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JAMES M. MARGOLIS

Engineering Plastics Handbook

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Preface

The *Engineering Plastics Handbook* is a one-of-a-kind book written by experts with many years of experience with engineering thermoplastics. They are the industry's crème de la crème of engineering thermoplastics science and technology. Engineering thermoplastics are used in every industry worldwide, primarily in the automotive, electrical or electronic, aircraft and aerospace, and plumbing; and in appliances, building/architecture and construction, lawn and garden, and other consumer products. Savings are increasingly being realized with engineering thermoplastics, with thin wall design; faster cycling; foam (cellular) products; the use of less material; and higher strength-to-weight ratios compared with steel, brass, aluminum, other metals, and ceramics—and as an alternative to glass. Long-term, load-bearing applications at elevated temperatures, and excellent electrical properties are hallmarks of engineering thermoplastics. Non-load-bearing applications, such as wire enamels, and clear products such as windows, are gaining in use. New grades based on blends and alloys, fiber and mineral-filled composites, and application-specific formulations are continually being introduced. Uses of engineering thermoplastics are increasing for new products, and as the preferred material-of-choice over metals.

The Introduction to the *Handbook* is comprised of four chapters on the four essential ingredients of engineering thermoplastics: 1) chemistry of polymerization, 2) products and design, 3) properties, and 4) processes. The four chapters, written by the *Handbook* Editor, are interrelated, and the fate of an engineering resin begins with polymerization technology. Finished product properties are largely allowable or disallowed according to the polymerization conditions. Chapter 1, "Chemistry of Polymerization," points out the important differences between small molecules, such as the styrene and propylene monomers, and polymeric macromolecules, such as engineering thermoplastics: Small molecules have an exact molecular weight (MW), while macromolecules have average MW. The chapter describes significant differences between the two primary polymerization methods for producing engineering thermoplastics:

polycondensation (step growth) polymerization and addition (chain growth) polymerization; and the many additional methods such as interfacial, solution, free radical, bulk (mass), solid state, emulsion, suspension, and ring opening. Chapter 2, “Products and Design,” connects the four introductory chapters with the statement, “Design opportunities begin with properties introduced by the chemistry of polymerization, and they continue through fabrication processes and assembly technologies.” The author provides a basis for understanding the unique combination of the elastic and viscous behavior of engineering thermoplastics by presenting a logical sequence of spring-and-dashpot models. The models begin with the simple Hookean spring element and Newtonian dashpot element, concluding with the more complex multielement models. The chapter presents a perspective for shear viscosity and shear modulus, Poisson’s ratio, the Boltzmann superposition principal, the Williams-Landel-Ferry (WLF) time-temperature superposition, master curve and shift factor, dynamic mechanical analysis (DMA), and design for assembly (DFA).

Chapter 3, “Properties,” identifies and lists American Society for Testing and Materials (ASTM International) and many International Organization for Standardization (ISO) standard test methods and specifications for engineering thermoplastics covered in the *Handbook*. Properties covered in Chap. 3 include details on dynamic mechanical properties, applied torque, shear, creep, and clear engineering plastics properties. Chapter 4, “Processing,” provides background for complex and critical decisions such as injection molding machine flight designs and other screw designs. Processing considerations provide readers with useful insight into processing engineering thermoplastics.

Chapter 5, “Polyacetals,” written by the Editor, describes similarities and differences between acetal homopolymers and copolymers, and the increasing replacement of metals by both polyacetals. Special attention is given to formaldehyde chemistry and its important functions in the polymerization of polyacetals. New polyacetal compounds narrow the gap between acetal homopolymers and copolymers such as thermal properties and toughness. New compounds are increasing the uses of decorated polyacetal resins for coated, painted, and metallized products. Selected processes in the chapter cover rotational molding, foam molding, overmolding, thermoforming, and powder metal injection molding (MIM).

Chapter 6, “Acrylonitrile-Butadiene-Styrene Resin,” from LG Chem, describes subjects of particular current importance, including flame retardant, transparent, heat resistant, and weatherable grades, especially ABS alloys such as ABS/PC, ABS/PVC, ABS/PA, and ABS/poly(methyl methacrylate). Flame-retardant compounds are used for components in electrical and electronic products, housings for computer monitors, printers, and copiers. The chapter provides special attention to environmental considerations for flame-retardant additives, particularly halogen-based and phosphorus-based compounds, and synergies with antimony trioxide flame retardant auxiliaries. The author provides an extensive and sophisticated view of transparent ABS: heat-resistant ABS grades with resistance up to 115°C (239°F), and current research on the compatibility and thermodynamics of ABS with an imide-based matrix. Many other relevant subjects are covered including new developments with extruded ABS compounds.

Chapter 7, "Polybutylene Terephthalate," from LG Chem, describes the science and technology of PBT blends, compounds, and composites. The chapter offers details on the advantages of different polymer blends, types of fiber, and mineral and fiber-mineral hybrid reinforcements as well as chemical and hydrolysis resistance, flammability, and other PBT attributes. The author states that "the most important applications of PBT are automotive and electrical, electronics and telecommunications, as well as precision engineering and general mechanical engineering," and concludes that "the ability to modify for various applications, combined with a range of reinforcement and blend, has enabled PBT as one of the most widely used engineering polymers."

Chapter 8, "Thermoplastic Polyetherimides," from GE Plastics, describes important differences in the chemistry and characterizations among thermoplastic polyetherimides (PEIs), especially biphenol-A dianhydride (BPADA)-based PEIs. GE Plastics produces and supplies Ultem® PEI worldwide. A key to thermoplastic polyetherimide melt flowability and flexibility is the three flexible linkages on the BPADA-MPD polymer: two ether links and the isopropylidene group of the BPA. From this molecular vantage point, the author develops the foundations for traditional and new PEI advantages such as higher glass transition temperatures (T_g). The author states "BPADA has been polymerized with a wide variety of other diamines and other dianhydrides to produce a family of polymers and copolymers." Significant members of the family of polymers and copolymers are covered in this chapter, which provides readers with an unbiased appraisal of the merits of PEI performance and processing conditions. The chapter describes four developments contributing to the increasing uses of PEI resins for new applications: 1) PEI blends with a growing number of resins, especially silicone-polyetherimide copolymers, lubricants, thermoplastic polyesters, polycarbonates, and PAEKs; 2) new formulations; (3) fiber and mineral-filled composites and (4) PEI resins as the preferred choice over metals, ceramics, glass, and thermosetting polymers.

Chapter 9, "Polyphenylene Ether Blends and Alloys," from GE Plastics describes traditional and new polyphenylene-ether grades based on GE Plastics' Noryl®. GE Plastics originally invented polyphenylene ether (PPE), its blends and alloys, and PPO® polyphenylene oxide. Noryl® is typically

PPE blended with polystyrene (PS) or high impact PS (HIPS). PPE/styrenic blends are commonly referred to as modified PPE. Noryl® grades are blended with other polymers such as polyamide (PA), and in the twenty-first century, with polypropylene (PP). PPE/PP grades are designated Noryl® PPX. The author describes the "novel compatibility [of PPE] with styrenic polymers" and "fortuitous and rather miscible, single-phase blend," which is contrasted to alloys based on PPE and PP that are not compatible with each other. Noryl® PPX grades are made possible by using General Electric's patent-pending compatibilization technology, which takes polyphenylene ether blends and alloys beyond the original PPE blends with polystyrene resins. "PPE/PP alloys offer product designers materials that fill the gap between the basic properties of high-end polyolefins and the stronger performance characteristics and attributes of engineering thermoplastics," according to the author. The chapter provides an abundance of information on Noryl® polyphenylene ether blends and alloys chemistry of polymerization, products, properties, and processes, including Noryl® ETX used as thermosetting resin property enhancers.

Chapter 10, "Thermoplastic Polyimide," from Mitsui Chemicals combines fundamental information with the special attributes of thermoplastic polyamide (TPI) resins, based on Mitsui Chemicals AURUM® TPI grades. The author gets right to the point in the first two paragraphs, describing the polymeric macromolecular differences between thermosetting polyimides, traditional TPIs, and the company's in-mold crystallizable super AURUM® TPIs, which were introduced in the early 2000s. The author states that "Super AURUM® TPI has better chemical and mechanical properties." TPI polymerization is "completed through an optimum of the monomer selection," according to the author. A description of typical polymerization of thermoplastic polyimide provides a good illustration of combining polycondensation, ring-opening polyaddition in solution, and subsequent solid state production of polyimides. The overall chemistry of polymerization highlights the nuances relating TPI macromolecular characterization to polymer properties. AURUM® can be polymerized without catalysts and it has no post-polymerization residual solvent, producing "outstanding cleanliness and can be used for semiconductor manufacturing equipment parts requiring tighter specs of cleanliness," according to the author. TPI high temperature resistance up to 235°C (455°F) is a principal reason this engineering thermoplastic is selected for high temperature semiconductor, wear/friction applications, automotive transmission, torque converter, and many other components described in this chapter. The chapter reports on carbon-fiber-reinforced TPI composites to replace ceramics and metals. Drivetrain components are at the cutting edge of new engineering thermoplastic automotive components. The author describes TPI replacing metal for automotive washers, TPI jet engine outer platforms replacing aluminum, and TPI plus metal hybrids. TPIs with wear resistance to mating metals and high temperature resistance are used for thrust washers and seal rings. Signaling the movement toward increasing use of non-load-bearing engineering thermoplastics products, the author includes extruded AURUM® TPI used for wire and cable covering, film, and fiber. The chapter includes optic fiber insulation, high heat and radiation resistant panels, woven and braided fabrics for high-performance aircraft, and industrial products. Specific melt processing conditions which the TPI processor needs to know are described.

