed by General Motors Research and Development Center. It is a protein-based biopolymer that has the lowest emissions of any organic foundry binder. CERP measured emissions are 0.073 lb HAP per ton. The process is a wet mix that is blown into heated tooling (100–200°C), and cures via dehydration.

18.8 General Remarks on Core/Mold Fabrication Processes Using Phenolic Resins

Discontinuous (batch) or continuous methods of mixing may be used for core sand conditioning and applies to all the processes mentioned here. Limits are placed on the mixing procedures by the binder level, as this varies quite widely in the process-specific core sands. The mixing procedure should permit uniform distribution even of solvent-free, high-viscosity liquid binder systems on silica sand. Unfortunately, the current state of the art of mixing equipment dictates that usable viscosities must be kept below 250–300 cps, which limits the ability of the resin chemist to eliminate solvents.

The question as to the extent of success of the cold curing and remaining hot curing processes on the market and to whether the situation of phenolic resins can still be maintained, as well as how near net shape castings will continue to be produced most economically, depends to a large extent on a number of factors; including, future environmental and workplace and worker exposure legislation, raw material pricing and availability, and the possibility of sand recovery and reuse.

Adequate specific data on used sand utilization – sand recycling – have been published by Krapohl [57] and Boenisch [58, 59]. The influence of various fresh core sands on the strength levels of green sand reported in the cited papers is of interest. According to these data, sand from the shell molding, epoxy-SO_2, and UCB cold-box processes offer benefits contributing to improvement of clay-bonded molding sands without exerting an adverse effect on wet tensile strength of the latter, although there are some data refuting beneficial effects of UCB on green sand [60, 61].

Krapohl notes that two main factors become apparent from a wide variety of individual results: interferences and the sensitivity to these. The high alkali of the resole processes represents such interferences. These interferences can present problems in sand reuse when using reclaimed sand into other types of binders and even back into the same system.

A major factor in problem-free use of recycled (thermally or mechanically regenerated) old sand is removal of dust fractions or stabilization of their levels. In practice, it is known that good castings of the desired quality may be produced when used sand is reasonably utilized and the used sand properties are matched to the specific types of core and mold fabrication processes in use and proper logistic procedures are applied.

With respect to raw material availability, products in which renewable raw materials are used [62, 63], for example, phenolic by-products from the timber industry and cellulose production such as tannin and lignin, will doubtless continue to be of interest for binders of the future. However, competing or companion materials produced by renewable sources may impact the availability and price; for instance, demand for ethanol from cellulose may adversely affect lignin.

Some current work being conducted at the University of Northern Iowa involves the examination of lignite and polysaccharide-based binders as a replacement of PF resin in polyurethane systems [64].

One can speculate that with the advent of tetraethyl silicate as a solvent in polyurethanes, perhaps the next generation of phenolic novolak and resole resins will incorporate silicon directly into their chemical backbones.

Other work [65] suggests that nanoparticles and core shells may offer unique chemical strategies to further strengthen phenolic polymers allowing significant reduction of binder levels with commensurate reductions in emissions and odor during pouring, cooling, and shakeout of castings.

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Chapter 19
Phenolic Resin for Refractories

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Abstract Refractories are used in furnaces and boilers that process steel, cement, or glass as well as incinerators that operate at high temperatures. A variety of binders is used when refractories are manufactured. In this chapter, the use of phenolic resin as a binder for refractories is described. There are several factors that support the use of phenolic resins in comparison to other refractory binders. These include the following:

1. Both adhesion and green body strength are high.
2. It is a thermosetting resin system whose strength on curing is high, and the size and stability of the resulting refractory component are good.
3. The ratio of fixed carbon is high and maintains high strength on carbonization. Phenolic resins are the preferred binder for carbon containing refractories.
4. The hazardous properties and industrial environmental issues are lower than those associated with the use of pitch binder.

19.1 Introduction

Refractories are inorganic nonmetallic materials which are used at high temperatures usually exceeding 1,000°C. The applications for which the refractory materials are used include linings for steel, glass melting furnaces, incinerators, and cement kilns. The production of the refractory during the last few years is quite

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Table 19.1 Production quantity of refractories in Japan

Year	Refractory bricks total (exceptmonolithic refractories) Production quantity (Unit: t)	Monolithic refractorie Production quantity (Unit: t)	Total Production quantity (Unit: t)
C.Y. 2003	4,44,614	15,038	4,59,652
2004	4,37,616	15,903	4,53,519
2005	4,42,277	17,356	4,59,633
2006	4,44,668	16,189	4,60,857
2007	4,50,660	15,918	4,66,578
2008	4,46,248	15,745	4,61,993

static. The production of the refractories in Japan is shown in Table 19.1 and confirms this trend [1].

19.2 Methods of Classification

Refractories can be classified either according to chemical composition or according to shape. There is a further classification and it relates to shaped and unshaped refractories.

19.2.1 Chemical Composition

Refractory chemical compositions consist of high alumina, fireclay, low alumina, silicate materials, etc., and depend upon the amount of components contained such as Al_2O_3, SiO_2, MgO, and CaO. Furthermore, there are carbon containing refractories that contain carbon with the above-mentioned metallic oxide aggregates. These carbon containing refractories have the features of low thermal expansion and a low permeability to slag. The added carbon also imparts high corrosion resistance, high resistance to thermal shock, and high physical impact resistance.

19.2.2 Refractory Shape

Refractories are classified as either shaped refractories or unshaped refractories. The shaped refractories are further classified in detail depending on the manufacturing process used. The unshaped refractories are classified in detail depending on the construction method. A photograph of unshaped refractories is shown in Fig. 19.1. Shaped refractories such as nozzles (Fig. 19.2), magnesia–carbon bricks (Fig. 19.3), and aluminum–carbon bricks (Fig. 19.4) demonstrate the different types of shaped refractories.

Fig. 19.1 The unshaped refractories (photograph: Shinagawa refractories CO., Ltd)

Fig. 19.2 The submerged entry nozzle (photograph: Shinagawa refractories CO., Ltd)

Fig. 19.3 The magnesia–carbon bricks (photograph: Shinagawa refractories CO., Ltd)

Fig. 19.4 The alumina–carbon bricks (photograph: Shinagawa refractories CO., Ltd)

19.3 Refractory Manufacturing Process

A general procedure for the manufacture of refractories is described below. Further, the manufacturing process for shaped refractories differs from the process to make unshaped refractories (unfired brick and fired brick).

19.3.1 Mixing

Flame resistant aggregates such as metallic oxides are processed in a pulverizer and screened to the prescribed grain size distribution. Carbon such as scale graphite is added to the mix, and additives such as metallic powder antioxidants also are added. The measured aggregate is mixed in a braid type high speed mixer and a pressurized roller (Simpson type) mixer. Afterward, phenolic resin or tar pitch binder is added and mixed. The desired mixture consistency should determine the mixing temperature, mixing time, and the kind of mixer used. For instance, graphite does not wet out easily when phenolic resin is used as the binder. Moreover, release of volatiles that occur during mixing might influence the physical properties of the refractory such as porosity. Therefore, it is necessary to determine the finishing point of the mixture in consideration of the type of refractory and the equipment. Unshaped refractory compositions are packed into containers immediately after satisfactory inspection.

19.3.2 Molding

Refractory mixtures are molded to produce shaped refractories. The kinds of presses used are chiefly impact pressure presses such as a friction press and static pressure presses such as oil hydraulic presses. Corrosion resistance is an important property of refractories. Corrosion resistance is influenced by the porosity of the molded refractory. Porosity, in turn, is influenced by molding conditions. Therefore, it is necessary to carefully select the appropriate molding conditions. When phenolic resin is used for the binder, the resin viscosity, mixing temperature, equipment, etc., should be considered.

19.3.3 Heating/Firing Refractory Brick

The molded refractory brick that is produced with phenolic binder is heated in the following manner. During the heating process, the phenolic resin cures and lower boiling point species such as low boiling solvents contained in the resin are volatilized out of the molded brick. High boiling point solvents such as the ethylene glycol are generally used in phenolic resin refractories. Therefore, problems can occur from solvent remaining in the brick if it is not heated long enough at temperatures of 200°C or higher. The trapped solvent can cause cracking to occur during baking or during use of the refractory. For unfired refractories, the manufacturing process ends in the above-mentioned heating and curing process. For fired refractories, the next step is a heat-treatment process called "firing." Firing is the heating of a refractory, typically in a tunnel kiln in a reducing atmosphere. The firing temperature is usually from 900 to 2,000°C, though the final temperature varies depending on the type of refractory. Strength of the refractories decreases rapidly from about 400 to 600°C when phenolic resin is used as the binder. The

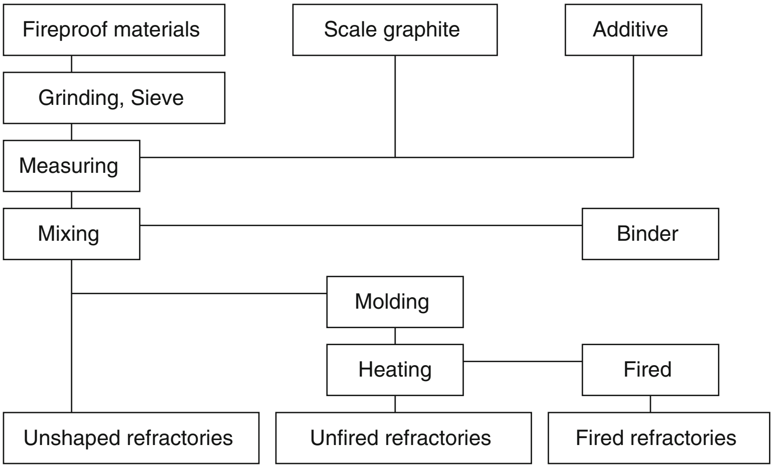

Fig. 19.5 The flow chart of the manufacturing processes for different types of refractory

decreasing strength is caused by pyrolysis. As pyrolysis occurs, bonding strength of the phenolic resin decreases. Moreover, as the phenolic resin pyrolyzes, gases of various aromatic compounds are generated. It is important to understand this to vent the exhaust appropriately. The flow chart of the manufacturing processes for different types of refractories is shown in Fig. 19.5.

19.4 Binder Used With Refractory

Inorganic and organic substances are used as binders for refractories. Inorganic binders used are bittern (mainly $MgCl_2$, with other salts), sodium phosphate, alumina cement, etc. They are chiefly used for the non-carbon containing refractories and as the binder for unshaped refractories. Organic binders used include molasses, polyvinyl alcohol, phenolic resin, furan resin, pitch, and others.

Because the fixed carbon is low, molasses and polyvinyl alcohol are chiefly used as a binder for the primary bonding agent. Because the fixed carbon is high, phenolic resin, furan resin, and pitch are chiefly used as a binder for carbon containing refractories. Chemical formulae of the principal components of typical binders are shown in Table 19.2.

19.5 Applications of Refractory

As previously described, the applications of refractories are the linings for steel, cement, and glass melting furnaces, and incinerators. The refractories used for steel account for about 70% of the total. In steel manufacturing, refractories of

Table 19.2 Chemical formulae of binders

Inorganic substance		Organic substance	
Binder	Chemical formulae	Binder	Chemical formulae
Bittern	$MgCl_2$	Phenolic resin	$(C_6H_5OH{\cdot}CH_{20})n$
Sodium phosphate	Na_3PO_4	Furan resin	$(C_5H_4O{\cdot}CH_2O)n$
Alumina cement	$(CaO){\cdot}(Al_2O_3)$	Pitch	$C_{10}H_{10}$ etc.

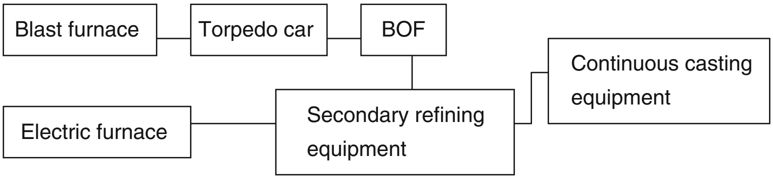

Fig. 19.6 Manufacturing processes for steel

various compositions are used for each type of steelmaking equipment. The steel manufacturing processes involve the blast furnace method and the electric furnace method. The processes are illustrated in Fig. 19.6. For either of these steel making processes, the refractory type and phenolic binder used are discussed below. In the blast furnace method, the first step is heating the iron ore with coke in the blast furnace. This reduces the iron ore to corresponding pig iron. Phenolic resin is used for the binder for the carbon brick used for the furnace bottom of this blast furnace. Phenolic resin is also used for the binder in the taphole mix that seals the taphole used to remove the pig iron from the blast furnace. The pig iron is transferred from the blast furnace to the basic oxygen furnace (BOF) by a piece of equipment called a torpedo car. Phenolic resin is used for the binder of the Al_2O_3–SiC–C bricks (Fig. 19.4) chiefly used in this Torpedo car. The use of BOF removes impurities such as C, Si, P, and S contained in the pig iron by blowing in oxygen. Phenolic resin is used for the binder of the MgO–C bricks (Fig. 19.3) used in the BOF. The molten steel is then moved with a ladle to continuous casting equipment, where it is formed into its prescribed shape. The continuous casting equipment includes equipment such as the sliding nozzle, sliding gates, and immersion nozzles used to control flow. Phenolic resin is used as the binder for the refractories used in this casting operation. In the electric furnace method, molten steel is obtained by melting steel scrap. The molten steel is adjusted in the secondary refinement equipment, similar to steel produced by the blast furnace method. The MgO–C brick is chiefly used in the furnace wall of an electric furnace and phenolic resin is used as the binder. Phenolic resin is used also for a part of the binder in unshaped refractories that are used as repair materials for each equipment type used by the blast furnace and the electric furnace.