Chapter 11, “Liquid Crystal Polymer,” from Toray Industries sums up the thermotropic LCP challenge to other engineering thermoplastics in the first sentence, which states, “Polyester-based liquid crystal polymer (LCP) is one of the most attractive materials in the field of engineering thermoplastics because of its superior heat resistance, stiffness, accuracy of dimensions, moldability, and the excellent balance of these properties.” Toray Industries produces and supplies SIVERAS® LCP grades worldwide. Describing the chemistry of LCP polymerization, the author points out that LCP polycondensation reactions can proceed without any catalyst; in some cases “metallic compound” catalyst is used. The chapter provides a clear description of the LCP science and technology history and future, and divides LCP into the conventional classes, Types I, II, and III. Toray Industries produces high-heat-resistant Type II LCP, with improved flowability. The company has developed “LCP, which has both the Type II comparable heat resistance and the Type III competitive cost …” according to the author.

The chapter includes Toray Industries’ new LCP series with improved weld strength and toughness using the company’s polymer nanotechnology. Among the numerous applications for LCP described in the chapter, are super-miniaturized electronics, components for SMT (surface mount technology), hard disc drive components, new automotive components, connectors, sockets, switches, and sensors. Valuable insight into SIVERAS® properties is provided regarding reinforced, specialty filler, low warpage (dimensional stability) grades and alloys. The high market potentials are shown for blends and alloys composed of incompatible polymers and LCP and polycarbonate/LCP using microcomposite technologies. Melt-processing conditions for LCP, especially for precision molding, are presented.

Chapter 12, “Polyamide-imide (PAI),” from Solvay Advanced Polymers is a comprehensive and detailed analysis of PAI chemistry of polymerization, products, properties, and processes. Solvay Advanced Polymers produces and supplies Torlon® PAI worldwide. The company is a subsidiary of Solvay America, which is part of Solvay SA, Brussels, Belgium. Early in the chapter, the author states, “All polyamide-imides that are fabricated in some fashion, whether it is an injection-molded part, an extruded rod, or thin coating, must be thermally cured in order for the material to reach its maximum properties." Polyamide-imide curing schedules for coatings and molded parts and graphs of cure cycle vs. tensile strength and cure cycle vs. flexural strength are valuable sources for information on proper curing and the effects of cure on strength properties.

A wide range of numerous PAI products is covered in the chapter, and several of these are given particular attention. These include a "primer" coating with good adhesion between metal and fluoropolymer for nonstick cooking pans and pots; wire enamel; friction and wear-resistant, high-speed bobbins and rotary compressor vanes; automotive transmission components, thrust washers, seal rings, and check balls; race car suspension bushings; aircraft air return valves, engine shrouds, thermal insulating fastener return mounts, and clip nuts; agriculture and construction vehicles and equipment, precision-machined poppets, and seats and spools in fluid (hydraulic) power systems; aerospace adhesives for honeycomb structures; and semiconductor test sockets. Tensile strength and flexural strength of reinforced Torlon® PAI at 204°C (399°F) are graphically compared with reinforced PES, PEI, PPS, and PAEK composites. Processing conditions for injection molding and compression molding PAI are described.

Chapter 13, "Polyarylethersulfones (PAES)," from Solvay Advanced Polymers covers basic and advanced developments of sulfone polymers, especially polysulfone (PSF), polyethersulfone (PES), higher performance with higher toughness polyphenylsulfone (PPSF), and, more recently, the higher temperature polyarylethersulfone Supradel™ HTS with a T_g of 265°C (509°F) and heat deflection temperature of 255°C (491°F). The company did not disclose the repeat unit at the time the chapter was written. Supradel™ HTS notched Izod impact strength is "on a par with that of polycarbonate" according to the authors. In addition to a comprehensive description of the chemistry of nucleophilic polycondensation polymerization, the chapter clearly relates the macromolecular characterizations of sulfone polymers with performance and processing properties. The authors observe that "the ether linkage that is common to the sulfone polymers imparts chain flexibility which allows for mechanical toughness and attractive melt rheological properties for thermoplastic fabrication." The authors describe further attributes of the ether linkage, sulfone moieties, and many other relationships between the sulfone polymers' characterizations and their properties. The chapter describes the unique combination of transparency, inherent flame resistance, and low smoke (particulate) emissions; electrical properties, ESCR (environmental stress crack resistance), radiation resistance (x-ray, electromagnetic, electron beam, gamma, microwave, and infrared), and solubility. Sulfone polymer performance properties are clearly related to applications. The authors state, for example, “The hydrolytic stability and heat resistance of PSF and PES make them suitable for use in a number of consumer and commercial food service items.” They also state, “The key feature for (plumbing) fittings is the excellent creep resistance and resistance to mineral buildup,” and “PPSF offers unique toughness, chemical resistance, and electrical properties to magnet wire insulation coatings.” The chapter discusses current trends in sulfone polymers applications and application-specific grades. These include an increasing emphasis on appearance and aesthetics, which is in addition to the functional aspects of sulfone polymers in high-performance applications; high-clarity polysulfones introduced in 2004; toughness enhancers in epoxy formulations; glass-fiber-reinforced sulfone polymers; hollow fiber membranes; and advancements in blends and alloys such as the company’s PSF-based Mindel® series and PSF + PPSF Acudel® series of blends and alloys. Melt-processing conditions for sulfone polymers are described, including the temperatures and times to anneal molded products in order to reduce molded-in stress.

Chapter 14, “Polycarbonates,” from GE Plastics is written by distinguished experts credited with many publications and patents on polycarbonates, which are assigned to General Electric, the global producer of Lexan® polycarbonates. The chapter has 207 references, including many references to the authors’ published works and to the works of Dr. Daniel W. Fox, the inventor of Lexan®, which heralded the beginning of General Electric’s engineering thermoplastics business. Dr. Fox was the inventor for 44 patents and he initiated the technical development of Noryl® polyphenylene ether polymers. His resume includes the General Electric Steinmetz Award and the Plastics Hall of Fame; he hired Jack Welch, former GE Chairman and CEO.

The chapter begins with early developments in aliphatic polyester, early developments in aliphatic and aromatic polycarbonate, and further developments in aromatic polyesters and polycarbonates; it continues with the chemistry of polymerization, in particular interfacial polymerization and melt transesterification. A large part of this chapter is devoted to properties of BPA-PC (bisphenol A-polycarbonate) blends, new and specialty polycarbonate resins, especially polyestercarbonates and other high heat polycarbonates, high melt flow copolycarbonates for thin-wall applications, PC siloxane block copolymers, biphenol-containing copolymers with polycarbonate, UV-resistant polycarbonate copolymers, and new copolymers for optical storage media. Typical applications for transparent grades, opaque grades, and polymer blends are also covered. The chapter includes part design and processing considerations including in-mold decorating (IMD), process controls, and equipment/machinery designs.

Informative and valuable sections of the chapter are "Reengineering the Molecule" and the previous sections to which this section refers, "Commercial Production of Polycarbonate," "Polycarbonate Properties: General-Purpose and Application-Specific Grades," "Applications using Polycarbonates" and "Processing Polycarbonate."

Chapter 15, "Reinforced Poly(Phenylene Sulfide)," from Chevron Phillips Chemical Company is authored by two experts with many years of first-hand experience in PPS. The chapter offers an insightful history of the invention and development of PPS, which was discovered by Phillips Petroleum Company in the mid-1960s. Reinforced PPS scientific and technological advancements are continuing at Chevron Phillips Chemical. Polymerization is much more complex than might be suggested, as the authors describe. While other engineering thermoplastics (except PET) are supplied in unreinforced and reinforced grades, engineering resin PPS grades are always reinforced. The authors sum up PPS properties stating that "commercial applications of reinforced PPS compounds generally exploit the plastic material's exceptional combination of resistance to thermal degradation, dimensional integrity at elevated temperatures, resistance to chemical attack, and inherent flame retardant behavior," and "as an alternative to using metals, reinforced PPS compounds offer the capability to mold complex shapes to tight tolerances, reducing production costs compared to extensive machining operations, while incorporating a reduction in part weight." Reinforced PPS with added glass fiber and mineral fillers can have UL94 flammability ratings of UL94 V-0 and UL94 5VA without incorporating flame retardant additives. Reinforced PPS thermal stability is compared with other engineering plastics by comparing their heat deflection temperature (HDT) and Underwriters Laboratories Relative Thermal Index (UL RTI). Reinforced PPS chemical resistance is described in the chapter by statements such as, "There is no organic solvent known to dissolve PPS at temperatures below 200°C (392°F)," and "the PPS polymer backbone may only be attacked and degraded by powerful oxidizing agents under extreme conditions of temperature and/or concentration." This statement is elaborated by the authors who note that above 100°C (212°F)" in water, the adhesion between glass fibers and PPS resin matrix may be weakened, and special PPS grades containing unique coupling agents have been developed to overcome this weakening at the fiber-matrix interface. A wide range of products fabricated from reinforced PPS compounds are referred to, with some emphasis on automotive components such as powertrain and transmission components, and precision-molded electrical and electronic components such as SMT (surface mount technology) applications.

The chapter discusses the development of new blends of PPS with polymers such as elastomeric impact resistant modifiers, polycarbonates, polyarylethersulfones, polyamide-imides, modified polyphenylene ethers, liquid crystal polyesters, poly(butylene terephthalate), polyamides, and PTFE. Work on these blends is amply referenced in the chapter, which points out that "of the various reported blends of PPS with other polymers, only blends of PPS with ethylene-copolymer impact modifiers, polyamides, and PTFE are beginning to show wide utility in applications for reinforced plastics."