19.6 Features of Phenolic Resin for Refractory

Features of phenolic resins as compared to other refractory binders are as follows:

1. Adhesion and green body strength are high.
2. As a thermosetting resin, it provides high green strength when cured. The size stability is good.
3. The ratio of fixed carbon is high and strength when carbonizing is high.
4. The hazardous properties and industrial hygiene concerns are lower than when pitch is used as the binder.

The ratio of fixed carbon and the environmental impact of the phenolic resin are discussed in more detail below.

19.7 Ratio of Fixed Carbon

One of the most important reasons why phenolic resins are used in carbon containing refractories is that the ratio of fixed carbon is high in phenolic resins. The ratio of fixed carbon of the typical organic compound that Riesz reports is shown in Table 19.3 [2]. The numerical value is a value after heat-treating the sample at 950°C.

The fixed carbon ratio of epoxy resin and urea–formaldehyde resin is low, considering they are also thermosetting resins. On the other hand, phenolic resin, furan resin, and pitch have high values. Phenolic resin includes both novolak and resole resins. Hexamethylenetetramine is usually used as a curing agent for novolak. The amount of hexamethylenetetramine influences the ratio of fixed carbon of the phenolic resin. Figure 19.7 shows the relationship between the amount of hexamethylenetetramine added to the novolak and the ratio of fixed carbon. The fixed carbon ratio of the novolak reaches its maximum when the added quantity of hexamethylenetetramine is increased to 12%. The reason is suggested as follows: The low molecular weight fraction of the novolak that usually volatilizes upon heating reacts with the hexamethylenetetramine and forms higher molecular weight, nonvolatile polymer. It is the decrease in the volatile polymer fraction that causes the yield increase. However, the fixed carbon decreases when the amount of hexamethylenetetramine increases further, because the fixed carbon of

Table 19.3 Ratio of fixed carbon of the organic compound

Type	Ratio of fixed carbon (%)	Type	Ratio of fixed carbon (%)
Coal tar pitch	52.5	Melamine resin	10.2
Phenolic resin	52.1	Epoxy resin	10.1
Furan resin	49.1	Urea–formaldehyde resin	8.2
Polyacrylonitrile	44.3	Natural rubber	0.6
Butadiene rubber	12.1	Polyester resin	0.3
Cellulose acetate	11.7		

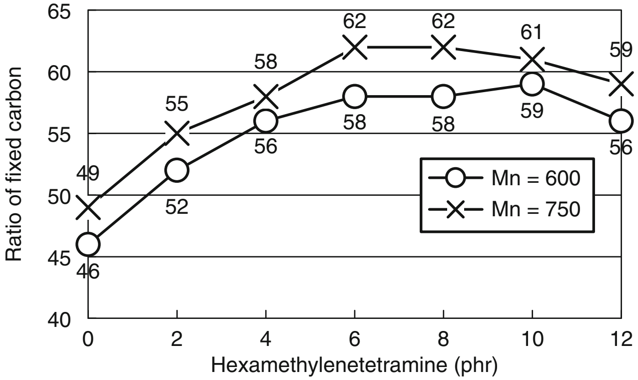

Fig. 19.7 The relationship between the amount of the hexamethylenetetramine added to novolak and the ratio of fixed carbon

hexamethylenetetramine is negligible. Therefore, it is necessary to adjust the amount of hexamethylenetetramine to an appropriate amount in relation to cure, fixed carbon, and cost.

19.8 Environmental Impact

When phenolic resin is used for the refractory binder, gases are generated during curing and firing. The key gases generated during curing are shown in Table 19.4.

In the case of resole resins, the volatiles are composed of water from resole condensation reaction, phenol, some formaldehyde depending on amount present in the resole, and solvent contained in the resin. In the case of novolaks, ammonia/amines from the reactive decomposition of the hexamethylenetetramine, solvent, and phenol contained in the resin are the main components. Therefore, the components that influence the environment are chiefly phenol and formaldehyde contained in the resin and ammonia/amines from the hexamethylenetetramine reaction, as shown in the Table 19.4. Therefore, areas for improvement in the reduction of odor are as follows:

1. Resin with low phenol and formaldehyde content.
2. Decreased amount of hexamethylenetetramine.
3. Use of resole with low phenol, and formaldehyde as a curing agent for the novolak.

Table 19.5 [3] below shows the volatile gases generated when novolak is cured and carbonized in a reducing atmosphere.

In the temperature region up to 350°C, the gas generated is primarily water from the condensation reaction and moisture in the refractory raw materials. In the temperature region of 400°C or more, the gas generated is mostly hydrocarbons and aromatic compounds such as methane or phenols released by decomposition of

Table 19.4 The main voltiles generated upon curing

Phenolic resin type	Main volatiles generated
Resole (ethylene glycol solvent)	Ethylene glycol, water, phenol, formaldehyde
Novolak (ethylene glycol solvent, added hexamethylenetetramine)	Ethylene glycol, water, phenol, ammonia/amines

Table 19.5 Volatile components emitted during novolak cure and carbonization (mol%)