Reinforced PPS-specific design considerations, and injection-molding and compression-molding parameters are described in this chapter. Woven-fabric-reinforced thermoplastic PPS compounds are thermoformed, filament wound, and pultruded; and new blow molding reinforced PPS compounds are being developed by Chevron Phillips Chemical according to the authors. Reference 135 (published in 2002) in the chapter cites blow-moldable PPS for large automotive ducting. The chapter describes machining and assembly methods for reinforced PPS compounds.

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Part

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Introduction

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Chapter

1

Chemistry of Polymerization*

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The fate of an engineering resin begins with polymerization technology. Finished product properties and applications are largely allowable or disallowed according to the choice of polymerization methods, monomers, polymerization process conditions, and catalysts. The changing choices for polymerization to improve polymer functionality and costs make information on the chemistry of polymerization especially important. Engineering thermoplastics polymerization methods influence polymer compositions, product design, properties, and processes. In Part 1, products and design are described in Chap. 2, properties in Chap. 3, and processes in Chap. 4. In Part 2, the chapters are written by experts at principal engineering resin producing companies worldwide that produce the polymer that is their chapter subject; except Chap. 5, "Polyacetals," which is prepared by the editor of this handbook, Jim Margolis of Margolis Polymers.

The chemistry of polymerization for polymeric macromolecules differs significantly from that of smaller molecules. Small molecules are assumed to be the same length and the same *molecular weight* (MW). Styrene monomer MW is 104.15 g/mol, and propylene monomer is

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*The chapter author, editors, publisher, and companies referred to are not responsible for the use or accuracy of information in this chapter, such as property data, processing parameters, and applications.

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42.08 g/mol. For these low-molecular-weight molecules MW = W/N, where W = total sample weight and N = number of moles in the sample. Macromolecule MW and molecular weight distribution (MWD) are affected by polymerization conditions. Macromolecules are polydispersed; i.e., macromolecules have different chain lengths and different molecular weights, even from the same polymerization reactor. Macromolecule molecular weight is determined from the number average (MW_n) and weight average (MW_w). Professor Hermann Staudinger awakened the world in the 1920s to macromolecules—molecules with 10,000 or more atoms. Prior to his discovery, molecular weights were thought to be no more than a few thousand, and materials such as cellulose and natural rubber were considered to be the combination of a lot of small molecules. Macromolecule molecular weight is calculated by various parameters, primarily as number average MW_n and weight average MW_w, using the following equations [1, 2, 4, 9]:

Number average molecular weight $$\mathrm{MW}_n = \frac{\Sigma_i n_i M_i}{\Sigma_i n_i}$$

Weight average molecular weight $$\mathrm{MW}_w = \frac{\Sigma_i n_i M_i^2}{\Sigma_i n_i M_i}$$

where n_i = number of moles of specie i
M_i = molecular weight of specie i

Number average molecular weight is determined by osmometry; and weight average molecular weight is determined by light scattering, *small-angle neutron scattering* (SANS), and sedimentation velocity [9].

A third way to determine MW is via the viscosity average molecular weight, determined by dilute solution viscometry, the intrinsic viscosity of a polymer solution [4].

Viscosity average molecular weight $$\mathrm{MW}_v = \left(\frac{\Sigma_i n_i M_i^{1+a}}{\Sigma_i n_i M_i}\right)^{1/a}$$

Here a is a Mark-Houwink constant for a given polymer. The exponent a is a function of polymer geometry with a range of 0.5 to 2.0, typically about 0.75 [5]. It is experimentally determined by measuring the intrinsic viscosity of several samples of a given polymer. Prior to measuring the intrinsic viscosity, the MW of the given polymer is determined by a method such as light scattering or osmometry (osmotic pressure). On a log graph, plot the log of intrinsic viscosity, 0.1 to 10 dl/g (y axis), versus log of MW, 10^4 to 10^6 g/mol (x axis) [5]. Fit a straight line to the experimental data. The slope of the line is a.

Intrinsic viscosity is frequently used for linear macromolecular characterization, and intrinsic viscosity number values can be used to determine the molecular weight [15]. The intrinsic viscosity number is the limiting value of the specific viscosity/concentration η_{sp}/c calculated to zero concentration [15]. To calculate intrinsic viscosity [9],

$$[\eta] = \lim_{c \to 0} \frac{\eta_{rel} - 1}{C} = \lim_{c \to 0} \frac{\eta_{sp}}{C}$$

where $[\eta]$ = intrinsic viscosity
$\lim_{c \to 0}$ = concentration of solution to zero
η_{rel} = relative viscosity
c = concentration of solution
η_{sp} = specific viscosity

Since viscosity is a measure of the time of flow using a Ubbeholde viscometer, viscosity is measured in its simplest form, in seconds.[1]

$$\eta_{rel} = \frac{\eta}{\eta_0}$$

where η = viscosity of a dilute concentration
η_0 = viscosity of pure solvent

and

$$\eta_{sp} = \eta_{rel} - 1 = \frac{\eta - \eta_0}{\eta_0}$$

A fourth molecular weight designation is *Z* average MW [9]. A different value for MW is obtained for the different molecular weight designations.

The two principal types of polymerization for thermoplastics including engineering thermoplastics are polycondensation polymerization and chain-growth polymerization. Both types can usually produce linear, branched, crosslinked; amorphous and semicrystalline; aromatic and aliphatic polymers [14].

Factors affecting the rate of polymerization and yield include:

1. Molecular configurations: linear, branched, crosslinking; ring structure; amorphous or semicrystalline; aliphatic or aromatic
2. Type of polymerization: polycondensation (step-growth) or chain-growth (addition); free-radical, ionic; solution including interfacial, emulsion, suspension, bulk (mass); continuous or batch; graft, solid state
3. Monomers, comonomers, monomer ratio
4. Initiators, catalysts

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[1] Paul J. Flory, "Viscosity of Linear Polyesters. An Exact Relationship Between Viscosity and Chain Length."

5. Chain terminators, end capping
6. Nucleating agents for semicrystalline polymers
7. MW and MWD
8. Solvent removal and by-product removal for polycondensation polymerization such as vacuum removal of H_2O.

Polycondensation Polymerization (Step-Growth Polymerization)

With polycondensation polymerization, two monomers join to produce dimers, trimers, tetramers, and higher oligomers; and finally polymers, plus a by-product which is usually H_2O. HCl, NaCl, CH_3OH, and other by-products can be formed instead of water. When a single monomer is used instead of two monomers, the reaction is self-polycondensation polymerization. Stoichiometry is monitored and controlled when two different monomers are polymerized, but stoichiometry is ensured with self-polycondensation. Most engineering thermoplastics can be produced by polycondensation polymerization: ABS, PET, PBT, polyamides (nylons), polycarbonate, PAI, LCP, TPI, PEI, PPS, PPE, PSU, and PAEK.

Cyclic, linear, branched, and crosslinked polycondensation polymers are produced with polyfunctional monomers, such as trifunctional monomers to produce branched polymers. Bifunctional monomers yield cyclic and linear polymers. When the ring has fewer than 5 atoms or more than 7 atoms, the polymer can be converted to linear [3]. Polycondensation polymerization can be an endothermic or exothermic reaction. MW is usually about 2000 to 25,000, lower than that of chain-growth polymerization [2]. Polymerization can take up to several hours and longer. The rate of the polymerization reaction is increased when the by-product is water, by carrying out polymerization in a vacuum to remove water.

The following examples illustrate specific polycondensation polymerizations: Polycondensation polymerization of ethylene glycol plus dimethyl terephthalate (DMT) to produce PET yields CH_3OH by-product. Crystallization is facilitated with organic and inorganic nucleating agents, such as organic nucleating agents, monocarboxylic acid salts and polycarboxylic acid, sodium chlorobenzoate, disodium terephthalate, diphenylamine, and epoxides; and inorganic nucleating agents, mica, silicate, clay, titanium oxide, magnesium oxide, and antimony trioxide. Nucleating agents include an array of fillers and reinforcing fibers as well as residual polymerization catalysts. Quick-quenching and *solid-state polymerization* (SSP) produce clear amorphous blow-molded, bottle-grade PET. Higher MWs are obtained by solid-state polymerization of pellets. Solid-state polymerization involves removing polycondensation by-product. PBT is typically the product of *polycondensation* of tetramethylene glycol (1,4-butanediol) with terephthalic acid or dimethyl terephthalate. Polycondensation polymerization provides effective use of the by-products CH_3OH and tetrahydrofuran. Higher MW is obtained with solid-state polycondensation.

Polycarbonates are produced by a number of polycondensation polymerization methods including interfacial polycondensation. Solid-state polymerization of polycarbonate is the subject of industrial and academic projects to produce semicrystalline and high-MW oligomers. One method uses supercritical CO_2 at temperatures down to 90°C (194°F) [8]. Thermotropic LCPs can be produced by phenyl esterification of the carbonyl group, and typically in two-phase polycondensation polymerization. Methods to produce polyphenylene-ether by polycondensation polymerization include oxidation of 2,6-dimethylphenol (2,6-xylenol) with H_2O by-product [4], or displacing the halogen from 4-halo-2,6-disubstituted phenols, to form the ether linkage. Polysulfone can be produced by polycondensation polymerization of a disodium salt of bisphenol-A and *p*-dichlorodiphenyl sulfone monomers. PAEK can be self-condensation polymerized, or polymerized through intermediates.

Solution polycondensation polymerization is used when the temperatures needed to melt the monomer are too high or when bulk (mass) polymerization is too exothermic and hazardous. With solution polymerization, monomers and polymerization initiators are dissolved in a nonmonomeric liquid solvent at the start of polymerization. The solvent is usually a solvent for the polymer and copolymer product.