Temp. (°C)	H_2O	CO	CO_2	CH_4	Phenol	Xylenol	Benzene	Toluene	H_2
100	1.47	–	–	–	–	–	–	–	–
150	0.75	–	–	–	–	–	–	–	–
200	0.48	–	–	–	–	–	–	–	–
250	0.57	–	–	–	–	–	–	–	–
300	1.28	–	–	–	–	–	–	–	–
350	3.44	–	–	–	–	–	–	–	–
400	3.44	–	–	0.05	0.46	0.13	–	–	–
450	5.42	0.21	–	0.15	0.81	0.25	–	–	0.76
500	3.35	0.44	0.09	0.75	2.72	0.75	0.02	0.08	1.47
550	2.44	0.87	0.11	1.29	1.62	0.38	0.06	0.13	2.18
600	0.40	1.30	0.32	2.61	0.79	0.14	0.06	0.05	3.65
650	0.26	1.19	0.51	2.35	0.44	0.10	0.03	0.04	5.17
700	0.13	0.77	0.26	1.32	0.21	0.05	–	0.01	5.88
750	–	0.54	0.17	0.83	0.09	–	–	–	6.64
800	–	0.26	0.11	0.40	–	–	–	–	7.35
850	–	0.20	–	0.20	–	–	–	–	5.88
900	–	–	–	0.08	–	–	–	–	4.50
950	–	–	–	–	–	–	–	–	3.65
1000	–	–	–	–	–	–	–	–	2.94
Total	23.4	5.5	1.6	10.0	7.1	1.8	0.2	0.3	50.1

the resin. Gaseous materials such as carbon monoxide, carbon dioxide, and hydrogen are generated by the carbonization of the resin. The carcinogen benzopyrene generated by tar pitch binder is not observed in the pyrolysis components of phenolic resin. It is important to note that the gas data might vary depending on the sample, the measurement conditions, and the instrumentation used.

19.9 Carbonization Mechanism of Phenolic Resin

A proposed carbonization mechanism of the phenolic resin is presented in Fig. 19.8 [4].

The dehydration reaction of the phenolic hydroxyl group commences at about 300°C. Dehydration and release of oxygen occurs initially. Carbonization progresses at about 400°C. Therefore, both a weight reduction and refractory strength reduction occur during pyrolysis. At 500°C and above, the resin carbonizes almost

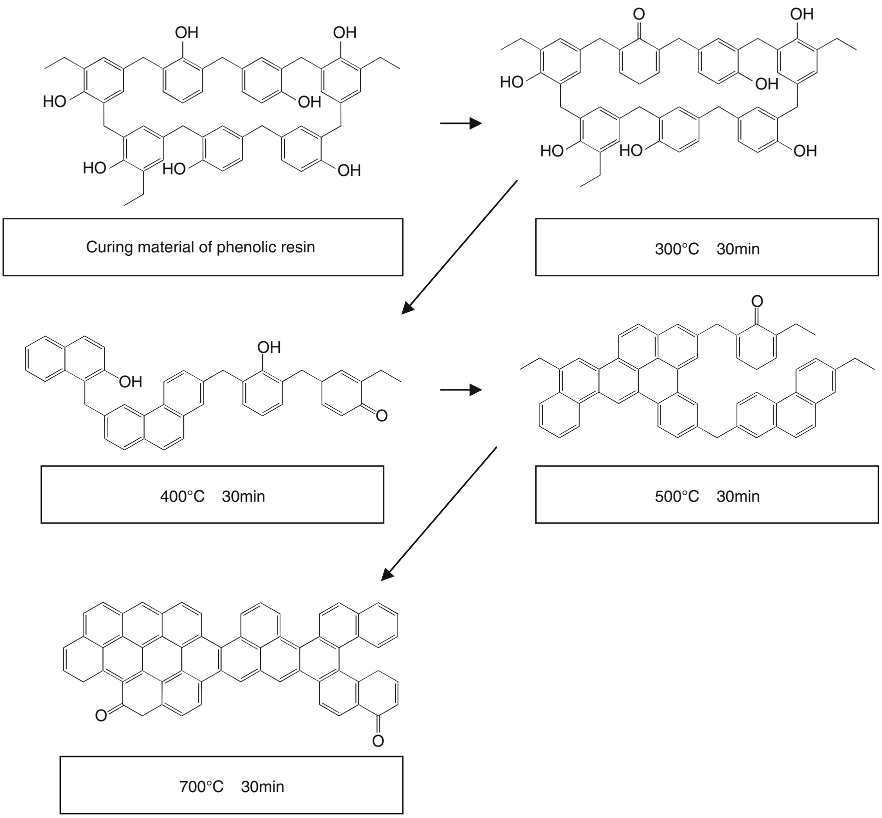

Fig. 19.8 Carbonization mechanism of phenolic resin

completely. However, some hydrogen, oxygen, etc., still remain in the carbonized material. When the phenolic resin carbonizes, it exists in the solid state. Otani et al. compared X-ray diffraction patterns of the phenolic resin charcoal and the black carbon lead [5]. In the carbonized phenolic resin, the diffraction pattern of about 26.5° that corresponds to the (002) diffraction line of the black carbon lead is not observed. Consequently, it is described as: “the net plane is small, and the thickness is extremely thin,” and results in an “ill defined structure in three dimensions.” This is because the phenolic resin does not melt during the heating and the movement of the molecule is constrained in the solid state before it carbonizes. Therefore, the phenolic resin is a nongraphitizable carbon material. The resulting carbon becomes vitreous or glassy carbon. Similarly, many other carbon containing thermosetting resins are nongraphitizable carbon materials. On the other hand, the graphitizable carbon such as pitch type materials melt on heating, and the carbonization advances in the molten state. Therefore, the resulting carbon is described as “the net plane of the aromatic series is wide and thick” and considerably different from the glassy carbon.

19.10 Use of Phenolic Resin for Refractories

It was stated previously in Sect. 19.5 that the phenolic resin is chiefly used as a binder for the carbon containing refractories of the refractory equipment for steel production. Both novolaks and resole resins are used. The resins are selected by the type of fire resistant aggregate used for the refractories or the process of manufacture for the refractories. The relationship between the type of phenolic resin and the kind of the refractories is shown in Table 19.6.

Various phenolic resins are used for the immersion nozzle. The amount of resin added is higher in the immersion nozzle. Therefore, various combinations of phenolics may be used such as those using liquid resole and powdered novolak that contains hexamethylenetetramine together, using liquid resole and liquid novolak together, or using a single liquid resole. In $MgO–Cr_2O_3$ brick, molasses and bittern are chiefly used as the primary bonding agent. However, there are shortcomings with these binders in that the yield of the refractory brick is lower because bonding strength is lower when these binders are used. Phenolic resin is used for a portion of these binders. However, because the price of the phenolic resin is higher than that of molasses and the bittern, its use is not widespread. The ratio of fixed carbon should be low for the phenolic resin used for $MgO–Cr_2O_3$ brick. This is opposite to the demand for carbon containing brick. If the ratio of fixed carbon is high, the carbon remains in the center portion of the brick after burning. Cracking occurs in the brick because the thermal expansion coefficient of the center part is different from that of the outer part. Currently, many phenolic resins are used as a binder for the MgO–C brick. Many resins used are combinations of a liquid novolak and hexamethylenetetramine. The reason why the novolak is used for the MgO–C brick is as follows: Because MgO aggregate is basic, when resole is used, the resole reacts too fast. Therefore, the change in the mixture state is fast. However, the novolak reacts slower than that of resole. In the Al_2O_3–C brick and the Al_2O_3–SiO_2–SiC–C brick, liquid resole is chiefly used. When resole is used, resole reaction is not fast, because Al_2O_3, SiO_2, and SiC are neutral in pH. Moreover, because molecular weight is comparatively lower than novolaks, resole can reduce the

Table 19.6 The relationship between the phenolic resin and refractories

Item		Novolak		Resole		Hexamethylenetetramine
		Powder	Liquid	Powder	Liquid	
Fired brick	Immersion nozzle	○	○		○	
	Ladle shroud				○	
	$MgO–Cr_2O_3$ brick				○	
Unfired brick	MgO–C brick		○			○
	Al_2O_3–C brick				○	
	Al_2O_3–SiO_2–SiC–C brick				○	
Unshaped refractories	Taphole mix		○			
	Plastic refractories		○			
	Gunning refractories	○		○		

amount of the binder used. Therefore, delamination does not happen as easily when molding it.

Very little phenolic resin is used for the unshaped refractories for the following reasons:

1. When phenolic resin is used, fluidity is low.
2. When the unshaped refractories are used, a lot of smoke is generated.

However, there is an example in which phenolic resin is used for the binder of a part of a taphole mix. The reason it is used is that the influence on the working environment is less than that in the case of the pitch, and when using it for taphole, the curing time is shorter than when using the pitch. Because the price is high, phenolic resin is not competitive in cost as compared with pitch. However, as the demand for improving the working environment continues, the amount of phenolic used is gradually increasing.

19.11 Future Development

Future trends for refractory materials are as follows:

1. The cost of steel manufacturing is decreasing and becoming extremely competitive.
2. Improvement in the hazards and emissions in the working environment.

Therefore, comparable or greater improvements such as those given below are required for the phenolic resin binder:

1. Improvement of ratio of fixed carbon
2. Improvement of bonding strength with aggregate
3. Decrease in refractory porosity when using phenolic resin as binder
4. Decreased amount of organic compounds such as free phenol being emitted or ethylene glycol used as solvent
5. Decrease in amount of phenolic resin used as binder
6. Use of silane coupling agents with phenolic resin may provide a remedy to many of the above proposed improvements

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Chapter 20
Recycling

Junya Goto and Michael Santorelli

Abstract Recycling systems are classified into those employing typically three methods, and the progress of each method is described. In *mechanical recycling*, powders of phenolic materials are recovered via a mechanical process and reused as fillers or additives in virgin materials. The effects to flowability, curability, and mechanical properties of the materials are explained. In *feedstock recycling*, monomers, oligomers, or oils are recovered via chemical processes and reused as feedstock. *Pyrolysis*, *solvolysis or hydrolysis,* and *supercritical or subcritical fluid technology* will also be introduced. When using a subcritical fluid of phenol, the recycled material maintains excellent properties similar to the virgin material, and a demonstration plant has been constructed to carry out mass production development. In *energy recovery*, wastes of phenolic materials are used as an alternative solid fuel to coal because they are combustible and have good calorific value. Industrial wastes of these have been in practical use in a cement plant. Finally, it is suggested that the best recycling method should be selected according to the purpose or situation, because every recycling method has both strengths and weaknesses. Therefore, quantitative and objective evaluation methods in recycling are desirable and should be established.

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20.1 Introduction

With current concerns for ecology and the environment, recycling systems are more important than in the past. In Europe, North America, and Japan, laws and regulations concerning recycling are being adopted.

In general, recycling can be classified into three methods:

1. *Mechanical recycling*: Powders of polymers are recovered via a mechanical process and reused as fillers or additives along with virgin materials. This system is sometimes called "material recycling."
2. *Feedstock recycling*: Monomers, oligomers, and/or oils are recovered from chemical processes and reused as feedstock. This system is sometimes called "chemical recycling."
3. *Energy recovery*: Thermal energy is generated by combustion of polymers and utilized as energy. In some cases, energy recovery is not considered a recycling system, but for this discussion, it is categorized as one of the three recycling systems. This system is sometimes called "thermal recycling."

These three systems will be discussed in detail below.

20.2 Mechanical Recycling

Thermoplastics can be recycled and processed several times by mechanical processes because they are melt-processable upon heating and soluble in organic solvents. Conversely, thermosets such as phenolic resins never melt and are insoluble after curing because they form an infusible network structure. Therefore, mechanical recycling systems are applied mainly to thermoplastics and cannot be applied to thermosets in terms of reprocessing via melt conditions. In the case of thermosets, they are powdered by milling or crushing and then used as fillers or additives. Mechanical recycling by milling or crushing has been applied to waste phenolic molding compounds generated during the molding process. This is called the "sprue" or "runner" and is obtained as excess scrap. The recycled powders are usually used along with the same materials that generated the waste.

When the powder is used as filler, the flowability, curability, and mechanical properties of the materials are affected. Hoffman reported that the flowability of materials tends to decrease when larger amounts are added [1]. Generally, the maximum amount of powder that is added is about 30% for compression molding and about 15% for injection molding to obtain satisfactory flowability. Concerning curability, Hoffman reported that the addition of larger amounts or larger particle size powder leads to shorter curing times [1]. Kalyon et al. [2] reported that the mechanical properties of materials are unaffected when adding amounts of the powder between 5% and 20%.

This recycling system by milling or crushing is a relatively simple process. It is profitable if the recycling target is limited to similar materials. However, the need for the products to be similar limits the commercial viability as does the low levels of recycled material that can be used.

20.3 Feedstock Recycling

Feedstock recycling can be very profitable for the recycling of thermosets. At present, there is no commercial use of feedstock recycling. Mass production development is being carried out on these systems and it is expected that they will be in practical use in the future.

The next section focuses on the three methods of feedstock recycling. It describes the methods and key features of each process.

20.3.1 Pyrolysis

Ordinary pyrolysis of phenolic resin without the introduction of a suitable solvent produces reactive radicals that react with each other. This results in a mixture of a solid residue as well as low molecular weight monomers. This makes it very difficult to achieve recovery of a high yield of liquefied product.