Interfacial polycondensation polymerization is an alternative to bulk polycondensation polymerization when bulk polymerization would require excessively high temperatures or generate high exothermic temperatures. Interfacial polycondensation polymerization is carried out at the boundary of two immiscible solutions. The monomer in one solvent at the interface reacts with the monomer in the other solvent at the interface of the two solvents. One solvent can be aqueous, and the other solvent is organic. When an emulsion is formed, the polymerization rate is determined by the diffusion rate and emulsion "capsule" surface area. Polymerization is very rapid.

Certain polymers such as poly(arylene-ether)s are produced by nucleophilic aromatic substitution, which involves the addition of a nucleophile during polymerization. Nucleophiles typically have negative ions (anions) that are attracted to, and attach to, a positive charge. A nucleophile (nucleus-friendly) is an electron-rich ion or molecule that donates electrons to, and reacts with, an electron-poor specie. The positive nuclear charge of an electron-poor specie is an electrophile (electron-friendly) [16, 17]. Electrons always go from a nucleophile to an electrophile. The reaction forms a new covalent bond [16, 17].

The following table compares polycondensation with chain-growth polymerization [2].

Polycondensation (step-growth)	Chain-growth (addition)
Long reaction times are needed to complete macromolecular polymerization.	Very fast reaction times are needed to complete macromolecule polymerization.
Reaction between different molecular species can occur independently.	Chain growth is entirely the addition of monomers to a growing chain.
Monomers disperse quickly to form oligomers.	Faster polymerization rate increases yield, but not average MW.
Oligomer sizes increase to termination of step-growth process.	During polymerization, mixture consists of macromolecules and unreacted monomer with few actively growing chains because polymerization rate is so fast.
Reaction mixture consists of different size oligomers—dimers, trimers, tetramers, and higher oligomers—in a distribution that is calculable by $f(\delta s/\delta t)$ with oligomer size s at a given time t.	

Chain-Growth Polymerization (Addition Polymerization)

Chain-growth polymerization produces thermoplastics such as polyacetal, polyethylene, polypropylene, polystyrene, methylmethacrylate, and PVC. Molecular weight can range from 25,000 to millions of grams per mole. Unlike in polycondensation polymerization, no by-product such as H_2O, HCl, CH_3OH, NaCl, or any other by-product is produced. Also unlike in polycondensation polymerization, chain-growth polymerization is extremely rapid and oligomers do not exist very long, if at all. Complete polymers can form in less than 0.1 s.

Three events are involved with chain-growth polymerization: catalytic initiation, propagation, and termination [3]. Monomers with double bonds ($-\mathrm{C}{=}\mathrm{C}-\mathrm{R}_1\mathrm{R}_2-$) or sometimes triple bonds, and R_1 and R_2 additive groups, initiate propagation. The sites can be anionic or cationic active, free-radical. Free-radical catalysts allow the chain to grow when the double (or triple) bonds break. Types of free-radical polymerization are solution free-radical polymerization, emulsion free-radical polymerization, bulk free-radical polymerization, and free-radical copolymerization. Free-radical polymerization consists of initiation, termination, and chain transfer. Polymerization is initiated by the attack of free radicals that are formed by thermal or photochemical decomposition by initiators. When an organic peroxide or azo compound free-radical initiator is used, such as *t*-butyl peroxide, benzoyl peroxide, azo(bis)isobutylonitrile, or diazo- compounds, the monomer's double bonds break and form reactive free-radical sites with free electrons. Free radicals are also created by UV exposure, irradiation, or redox initiation in aqueous solution, which break the double bonds [3].

The free electrons are relayed along the polymer chain to the end of the polymer where the free electrons continue to chemically bond, forming polymers. Monomers with reactive free radicals keep adding on to the growing polymer chains until either the reactive monomers or the initiator is consumed. With chain-growth free-radical polymerization, monomers are added to the free-radical ends of growing molecules which are effectively long-chain free radicals. Two growing free radicals combine (coupling) or disproportionate, causing termination of chain growth.

Free-radical polymerization can be terminated with a transfer agent such as benzoquinone which consumes free radicals. Mercaptans (thiols) such as butyl mercaptans are commonly used transfer agents. Free radicals at macromolecule chain ends can selectively react with transfer agents to terminate chain growth; but the free radical is transferred to another macromolecule that continues to grow. Transfer can occur with the initiator, monomer, macromolecule, and solvent. Monomer propagation and transfer to the monomer are

$$\text{Propagation}\quad R' + CH_2 = CHX \rightarrow RCH_2 = C'HX$$

$$\text{Transfer}\quad R' + CH_2 = CHX \rightarrow RH + CH_2 = C'X$$

The relationship between kinetic chain length with chain transfer and without chain transfer is expressed by the Mayo equation [9]

$$\frac{1}{\nu_{\mathrm{tr}}} = \frac{1}{\nu} + C_{\mathrm{SX}}\left(\frac{[\mathrm{SX}]}{[M]}\right)$$

where ν_{tr} = kinetic chain length with chain transfer
ν = kinetic chain length without chain transfer
C_{SX} = chain transfer constant
[SX] = concentration of chain transfer species
$[M]$ = concentration of monomer

The Mayo equation is also expressed as

$$\frac{1}{\mathrm{DP}_n} = \frac{1}{\mathrm{DP}_{n0}} + C_S\,[\text{transfer agent} / \text{monomer}]$$

where DP_n = degree of polymerization with a transfer agent
DP_{n0} = degree of polymerization without a transfer agent
C_S = chain transfer constant

Pulsed laser photolysis synthesis and *gel permeation chromatography* (GPC) are used to determine propagation rate constants for free-radical polymerizations. Free-radical polymerization used for industrial production of polymers shows better tolerance to trace amounts of oxygen and impurities compared with other processes [11].

Free-radical polymerization is used to produce graft copolymers. Free-radical sites on the macromolecule provide sites for an unsaturated copolymer to graft, a method commonly used for polyolefins [9, 14].

Ionic polymerization uses anionic or cationic catalysts. Monomers with electron-accepting groups at the double bonds such as vinyls are catalyzed by anionic catalysts such as organometallic compounds [16, 17]. Monomers with electron-donating groups at the double bonds are catalyzed by cationic catalysts such as Lewis acids, Ziegler catalysts, and Friedel Crafts catalysts [16, 17]. Polyacetals are linear polymers that can be produced by anionic or cationic chain-growth polymerization of formaldehyde [2, 14].

Two strategic parameters for semicrystalline polymers are the polymerization reaction rate and degree of crystallization [10].

The *specific reaction rate* (isothermal kinetic data) is obtained from *differential scanning calorimetry* (DSC) data. When isothermal thermogravimetry is used, the specific reaction rate is directly related to sample weight at a given time.

$$k = \left(\frac{dC}{dt}\right)(1-C)^n = \frac{(dW/dt)(W_0 - W_f)}{(W - W_f)(W_0 - W_f)^n}$$

where k = specific reaction rate
C = fraction of conversion
t = reaction time, s
n = reaction order
W = sample weight at a given time (dW/dt), g
W_0 = initial sample weight, g
W_f = final sample weight, g

When this equation is valid, a straight-line plot of $(1 - C)^n$ versus dC/dt is obtained for the value of n, and k is calculated from the slope. Rate constants determined for more than one temperature can be used to calculate the Arrhenius activation energy constant. The Arrhenius equation predicts the rate of a chemical reaction at a given temperature (Kelvin temperature). The equation is a function of a frequency factor or preexponential factor A, mathematical quantity e, gas constant R, temperature T in kelvins, and activation energy E.

The specific reaction rate is related to the Arrhenius activation energy and temperature by [10]

$$k = A\exp\left(\frac{-E}{RT}\right)$$

where k = specific reaction rate
A = preexponential factor
$-E$ = Arrhenius activation energy, kJ/mol
R = universal gas constant, 8.314 J/(mol · K)
T = temperature, K

(Arrhenius activation energy and gas constant units differ by a factor of 1000.)

The equation for k is expressed in a variety of ways, but they all have the same parameters. Arrhenius is credited with defining this relationship (in 1899) and proposing the specific reaction rate model which shows the reaction rate k is a function of E and T. Rate constants are plotted at several temperatures. The ln k (natural log of k) [y axis] is plotted at several temperatures as $1/T$ [x axis] to obtain the slope.

The *degree of crystallinity* (DC) is determined from a polymer's heat of fusion

$$\mathrm{DC} = \left(\frac{\Delta H_f}{\Delta H_\mu}\right)100$$

where ΔH_f = heat of fusion of polymer, Kcal/mol
ΔH_μ = heat of fusion of perfectly crystalline polymer, Kcal/mol

The ΔH_f is determined by *differential scanning calorimetry* (DSC), and ΔH_μ is determined by *differential thermal analysis* (DTA) and from heat of fusion tables such as values obtained by Flory's method.

The *rate of crystallization* is a function of temperature, free energy, and activation energy. The rate of nucleation or crystal growth is associated with chain folding (lamella growth), which is associated with the three conditions of temperature, free energy, and activation energy. Turnbull and Fischer equated the rate of nucleation or crystal growth to the following parameters [10]:

$$I = I^0 \exp\left(\frac{-\Delta G}{kT}\right)\exp\left(\frac{-\Delta E}{kT}\right)$$

where I = rate of nucleation or crystal growth
I^0 = temperature-independent constant
$-\Delta G$ = free-energy change for the formation of a nucleus of critical size
k = thermodynamic function (Boltzmann's constant)
T = thermodynamic absolute temperature, K
$-\Delta E$ = viscosity factor

Knowledge of the variation and complexity of crystalline shapes opens a universe of new polymers and properties. H. D. Keith and F. J. Padden, Jr., observed that crystalline characteristics are a function of crystal growth rate, and crystalline transformation occurs when a single crystal grows to predictable size. To calculate a predictable crystal size from melt for homopolymers [10],

$$\delta = \frac{D}{G_r}$$

where δ = single crystal size when transformation occurs
D = diffusion coefficient in crystalline medium (coefficient of self-diffusion)
G_r = crystalline growth rate

Spherulite and lamella characteristics vary from polymer to polymer.[2]

Many semicrystalline polymers have an optimum crystallization temperature. Above the optimum crystallization temperature, the nucleation rate slows, limiting crystallization; below the optimum crystallization temperature, viscosity increases, which also limits crystallization. The rate of crystallization is affected by several methods, such as adding a nucleating agent to increase crystallization. Quick-quenching polymers such as PET produce amorphous PET, as noted earlier. To calculate the crystallization rate for a given polymer as a function of temperature [10],

$$K = B - \left(\frac{4E_p}{KT_c}\right)\left[\left\{\frac{\left(DT_m^2\right)}{T_c}\right\}(T_m - T_c)^2\right]$$

where K = crystallization rate constant
B = constant for a given polymer

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[2] See H. D. Keith and F. J. Padden, Jr., "A Phenomenological Theory of Spherulite Crystallization," Bell Telephone Labs Inc., Murray Hill, N.J., USA, published by The American Institute of Physics in 1963; and other reports on the crystallization phenomenon from the 1950s to 2004.

E_p = activation energy for segmental diffusion
T_c = crystallization temperature, °C (°F)
D = constant for a given polymer
T_m = melt temperature, °C (°F)

The crystallization rate at constant temperature is calculated with the Avrami equation [10]

$$\ln(1-\theta) = Kt^n$$

where θ = degree of crystallization
K = Avrami constant
t = crystalline time interval
n = Avrami exponent related to crystallization process—nucleation type and spherulite growth form (see table)

Relationship of Avrami Exponent *n* to Crystalization Growth Form

n	Nucleation type	Growth form
1	Predetermined	Fibrillar
2	Sporadic	Fibrillar
3	Predetermined	Discoid
4	Sporadic	Discoid
5	Predetermined	Spherulite
6	Sporadic	Spherulite
7	Predetermined	Sheathlike
8	Sporadic	Sheathlike

Beyond polycondensation and chain-growth polymerizations, further selections must be made: whether to use bulk (mass), solution, emulsion or interfacial, suspension, graft and solid-state polymerizations; ring opening, free radical, anionic or cationic.

For example, SAN is an emulsion or suspension polymerized from styrene plus acrylonitrile, and SAN is graft-polymerized to polybutadiene to form ABS. Antioxidants can be introduced during polymerization as well as during compounding, to protect the double bonds in polybutadiene and acrylonitrile. Block and graft in situ polycondensation polymerization can be used to produce ABS composites and other engineering thermoplastic composites reinforced with poly-*p*–phenylene terephthalamide (PPTA) liquid crystal fibers at the molecular level [4].

The choices are not always optimal. Solution and interfacial polycondensation polymerizations are used when bulk polymerization is too exothermic, as noted earlier. Polymerization combines processes such as polycondensation, bulk, graft, and solid-state polymerization or copolymerization. Three solid-state polymerization methods include

(1) fluidized bed, (2) stationary bed, and (3) vacuum. Polymerization systems influence the molecular architecture and configuration, such as aliphatic or aromatic, semicrystalline or amorphous, linear or branched; and other important molecular characteristics such as MW and MWD.

Bulk (mass) polymerization is the polymerization of monomers to polymers without the presence of solvents or dispersants. Bulk polymerization is typically exothermic. Polymerization requires only monomer and a catalyst or accelerator. Bulk polymerization is used for many polycondensation polymerizations and chain-growth polymerizations. It is used with liquid monomers and also with gases and solids. Heat stabilizers can be introduced during high-temperature polymerizations.

The *Tromsdorf effect*, also called the *Norrish effect* or *gel effect*, is associated with exothermic reactions during bulk polymerization. Autoacceleration of the polymerization rate can occur with medium to high polymerization conversions. This phenomenon inhibits termination. Strength of the Tromsdorf effect is calculated as the *gel effect* index [12]

$$\gamma = \frac{R_p}{R_{p0}} - 1$$

where γ = gel effect
R_p = rate of polymerization with no gel effect (theoretical)
R_{p0} = rate of polymerization with gel effect

The Tromsdorf effect can occur in suspension polymerization of PVC, but it is not as significant as it is with bulk polymerization.

During conversion from monomer to polymer in bulk polymerization, the volume of the reaction mixture shrinks. There is less volume shrinkage with increasing number and length of side chains. To calculate the specific volume of a reaction mixture during bulk polymerization at a given temperature [12], use

$$\nu = \nu_n(1 - \varepsilon\chi)$$

where ν = specific volume of a reaction mixture, cm^3/g (in^3/oz)
ν_n = specific volume of monomer, cm^3/g (in^3/oz)
ε = contraction constant for a given polymer
χ = degree of conversion, %

Ring-opening polymerization

Ring-opening polymerization can be a chain-growth polymerization or condensation polymerization, catalyzed by metal catalysts such as a tungsten, molybdenum, or rhenium catalyst. With a cyclic polymer, ring opening is caused by ring strain, which is due to the angle between ring "sides." More ring sides have more ring strain, so a three-member ring has less strain, while a seven-member ring such as ε-caprolactam used to polymerize polyamide-6 has greater ring strain, which facilitates polymerization [3, 6, 13]. Polyamide-6 can be produced by ring-opening chain-growth ionic polymerization of caprolactam. It can be produced by hydrolytic bulk polymerization of ε-caprolactam in the presence of water, acid, alkali (ionic polymerization), or alcohol, which breaks the caprolactam ring. Polyamide-12 is produced by ring-opening polymerization of laurolactam. Poly(ethylene-imine) (PEI) and aliphatic polyesters can be polymerized by ring-opening mechanisms [4].

Aromatic engineering thermoplastics are produced from macrocyclic oligomer precursors by ring-opening polymerization without by-product formation during polymerization [6]. Selection of amine catalysts such as Et_3N (triethylamine) is a factor in getting high cyclic oligomers and low linear oligomer yields [13].

Macrocyclic oligomer precursors of polycarbonates, PET, polymers of amides, etherketones, and ethersulfones are candidates for further study of macrocyclic oligomer polymerization thermodynamics [6]. Research extends to cyclic arylates (cyclic aryl-aryl esters) and cyclic alkyl aryl esters going back to isolating a cyclic trimer of poly(ethylene-terephthalate) in 1954 [13]. Much of the work on macrocyclic oligomers as precursors to high-MW macromolecules starts with spiro(bis)indane (SBI) biphenyl monomer to produce macrocyclic carbonates.

The 80,000-MW polyethersulfone was produced by heating an SBI-based cyclic oligomer mixture at 380 to 400°C (716 to 752°F) in the melt with 1.0 mol % bisphenol A disodium salt [6]. In 1990, an etherketone macrocyclic mixture was prepared by an aryl-aryl coupling; and nickel(0) catalyzed aryl coupling of selected bis-arylchlorides can produce about 40% cyclic etherketones by applying pseudodilution methods [13]. Macrocyclic aramids (aryl-aryl aramids) have been prepared from SBI-based diamines and other starting materials. Findings with gel permeation chromatography were used to analyze macrocyclic oligomers [13]. GPC is used to determine polymer properties and kinetic data. Together with light-scattering detection, GPC offers more precise MW determinations than alternative methods [11].

Reaction conditions needed to form selective cyclics include maintenance of the right hydrolysis, condensation ratio, and the right amine catalyst [13].

Structural characterizations of macrocyclic aromatic sulfide oligomers were studied jointly at Guangzhou Institute of Chemistry and McGill University Department of Chemistry. The studies used matrix-assisted laser desorption and ionization time of flight mass spectroscopy (MALD ITF-MS), which the researchers said was a powerful tool to analyze the macrocyclics [13].

Polymer Characterization [6]

Includes:

1. Polymer architecture
   - Atomic force microscopy, e.g., crystal structures.
   - Electron microscopy.
   - X-ray diffraction, e.g., crystal structures.
   - Optical microscopy.
2. Determination of MW by dilute solution viscosity
   - *Dilute solution viscosity*. Dilute solution polymers typically have a dilute solution viscosity greater than 0.1 dL/g. Dilute solution viscosity measurements are used for initial characterization.
   - Viscometry.
   - Gel permeation chromatography.
3. Chain structure
   - NMR spectroscopy.
   - IR spectroscopy is a practical method to obtain data from thin film specimens.
4. Thermal transition
   - Thermal microscopy.
   - Differential scanning calorimetry. DSC is used to obtain the glass transition temperature, but not the melt points, for amorphous polymers. Melt points are created in the crystalline segment of semicrystalline polymers.
5. Polymer degradation
   - Differential thermal analysis.
   - *Thermogravimetric analysis* (TGA).
   - Chemical hydrolysis and viscometry.

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Chapter 2

Products and Design*

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Design opportunities begin with properties introduced by the chemistry of polymerization, and they continue through fabrication processes and assembly technologies. The designer of engineering thermoplastics for a given product is concerned with every aspect of the product including process options and property requirements, such as mechanical properties—tensile, compressive, flexural, torque, and shear strength and modulus; creep; and stress relaxation. Engineering plastics are frequently called upon for long-term applications that challenge the viscoelastic properties that go beyond the elastic limit. Long-term properties transcend the conventional short-term tests provided by the American Society for Testing and Materials (ASTM), International Organization for Standardization (ISO), and other recognized short-term test methods. The designer is involved with details of processing, e.g., with melt volume change during injection molding, and mold designs such as gate type, size, and locations. Engineering plastics are successfully designed into thousands of products owing to their properties such as elevated temperatures, sustainable high loads, and electrical aspects. Engineering thermoplastics products are used in every industry, affecting virtually all aspects of our daily lives. They

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allow us to perform a vast number of activities that would not be possible without engineering thermoplastics. Engineering thermoplastics are often associated with load-bearing and semistructural products, but their uses in other applications are increasing, such as wire coatings and clear sheeting, which are included in this handbook.