In order to improve the ordinary pyrolysis, liquid phase cracking with hydrogen donor solvents has been developed. In this method, polymers are decomposed in the presence of hydrogen donor solvents, such as tetralin, at high reaction temperatures, which leads to reactive radicals that react with the hydrogen from the hydrogen donor solvents. This prevents production of residue, and the recovery yield of liquefied products increases significantly. Sato et al. [3] described the effects of solvents on the liquid phase cracking of thermosets in the presence of tetralin (hydrogen donor solvent) or decalin (nondonor solvent), with a reaction time of 60 min at 430°C–450°C. In the presence of tetralin, both novolak phenolic resins and resol phenolic resins are converted to liquefied products with almost 100% yield. The products contain phenolic monomers such as phenol, cresol, and xylenol. The total yield of these phenolic monomers from a novolak is about 76% and that from resol is about 57%. In the absence of tetralin, liquefied product yield and monomer yield are much lower than in the presence of tetralin [3].

Liquid phase cracking is considered to be related to coal liquefaction technology. For feedstock recycling of thermosets, liquid phase cracking process is composed of several unit operations: reaction, refinery of products, and regeneration of reacted hydrogen donor solvents, which are similar to those of coal liquefaction. In addition, the operating conditions of liquid phase cracking, such as reaction temperature, reaction pressure, and reaction time, are also similar to those of coal liquefaction. Therefore, it is possible that research and development from coal liquefaction can be applied to the design of recycling process and plant with liquid phase cracking.

20.3.2 Solvolysis/Hydrolysis

Solvolysis is as important for feedstock recycling as pyrolysis. Hydrolysis, with a dilute alkali solution or solvolysis, with phenol (phenolysis), and with an acid catalyst, was studied for feedstock recycling of phenolic resin.

Summers [4] reported that hydrolysis of cured phenolic resin in dilute sodium hydroxide solution yields novolak resins with 70–80% recovery. Recovered novolaks have the same composition as conventional novolaks made by acid-catalyzed polymerization. These recovered novolaks are soluble in organic solvents and they cure when heated with 10% hexamethylenetetramine. Weight-averaged molecular weight of the recovered novolaks varies from 1,100 to 3,100 depending on the reaction time and the reaction temperature of hydrolysis [4].

Horiuchi et al. [5] described several cured phenolic materials heated with a large excess of phenol and with a small amount of acid catalyst (*p*-toluene sulfonic acid). As the reaction proceeds, insoluble phenolic resin gets converted to soluble low molecular weight resin in a phenol solution. It requires from 3 h to 5 h to complete the reaction. Phenolic solutions containing the recovered resin react with formaldehyde to produce higher molecular weight resins (novolaks). The recovered novolaks were formulated with hexamethylenetetramine and other additives into satisfactory molding compounds. The mechanical and electrical properties of the molding compounds had similar characteristics to those of conventional molding compounds [5].

20.3.3 Supercritical or Subcritical Fluid Technology

Presently, feedstock recycling with a supercritical or subcritical fluid as a reaction medium is being studied. A supercritical fluid is defined as a fluid at a temperature and pressure above its thermodynamic critical point. A subcritical fluid is a fluid that is slightly below its critical point. In these fluids, remarkably rapid chemical reactions can occur. Though feedstock recycling with a supercritical or subcritical fluid may be categorized into the wide definition of solvolysis, there are differences.

Supercritical or subcritical water and methanol are usually used for recycling of condensation polymers, such as polyethylene terephthalate (PET). When PET is decomposed in the supercritical or subcritical fluid, the hydrolysis or methanolysis of ester linkages of PET leads to a high recovery yield of the monomers in a short reaction time.

Water has a critical temperature of 374°C and a critical pressure of 22.1 MPa. Suzuki et al. [6] reported that when phenolic molding compounds containing about 50% phenolic resin are decomposed in supercritical water with a reaction time of between 60 and 90 min at 430°C, phenolic monomers such as phenol, cresol, and xylenol are produced by the hydrolysis of methylene linkages in the phenolic resin.

The total yield of phenolic monomers is about 15%. Addition of sodium carbonate as an alkali catalyst increases the yield to 25%. The yield of 25% monomer recovery means that one-half of phenolic resin is recovered as phenolic monomers, as the phenolic molding compounds contains about 50% of phenolic resin [6]. The authors studied the reaction mechanism of the phenolic resin decomposition in supercritical water. It is suggested that complete decomposition of phenolic resin is difficult in supercritical water because recombination, which is the reverse reaction of hydrolysis, occurs with the methylene linkages of the phenolic resin. Therefore, the maximum conversion of phenolic resin into liquid is about 70% when the reaction temperature rises to 480°C.

In another study, supercritical methanol was examined as the reaction medium. Methanol has a critical temperature of 240°C and a critical pressure of 8.1 MPa, which are lower than those of water. Ozaki et al. [7] reported that several phenolic resins were decomposed in supercritical methanol with a reaction time of between 30 and 150 min and at a reaction temperature of between 300°C and 420°C. When the reaction temperature is above 300°C, decomposition occurs and the conversion of phenolic resin to liquids reaches 94% at 420°C. The liquid products contain phenol, cresol, and xylenol [7].

In addition to these methods, the authors have developed a novel method in which supercritical or subcritical phenol is used as the reaction medium. This method gives a high yield recovery of oligomer, rather than monomer, in a very short reaction time. The recovered oligomer can be converted into a conventional novolak. Phenol has a critical temperature of 421°C and critical pressure of 6.1 MPa. The critical temperature is so high that subcritical fluid conditions are considered feasible for feedstock recycling. Cured phenolic molding compound decomposes to soluble products containing oligomers in a subcritical mixture of water and phenol within a reaction time of 20 min at 340°C (Fig. 20.1). M_w of the oligomers reached a maximum value and then decreased to a constant value (Fig. 20.2). It is believed that the unusual behavior of M_w is caused by two consecutive reactions. In the first reaction, the three-dimensional cross-linked phenolic resin component of phenolic molding compound is decomposed into oligomers which are soluble in the reaction medium. In the second consecutive

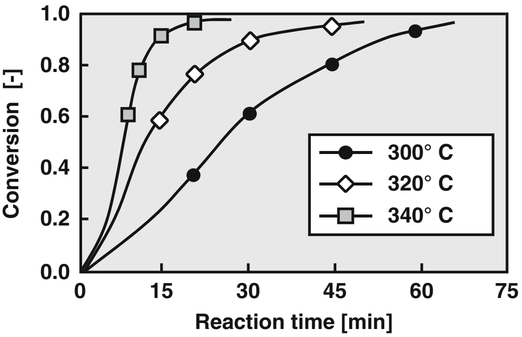

Fig. 20.1 Influence of reaction time on conversion of cured molding powder to soluble oligomers at different temperatures