Product designs are essential to the ongoing success of engineering plastics products. Underlying the design considerations for every engineering thermoplastic is the effect of *viscoelasticity* on long-term applications under applied loads at elevated temperatures. Spring-and-dashpot models provide an understanding of the important subject of viscoelastic behavior. Spring-and-dashpot models are described in this chapter in a logical sequence, starting with the hookean spring element and newtonian dashpot element and progressing to multielement models. The spring element indicates short-time tensile properties, and the viscous dashpot indicates time-dependent properties. Below the elastic limit where there is a linear relationship between stress and strain, a thermoplastic material returns to its initial form for small strains. Beyond its elastic limit, a thermoplastic does not return to its initial form. In fact, at a constant applied stress, deformation (strain) continues to increase. Steel and aluminum are elastic, not viscoelastic, materials. *The significance of thermoplastic behavior beyond the elastic limit relates to the viscous properties for long-term applications under stress. Engineering thermoplastics are typically (not always) used for long-term applications and at elevated temperatures.* Short-term test methods provide data for initial selection and elimination of resins and compounds and a starting point for application-specific compounds.

Solutions for beam and flat plate formulas are based on traditional engineering design and require safety factors to comply with the effects of viscoelasticity. Beam bending calculations consider the second moment of inertia and stiffness. I beams, T beams, and hollow-center beams have a high second moment of inertia and allow the use of less material [1]. The second moment of inertia is an area moment of inertia. It is the second moment of a cross-sectional area around a given axis, and it is a measure of a beam's capacity to resist bending. The larger the second moment of inertia, the more resistant the beam is to bending [2, 3]. The bending moment of a section M is directly proportional to the second moment of inertia I. The polar moment of inertia J_z of the cross section of a beam is a measure of a beam's capacity to resist torsion. The larger the $J_{z,}$ the more resistant the beam is to twist.

Sandwich panels constructed of a cellular or honeycomb core and laminated outer skins are treated as I beams to calculate the moment and modulus. The laminate skin is the I beam flange, and the core is the beam shear web in calculations. Under a bending load, the flexural stiffness of a sandwich panel is proportional to the cube of its thickness [4]. For these reasons, modified "I beams" constructed as a foam core–outer skin sandwich panel should have high application potential in industries ranging from building and construction to transportation to furniture. PEI/PES core laminates are used for aircraft and railroad car interior panels. They have a service temperature range from –194 to 180°C (–317 to 356°F) and fire resistance. The core is primarily under shear stress on bending. The upper skin is under compression stress, and the lower skin is under tensile stress.

SP Systems developed Core-Cell®, a structural foam composite based on heat-stabilized SAN copolymer used for thermal and sound insulation [4]. The foam composite has high impact resistance and toughness, and it is thermoformable. Core-Cell® was developed for marine applications, and its applications extend to more transportation products. SP Systems (Isle of Wight, UK) produces composites and technology for core materials and services including structural design and process engineering. The company was a force in converting from aluminum to *fiberglass-reinforced* unsaturated *polyester* (FRP) for boat hulls. An analogy, looking "back to the future," is to convert the decades old, aluminum *honeycomb before expansion* (HOBE) used in airframe construction to HOBE using engineering thermoplastics.

Fundamental design equations are given in this chapter. More complex models use calculus, linear *finite element analysis* (FEA), and CAD/CAE. Linear FEA for structural analysis and testing is used with elastic materials, which includes plastics in the elastic region and metals. Nonlinear FEA is used with elastomers because these materials have no stress-strain curve linear portion. Linear FEA uses Young's modulus and Poisson's ratio. Data for Young's modulus are more abundant than for Poisson's ratio. Three-dimensional modeling FEA codes and *finite element modeling* (FEM) services are provided by

1. Algor Inc., Pittsburgh, Pa., USA
2. Abaqus Inc., Pawtucket, R. I., USA
3. Ansys Inc., Canonsburg, Pa., USA
4. ATA Engineering Inc., San Diego, Calif., and Herndon, Va., USA
5. Engineering Mechanics Research Corporation, Troy, Mich., USA

Algor software and services include *manufacturing execution systems* (MES) software that combines large-scale motion and stress analysis of an FEM model in a single process, simulating real-world deformation and failure analysis, and "Superflow," a CAD-like program for high-precision FEM modeling. ABAQUS/Standard® is used for solutions of traditional implicit FEA of static, dynamic, and thermal properties, and it is integrated with third-party software for injection molding analysis. Ansys DesignXplorer VT® is used by designers of engineering plastics products addressing multiple competitive objectives including geometric CAD, ANSYS ParaMesh™, materials properties, and shell thicknesses. The company's proprietary Variation Technology™ is used for structural analysis of alternative design parameters. ATA Engineering services include assembly tasks, FEA, and I-DEAS® for design and manufacturing tasks such as configuration illustration and drawing creation. I-DEAS® software was developed by SDRC, which was acquired by EDS, the parent company of UGS Corporation. EDS provides Unigraphics Solutions. Principal competitors include PTC's Pro/Engineer and Dassault's CATIA. The consulting firm Engineering Mechanics Research Corporation develops FEA and CAE software for design analysis of fatigue and fracture configurations for dynamic systems. The company uses the NISA family of FEA software programs. Following is a list of design considerations.

Design Considerations

1. Final product application
2. Final product performance requirements
3. The number of functionalities the part will perform
4. Type of applied loads: constant, dynamic; intermittent, cyclical
5. Stress and strain
6. Maximum allowable deflection
7. Wall thickness
8. Wall taper from thicker to thinner walls
9. Radii
10. Ribs and bosses: geometry, locations, spacing between ribs or bosses
11. Draft angles for part demolding
12. Tolerances
13. Environmental requirements (e.g., humidity, weatherability, underwater, space, multiple environments)
14. Temperature range
15. Chemical resistance
16. Finishing, e.g., oven cure, *in-mold decorating* (IMD)
17. Component integration versus joints
    - In-mold assembly (IMA)
    - Joint design
    - Method of joining, e.g., ultrasonic, spin welding
    - Seam location
18. Code requirements
19. Process selection
20. Mold and tool design, e.g., gate selection and location
21. Product life expectancy
22. Use abuse (safety factor)

SOURCE: Based on "Designing with Plastics and Advanced Composites—Technical Advances in Vehicle Design," *Proceedings of the International Association for Vehicle Design*, and D. V. Rosato, "Designing with Plastics: A Guide to Product Design," Interscience Enterprises Ltd., Geneva-Aeroport, Switzerland, 1986.

Design engineering has three primary objectives: (1) satisfying the application performance requirements, (2) preventing product failure, and (3) containing costs.

Elastic Region

Stress-to-strain proportionality

Stress-to-strain proportionality is limited to the elastic region, for very low strains where Hooke's law applies.

To calculate the modulus of elasticity E in the elastic region, use the following [7–9]:

$$\text{Young's modulus } E = \frac{\sigma}{\varepsilon} = \frac{F/A}{L/\Delta L} \qquad \text{MPa (psi)}$$

where σ = stress, MPa (psi)
ε = strain, cm/cm (in/in) %
F = applied force (load), N (lb)
A = area of applied force, cm^2 (in^2)
L = unit length, cm (in)
ΔL = change in length due to stress, cm (in)

Beyond the Elastic Limit (Beyond the Proportional Region)

In the proportional (elastic) region, Hooke's law applies, and Young's modulus $E = \sigma/\varepsilon$. Beyond the elastic limit there is no stress-to-strain proportionality, and Hooke's law does not apply. Beyond the elastic limit, stress can be constant while strain continues to increase. A viscoelastic solid plastic has viscous fluid characteristics beyond the elastic limit.

Spring-and-Dashpot Models

Hookean spring element

The simplest mechanical model, the hookean spring element, has an elastic response. The spring is an energy storage element. It releases its energy when it returns to its original form. When subjected to an instantaneous stress σ_0, the spring has a response with a strain ε_0 [10]:

$$\text{Young's modulus } E = \sigma_0/\varepsilon_0$$

Newtonian dashpot element

The simplest linear viscous model is Newton's model. This is shown by a piston-dashpot element [10]. The dashpot is an energy dissipation element, and it represents a viscous damping force. It relates the translational and rotational velocity of a fluid (oil) between two points, and an applied load, by using a damping constant.

Maxwell spring-and-dashpot model

The Maxwell model integrates the elastic and viscous behavior of a thermoplastic by combining the spring and dashpot, providing a simple model for viscoelastic polymers. The spring and dashpot are in series [10].

$$\text{Stress}_{\text{spring}} = \sigma_s = E\varepsilon$$

$$\text{Stress}_{\text{dashpot}} = \sigma_d = \eta \frac{d\varepsilon}{dt}$$

where E = Young's modulus, MPa (psi)

η = viscosity of newtonian fluid (oil) in dashpot, Pa·s

Total strain ε = strain in the spring ε_s + strain in the dashpot ε_d

The Maxwell model represents elastic creep, elastic recovery, and permanent set. In general, the Maxwell model provides reasonable expressions for stress relaxation, and the Voigt-Kelvin model provides reasonable expressions for creep behavior. Creep occurs when a constant stress is instantly or rapidly applied over a period of time, and a corresponding strain increases over that time. The instant or rapid application of stress to a Maxwell model causes instantaneous stretching of the spring, which reaches an equilibrium strain ε. Under constant stress the dashpot continues to extend with time. When the stress is released, the spring immediately contracts to an amount equal to its extension, which is elastic recovery. The dashpot does not recover, leaving a permanent set, which is the amount that the dashpot extended during the time the constant stress was applied. This model may not be easy to fit to experimental quantitative data, but it demonstrates some viscoelastic characteristics [11, 12].

Voigt spring-and-dashpot model

The Voigt model spring and dashpot are parallel. The model is a conventional concept for understanding stress and strain relationships when load is applied to a viscoelastic material [10].

Voigt-Kelvin spring-and-dashpot models

Spring-and-dashpot models are extended by the Voigt-Kelvin (V-K) model, which broadens linear viscoelastic concepts. The spring and dashpot are always in parallel. The V-K spring-and-dashpot models are useful for understanding creep behavior [11].

$$\sigma = \sigma_s + \sigma_d$$

where σ = total stress acting on a V-K spring-and-dashpot model, MPa (psi)

σ_s = stress acting on spring element, MPa (psi)
σ_d = stress acting on dashpot element, MPa (psi)

Total strain ε in a Voigt-Kelvin spring-and-dashpot model [11] is

$$\varepsilon = \varepsilon_s + \varepsilon_d$$

where ε_s = strain in spring element, cm/cm (in/in) %
ε_d = strain in dashpot element, cm/cm (in/in) %

Three-, four-, and five-parameter models

Spring-and-dashpot models developed for three-, four-, and five-parameter models evolve from the linear elastic (spring) and viscous (dashpot) elements in Maxwell and Voigt-Kelvin models. A larger number of hookean spring and newtonian dashpot elements may be needed to obtain a more accurate description of viscoelastic responses. An example of a three-element *standard linear solid model* (SLSM) has a second hookean spring element added parallel to the conventional hookean spring and in series with the newtonian dashpot element. The three-element model depicts a more realistic stress relaxation time and creep behavior with addition of the second spring [11–13].

To calculate the stress relaxation time for the standard linear solid model with a second spring added parallel to the initial spring, use

$$\tau^* = \eta_m \left(\frac{1}{E^*} + \frac{1}{E_m} \right)$$

where τ^* = stress relaxation time
η_m = viscosity of Maxwell dashpot oil, Pa·s (cP)
E^* = modulus of additional spring, MPa (psi)
E_m = modulus of Maxwell spring, MPa (psi)

To calculate the stress relaxation time for the Maxwell model alone, use

$$\tau^* = \frac{\eta_m}{E_m}$$

To calculate the shear modulus of elasticity G at any given time t, use

$$\mathrm{G} = \frac{\tau}{\gamma} = \frac{\eta}{t}$$

where τ = shear stress
γ = shear strain
η = newtonian shear viscosity

To calculate the shear modulus for the elastic portion (below the elastic limit), use

$$G = \frac{\Delta\tau}{\Delta\gamma}$$

where G is the slope of the curve.

Formulas for linear viscoelastic models can be applied to tensile deformation as well as shear deformation by replacing the shear stress τ with tensile stress σ, shear strain γ with tensile strain ε, shear modulus G with Young's tensile modulus E, and newtonian shear viscosity η with Trouton's tensile viscosity η_e [11–13].

Shear viscosity and shear modulus

Shear viscosity with the dashpot depicting a linear newtonian fluid is calculated by

$$\eta = \frac{\tau}{\gamma^*}$$

where η = shear viscosity of a newtonian fluid in dashpot, Pa·s (cP)
τ = shear stress, MPa (psi)
γ^* = shear strain rate, s^{-1}
10 P = 1000 centipoise (cP)

Two conditions are that (1) a constant stress is suddenly applied, and (2) strain is assumed to be zero when the stress is applied. Shear modulus G from a linear elastic model depicting a hookean solid is determined by $G = \tau/\gamma$ [11].

Poisson's Ratio

Poisson's ratio ν is the ratio of transverse contraction to longitudinal extension in the stretching direction. For the purposes of visualization only, picture a tough rubbery sheet, push a dull thin rod into the sheet, and you have transverse contraction and longitudinal extension. In a practical mode, Poisson's ratio is about 0.33 for many solid plastics and just under 0.5 for elastomers.

$$\nu = \frac{-\varepsilon_{\text{transverse}}}{\varepsilon_{\text{longitudinal}}}$$

The transverse strain $-\varepsilon_{\text{transverse}}$ is defined as negative, and the longitudinal strain $\varepsilon_{\text{longitudinal}}$ is defined as positive so that ν has a positive value.

Poisson's ratio can be viewed, in simple terms, as directly related to the modulus of elasticity E and inversely related to the shear modulus G:

$$2(1+\nu)=\frac{E}{G}$$

The Boltzmann Superposition Principle

This superposition principle states that the response of a viscoelastic plastic to a load is *independent* of any other load already applied to the plastic. Further, strain is directly proportional to applied stress when the strains are observed at equal time intervals. The Boltzmann superposition principle quantifies creep strain as a function of stress and time at a given temperature. Constitutive equations express the relationships among stress, strain, and time [12].

$$\varepsilon(t) = D(t-\tau_1)\sigma_1 + D(t-\tau_2)(\sigma_2-\sigma_1) + D(t-\tau_n)(\sigma_n-\sigma_{n-1})$$

where $D(t)$ is a compliance function of a polymer at initial stress and a specific temperature. Long-term stress and strain, creep, and stress relaxation at different temperatures are described by Ferry [13].

Williams-Landel-Ferry (WLF) Equation

This equation is the WLF time-temperature superposition principle. When shear compliance versus frequency is plotted for a given frequency, the curves can be superposed at different temperatures by keeping one curve fixed and shifting all other curves along the frequency axis. This superposition creates a *shift factor*, expressed as [14, 15]

$$\text{Log}\ aT=\frac{-C_1\,(T-T_r\,)}{C_2\;+\;(T-T_r)}$$

where aT = shift factor = $\eta T/(\eta T_r)$
C_1 = constant
T = temperature for plotting shear compliance versus frequency
T_r = reference temperature
C_2 = constant
ηT = viscosity at temperature T
ηT_r = viscosity at reference temperature T_r

This is a standard empirical equation of the WLF time-temperature superposition principle. By using the shift factor to create curves along the frequency axis, a master curve can be produced. The master curve is used to predict mechanical characteristics of the thermoplastic beyond the range of the available data. The equation is suitable for thermoplastics at temperatures near the glass transition temperature T_g [16].

Dynamic Mechanical Analysis

DMA calculations are applied to data in the linear region of a stress-to-strain curve. The calculations are most suited for low-amplitude sinusoidal strain when the sinusoidal strain is out of phase with sinusoidal stress. Design considerations for dynamic mechanical applications use values for the stress, strain, phase angle, storage modulus, and loss modulus [14, 15, 17, 18].

To calculate strain,

$$\varepsilon = \varepsilon_0 \sin \omega t$$

where ε = applied strain at time t, %
ε_0 = applied initial strain, %
ω = frequency of applied strain, Hz
t = selected time for calculating applied strain

To calculate stress,

$$\sigma = \sigma_0 \sin (\omega t + \delta)$$

where δ = phase angle between stress and strain.

Stress can be expressed with two components:

$$\sigma = \sigma_0 \cos \delta \sin \omega t + \sigma_0 \sin \delta \cos \omega t$$

Component 1 is in phase with strain:

$$\sigma_0 \cos \delta$$

Component 2 is 90° out of phase with strain:

$$\sigma_0 \sin \delta$$

where σ = stress at time t and σ_0 = initial stress.

Information on dynamic mechanical analysis and properties is found in Chap. 3, “Properties,” and Chap. 4, “Processes.”

Beam Equations

To return to beam equations, the same equations used for steel are used for plastic beams. Steel is an elastic material and thermoplastics are viscoelastic. The solutions of beam equations for plastic beams are based on the linear elastic region and must be compensated with safety factors, especially for long-term applications and elevated temperatures [5]. Beam equations are based on the following conditions:

1. Perpendicular loads are applied to straight beams with symmetric uniform cross sections.
2. Deflection is due to bending.
3. Neutral axis for the beam is a central horizontal axis where both tensile and compressive strain (and stress) are considered to be zero.

Types of beams

- Simple supported beam, load at center of beam. Beam is supported at both ends. To calculate the maximum deflection for a beam supported at both ends and center-loaded, use

$$\Delta_{\max} = \frac{CL^3F}{4bd^3}$$

where $\Delta_{\max}$ = maximum deflection, cm (in)
C = compliance factor, cm (in)
L = length of beam between two supports, cm (in)
F = applied load at center of beam, N (lb)
b = beam width, cm (in)
d = beam thickness, cm (in)

- Simple supported beam, load off-center
- Simple supported beam, two equal loads symmetrically located between center and the two supported ends
- Simple supported beam, load spread uniformly along beam length
- Beam fixed at both ends, load at center of beam
- Beam fixed at both ends, load spread uniformly along beam length
- Beam fixed at both ends, load at any point along beam
- Beam fixed at both ends, uniform load per unit length
- Cantilever beam, load at free end
- Cantilever beam, load spread uniformly along beam length
- Cantilever beam fixed at one end, free at other end

Deflection in beam bending

Deflection of bending beam equations is used for designing panels, doors, floors, columns, other building and architectural products, rails, shafts, and platforms [19].