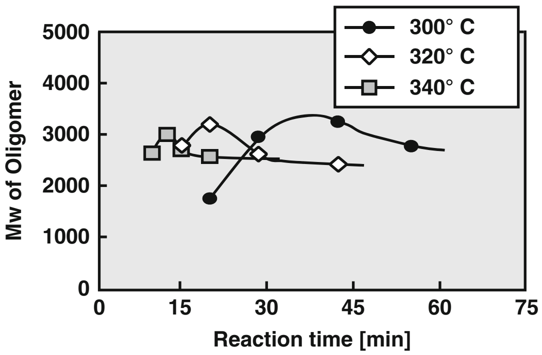

Fig. 20.2 Influence of reaction time on M_w of oligomer at different temperatures

Table 20.1 Comparison of properties of recovered oligomer with conventional novolak

		Recovered oligomer	Conventional phenol novolak
M_n	–	5.2×10^2	9.1×10^2
M_w	–	2.6×10^3	4.6×10^3
M_w/M_n	–	5.0	5.0
Gelation time at 150°C[a]	s	113	126

[a] with hexamethylenetetramine (15 phr)

Table 20.2 Comparison of properties of recycled material and virgin material

	Recycled material	Virgin material
Flexural strength (MPa)	83	90
Flexural modulus (MPa)	6,600	7,000
Charpy impact strength (k J/m^2)	2.3	2.5
Insulation resistance (Ω)	9.5×10^{12}	3.7×10^{12}
Heat deflection temperature (°C)	170	175

reaction, the oligomers are decomposed further to much lower molecular weight materials. It suggests that the molecular weight of oligomers can be controlled by the reaction time. The oligomers have curing behavior comparable to a conventional novolak. The recycled material made from the recovered oligomers maintains excellent properties similar to the virgin material made from a conventional novolak (Tables 20.1 and 20.2).

A demonstration plant utilizing this method has been constructed in Japan (Fig. 20.3). The plant has a capacity of about 33 MT/month of waste polymers and mass production development has been carried out.

The authors consider that feedstock recycling can satisfy a wider application area and is suitable for recycling larger amounts of materials than the mechanical recycling method. Yet there are technical issues related to the design of a suitable chemical process and the subsequent construction of the chemical plant. These considerations must be balanced with the investment and economy of operation.

Fig. 20.3 A photograph of the demonstration plant

20.4 Energy Recovery

Energy recovery is not a primary system as a recycling method of polymer waste. However, it can be very useful if the waste is mixed or assembled with other materials, such as other polymers or metals. Cured phenolic resin is a solid, combustible material and has a calorific value similar to that of coal. Therefore, waste phenolic resin product can be used as an alternative solid fuel to coal, and, in some cases, it is used as such.

For example, a phenolic molding compound industrial waste that is generated during thermoset processing is utilized in a cement plant in Japan. In this example, resin and other organic filler components are utilized for solid fuel. Additionally, the inorganic filler components are utilized as raw material in the cement manufacture. This process is sometimes called “Material and Thermal Recycling.”

In some instances, energy recovery may be the only practical system, so its importance should be considered. However, it should not be overlooked that the potential value of recycling polymers as materials or feedstock is lost by this method.

20.5 Summary

In general, time, location, and circumstances influence the motivation for recycling. In some cases, recycling is related to economic issues. In other cases, it is related to ecological issues such as reducing waste, saving fossil resources, or reducing CO_2 emissions. In the future, it is expected that recycling will have a closer relationship to ecological issues than in the past.

The three typical recycling methods presented have both strengths and weaknesses, so the best method should be selected according to purpose or situation. It is suggested that quantitative and objective methods for evaluating of each method should be established. In regard to fossil resource consumption or CO_2 emission, life cycle assessment (LCA) is necessary and profitable. Further advance in LCA with regard to recycling systems is desired.

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Chapter 21
Future Aspects

Louis Pilato

There are some disturbing signs that appear on the horizon as phenolic resins enter their second century of existence. The large area of wood adhesives application (~60% of the total volume of phenolic resins in North America) is under intense pressure due to many factors that are contributing to continuing reduction in the sales volume of wood adhesives. These factors include the known slow cure speed of phenolic resins compared to Urea Formaldehyde (UF), Melamine Formaldehyde (MF), or Methylene Diphenyl Isocyanate (MDI); installation of new machinery/equipment with fast continuous lines; continued decrease in plywood consumption at the expense of Oriented Strand Board (OSB) where phenolic resin is the preferred adhesive for plywood; further reduction in formaldehyde emissions through California Air Resources Board (CARB) Phase I and Phase II; uncertainty of whether formaldehyde will be identified as a human carcinogen pending the anticipated 2009 study; and the environmental movement to reduce or eliminate formaldehyde-containing resins in wood and thermal insulation consumer products (U.S. Green Building Council and other Environmental groups like the Sierra Club). Consumers are being urged by environmental organizations to purchase composite wood products with lower formaldehyde emission levels or none at all. This is illustrated by examining the news media reports after the Hurricane Katrina in 2005. The home trailers provided by the Federal Emergency Management Agency (FEMA) that were used for Louisiana and Mississippi residents after Katrina hurricane as temporary housing further accelerated concerns over formaldehyde emissions since higher than typical indoor exposure levels of formaldehyde in travel trailers and mobile homes were determined for the FEMA trailers. Incidents like this gained national and international press coverage and heightened consumer concerns of formaldehyde emissions to consider banning all formaldehyde-containing materials for use in wood products and thermal insulation.

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Coupled with these considerations, there is a shift of wood composite manufacture to South America (primarily Brazil), China, Russia, and India where favorable low-cost production is possible, and less environmental constraints are imposed. New and alternative technologies are being developed involving phenolic resins as one of the components leading to hybrid systems containing other resinous species such as UF, MF, MDI, and even protein-based (Soyad, "As Wood," etc.) combinations with phenolic resins. These hybrids contain phenolic resins but at a reduced level.

Another application market area that has been affected by consumer awareness to formaldehyde emissions is fiberglass thermal insulation. "Formaldehyde-free" fiberglass insulation is available to consumers involving a cross-linked acrylate resin system. It is not clear whether emissions and/or formaldehyde categorization as a human carcinogen will lead to a further shift in the use of phenolic resin in the fiberglass insulation area.

There are also shifts in the manufacturing of phenolic-based components to low labor locations and has contributed to the erosion of abrasive resins' sales volumes and leading to increased resin sales in many developed countries like China, India, and Thailand. This is mentioned in the Abrasives Chapter.

21.1 All is Not Negative for Phenolic Resins as they Enter the Twenty-first Century!

New developments in molding compounds through the use of long glass fiber or carbon fiber will expand market opportunities in displacing metals, ceramics, and filled high-performance thermoplastic resin systems in many applications where weight reduction and fuel efficiency are vital – auto and aircraft industries. Molding materials containing long fibers and carbon fibers represent some exciting newly introduced phenolic reinforced compositions that exhibit significantly higher impact strength and high mechanical strength at high temperatures for further displacement of metals and ceramics by these newly developed materials.

Fiber-reinforced composites with phenolic resins will flourish with the expected increase in new aircraft by Boeing and Airbus (787, A380, and A350) requiring aircraft interiors, cargo liners (both new and retrofit), increased volume in honeycomb manufacture and light weight paneling for aircraft, pultrusion of oilfield grating, filament-wound deluge pipe for oilfield, and potential use of pultruded high-density phenolic foam as a replacement for balsa sandwich panels. The development of carbon foam is expected to expand into composite related areas such as tooling and high-temperature paneling.

The emergence of benzoxazine (BZ) and phenylene bisoxazoline (PBO) type materials will facilitate an expansion into those areas where phenolic resins have not succeeded sufficiently because of water by-product emissions causing voids, compromised properties, and unacceptable number of rejected parts. BZs undergo cure without the release of volatile water by-product and possess excellent dimensional stability. Cured BZ products exhibit low water absorption and stable low dielectric properties – of considerable value to the electronics industry. It is anticipated that many of the product features will be transferred in fiber-reinforced composites. Co-reaction of either BZ or PBO with epoxy, isocyanate, or BMI will contribute to their growth in composites and other related areas. Efforts continue unabated in benzoxazine chemistry because of the favorable characteristics of the BZ structure and resulting resin properties, with many phenolic resin manufacturers providing BZ resins. Besides the introduction of other new BZ-type compositions, additional co-reactions of BZ with selected resins such as epoxy, isocyanate, BMI, and BPO are expected and will lead to new materials.

Opportunities exist for high-heat-resistance phenolic resins (friction, abrasives, molding compounds, refractory, carbon–carbon composites, others) and it is possible that nanomodification may provide more thermal stability to phenolic resins with the introduction of low amounts of selected nanoparticles. The use of nanoparticles is costly. In fact, even the least expensive nanoclay is more expensive than most phenolic resins. However, the addition of small amounts ($\leq 5\%$) may be sufficient for improved thermal stability and provide other key improvements to the resulting nanomodified phenolic resin. Nanotechnology will contribute to the development of new phenolic and related materials (resole, novolak, BZ, and CE) exhibiting multifunctionality in resin performance with relatively low amounts of nanoparticles added. It is anticipated that nanomodification of phenolic materials used as matrix resins for fuel cells will increase the performance of the fuel cells and provide longevity. Seemingly other niche application areas will benefit using the "chemical toolbox" of nanomodification for phenolic resins.

The quest for a more reactive phenolic resin persists to be a key objective for phenolic resin manufacturers. In view of the escalating cost of energy as well as the availability of more reactive, competitive formaldehyde-containing resins such as urea formaldehyde and melamine formaldehyde resins, studies related to the addition of formaldehyde to phenol solely to prepare highly methylolated phenols (highly reactive phenolic species) via continuous stirred-tank reactor (CSTR) conditions may be a viable way to improve the reactivity of phenolic resins. These highly methylolated phenols may be suitable as mineral wool binders (Chap. 10) or combined with resole as a bimodal composition for wood adhesives (Chap. 8). Further, the use of latent catalyst system mentioned in Chap. 4 offers opportunities of lower temperature cure versus traditional high-temperature (~150°C) cure conditions.

The announced new novolak process by Asahi Phosphoric Acid Phase Separation (PAPS) involves some "trade-offs" or favorable versus unfavorable features that must be considered for full acceptance of the PAPS process. These favorable features consist of narrow molecular weight distribution (MWD), low free phenol, low dimer, fast manufacturing process, low bulk viscosity, better thermal stability, high para content, but must be compared with unfavorable features such as slower cure rate with hexa, recycle of large amount of phosphoric acid, and treatment of water washings. Yet it appears to be a convenient method to prepare a high yield of the "much sought after" bisphenol F without using a large excess of phenol. Further the PAPS method allows the preparation of narrow MWD cresol novolaks as resists for photolithography and other substituted phenols.

Bisphenol F continues to be a desirable compound for a variety of areas such as a low-viscosity epoxy diluent, monomer component in polycarbonate resin, and high-performance epoxy resin matrix. A more streamlined process for bisphenol F may be possible through the use of the proposed newly developed PAPS novolak process.

Although the PAPS novolak process is in its early developmental stages, PAPS novolaks may offer opportunities in the use of novolak with narrow MWD, lower bulk viscosity, better thermal stability, lower free phenol, yet lower reactivity with hexa as compared to conventional novolak.

Renewable raw materials such as cashew, lignin, tannin, and others have not emerged as phenol monomer replacement as was originally anticipated other than the use of these materials in modest amounts as co-reactants and/or additives. It is very unlikely that these materials will be used in large amounts in any resin preparation because of the variability in global availability and product specifications and, in most examples particularly with cashew and lignin, the properties of the resulting modified phenolic resin are compromised. However, the continued use of these renewable raw materials cannot be emphasized sufficiently. These renewable materials have been identified with phenolic resins from the early days of phenolic resin commercialization and will continue as a low-cost co-reactive and/or additive component for a diversity of application areas.

Continuing or escalating cost of energy for domestic and industrial facilities will benefit by the use of phenolic foams as thermal insulation based on continuing success of the Oak Ridge National Labs Consortium for the US as well as ongoing success of phenolic foam in Europe, especially in the UK.

Phenolic polymer network studies by Sumitomo Bakelite (SB) suggest that additional studies are necessary to obtain higher cross-link-density phenolic materials. The SB preliminary studies point to the preparation of a wholly linear novolak with little or no branching for high cross link density with hexa curing agent. Yet network novolak cure studies suggest that more resin structure design is warranted to achieve a complete cure of novolak and performance of ultimate mechanical properties. Whether a fully linear novolak with little or no branching can be achieved commercially and cured with hexa for maximum properties remains to be accomplished.

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