Deflection in beam bending is determined by the second moment of inertia I and section modulus, by using the geometry of the cross section, illustrated with (1) polygons—square, rectangle, hollow rectangle, triangle, pentagon, hexagon, and octagon—and (2) beams of I, U, and T shapes—circular and hollow circular. Section modulus is a function of the cross-sectional area of a beam, independent of the type of material used. It can be expressed as

$$I = \frac{M}{d}$$

where I = section modulus, cm^3 (in^3)
M = moment of inertia of a cross section about a neutral axis, cm^4 (in^4)
d = distance from neutral axis to outermost fibers, cm (in)

Types of Circular and Rectangular Flat Plates

Flat plate equations are based on the following conditions:

1. Perpendicular loads are applied to flat plates with uniform cross sections.
2. Deflection is less than one-half the plate wall thickness.
3. Resin is homogeneous and isotropic.

- Circular flat plate, simply supported around circumference, load applied at the center of the plate. To calculate the maximum deflection for a circular flat plate simply supported around the circumference when a load is applied at the center of the plate, use

$$\Delta_{\max} = \frac{3(3+\nu)(1-\nu)^2}{4\pi(1+\nu)E}\,\frac{Fr}{d^3}$$

where $\Delta_{\max}$ = maximum deflection, cm (in)
ν = Poisson's ratio
E = flexural modulus, MPa (psi)
F = applied load at center of circular plate, N (lb)
r = radius, cm (in)
d = beam thickness, cm (in)

- Circular plate, simply supported around circumference, load uniformly distributed
- Circular plate, fixed around circumference, load uniformly distributed

- Rectangular plate, all four edges fixed, load uniformly applied
- Rectangular plate, all four edges simply supported, load uniformly applied

Design for Assembly

Press-fitting

Press-fit assemblies are extensively used in high-performance applications. PAI press-fit suspension bushings are used in race cars [20]. Drill bushings are press-fit assembled [21]; solderless connectors are press-fit into printed circuitboards [22]; compliant press-fit connectors are assembled with bi-spring press-fit contacts [23]; security magnet sensors with crush-proof plastic casings are press-fit installed on doors, windows, and cabinets [24]; and General Electric Home Security sensors are press-fit assembled [25].

The maximum allowable diametral interference between a shaft and a hub for press-fitting assembly is a function of part geometry, stress, modulus of elasticity of shaft and hub, and Poisson's ratio for shaft and hub materials. When the shaft and hub are made of the same material, the moduli of elasticity are the same and Poisson's ratio is the same for the shaft and hub, simplifying the equation for maximum diametral interference. Calculating diametral interference is simplified when the shaft is made of high-modulus material.

Temperature variations during operation cause total interference changes with dimensional changes of the shaft and hub. Total interference at a given temperature above room temperature is determined with the following equation [6]:

$$i^T = 2({R_s}^T - {R_i}^T)$$

where i^T = interference at a given temperature, mm (in)
${R_s}^T$ = inside radius of shaft at given temperature, mm (in)
${R_i}^T$ = radius of hub at given temperature, mm (in)
T = given temperature, °C (°F)

Optimum insertion force is a high-value property for press-fit assembly. It is determined by the following equation [6]:

$$F_{\text{in}} = 2\pi\mu h R_s p_c = F_{\text{out}}$$

where F_{in} = insertion force, N (lb)
μ = coefficient of friction
h = joint depth, mm (in)
R_s = radius of shaft, mm (in)

p_c = contact surface pressure between hub and shaft, MPa (psi)
F_{out} = pull-out force, N (lb)

In some applications, torsion is applied to a press-fit assembly. Transmitted torque M is calculated by [6]

$$M = F_{\text{in}} R_s = 2\pi\mu h R_s^2 p_c = F_{\text{out}} R_s$$

Snap-fit designs

A classical beam theory applied to snap-fit designs uses cantilever beams with an overhang at the free end. Depth of overhang determines the amount of deflection, which has an entrance side angle a and a retraction side angle b. The mating force is a function of a and b.

Here are suggestions for excellent snap-fit performance:

1. Wall thickness should be uniform.
2. Place snap-fit in area where the undercut section can expand easily.
3. Circular geometric shape is ideal.
4. Avoid weld lines in the area of the undercut.

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Chapter

3

Properties

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Property Checklist

Properties of engineering and other plastics are shown in Table 3.1.

Selected ASTM and similar ISO standards are shown in Table 3.2. Some test methods and specifications shown are prior to or after the year 2000.

The ASTM and ISO standard test methods and specifications shown in Table 3.3 refer specifically to engineering thermoplastics.

Medical grades are supplied with other engineering plastics such as Radel® poly(phenylene sulfone) and Lexan® polycarbonate.

Typical ASTM test methods used in suppliers' property tables for U.S. markets are given in Table 3.5.

Bulk modulus K is the ratio of change in pressure/volume compression (fractional change in volume), where $K = V(\Delta P/\Delta V)$. For solids, applied stress is used instead of pressure, and K is a constant for a given material. When there is an adiabatic exchange of heat, we have bulk modulus at constant entropy [13]. When the bulk modulus is determined at constant temperature, we have the isothermal bulk modulus [13].

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*The chapter author, editors, publisher, and companies referred to are not responsible for the use or accuracy of information in this chapter, such as property data, processing parameters, and applications.

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TABLE 3.1 Properties—Engineering and Other Plastics

Specific gravity, density
Tensile strength
Flexural strength
Compressive strength
Shear strength
Torque strength
Tensile modulus
Flexural modulus
Compressive modulus
Bulk modulus
Shear modulus
Dynamic mechanical properties, sinusoidal, intermittent
Stiffness, rigidity (flexural modulus)
Brittleness
Percent elongation
Impact strength, Izod, notched, unnotched, Charpy
Impact resistance, free-falling dart (Gardner impact)
Hardness
Wear resistance
Abrasion resistance
Coefficient of friction, static (initial), kinetic (in motion)
Tear resistance
Puncture resistance
Coefficient of (linear) thermal expansion
Chemical resistance
Permeability to gases
UV resistance
Radiation resistance
Deflection temperature under load (DTUL)
Melt point
Glass transition temperature
Continuous-use temperature
UL relative temperature index
Vicat softening temperature
Heat capacity
Resistivity, volume
Resistivity, surface
Dielectric constant (relative permittivity), the dielectric constant normalized to the absolute permittivity $\varepsilon = \varepsilon_r \varepsilon_0$, with ε = permittivity, ε_r = relative permittivity, ε_0 = absolute vacuum permittivity
Dielectric strength
Dissipation factor
Voltage, maximum before breakdown
Flame retardance
Ignition resistance
Limiting oxygen index
Optical, haze, light transmission, refractive index
Water absorption
Melt flow index, melt flow rate
Melt strength
Mold shrinkage
PVT (pressure-volume-temperature) relationship

TABLE 3.2 Selected ASTM and Similar ISO Standards [1]

ASTM/2000 Standard test methods and specifications		ISO
Committee D-20	Plastics (except “E” Standards)	
E 096	Test method for *vapor transmission*	
D0149	Differential scanning calorimetry (*DSC*)	IEC60243
D0149	*Dielectric strength*	—
D0150	A-C *loss characteristics and permittivity (dielectric constant)*	—
D0256	Determine pendulum *impact resistance* of notched Izod impact, unnotched Izod impact, reversed notched Izod, Charpy impact strength; also see D4812	180
D0257	Surface *resistivity*, volume resistivity	—
D0495	*Arc resistance*	—
D0523	Associated with capability of a surface to *reflect* more light in some directions than in other directions; use gloss meter; see D2457	
D0542	*Index of refraction* of transparent organic plastics	489
D0568	*Rate of burning* and/or extent and time of burning of flexible plastics	
D0570	*Water absorption* 24 h	
D0621	*Compressive* modulus, compressive deformation	—
D0635	*Rate of burning* and/or extent and time of burning of self-supporting plastics in a horizontal position; see D0568 and ISO 3795	1210
—	*Flammability* of interior materials for road vehicles, tractors, machinery for agriculture and forestry	3795
D0638	*Tensile properties*; Poisson’s ratio	527-1,2
D0648	*Deflection temperature* under flexural load	75-1,2
D0695	*Compressive properties* of rigid plastics	604
D0696	Determination of coefficient of linear thermal expansion (*CLTE*)	—
D0732	*Shear* test; see D2344	
D0746	*Brittleness temperature* by impact	974
D0785	Rockwell hardness of plastics and electrical insulating materials	2039-2
D0789	Determination of *relative viscosity and moisture* content of polyamide (PA)	[960] [water content only]
D0790	*Flexural properties* of unreinforced and reinforced plastics and electrical insulating materials	178
D0792	*Specific gravity, density*	1183
D0794	Maximum *continuous-use temperature*	—
D0882	*Tensile properties* of thin plastic sheeting	527-3
D0953	Determining the *bearing strength* (bearing stress to cause 4% strain)	—
D0955	Measuring *mold shrinkage*	294-4

(*Continued*)

TABLE 3.2 Selected ASTM and Similar ISO Standards [1] (*Continued*)

ASTM/2000	Standard test methods and specifications	ISO
D1003	Haze and *luminous transmittance* of transparent plastics (hazemeter or spectrometer)	14782/13468
D1043	*Stiffness* properties of plastics as a function of temperature by means of a torsion test (apparent modulus of rigidity, equated to modulus of elasticity)	458-1
D1044	Resistance of transparent plastics to surface *abrasion*	9352
E1131	Compositional analysis by thermogravimetric analysis (*TGA*)	11358
D1238	*Melt flow rate* of thermoplastics by extrusion plastometer	1133
D1242	Determining *abrasion resistance* as volume loss of plastic due to abrasion	—
E1356	*Glass transition temperature*	—
D1434	*Gas permeability* (gas transmission rate) through film, sheet, laminate, plastic-coated paper, plastic-coated fiber	—
D1505	*Density* of plastics by the density-gradient technique	1183
D1525	*Vicat softening* temperature of plastics	306
D1621	*Compressive* properties for rigid foam (apparent modulus of elasticity in compression)	—
D1622	*Density* of rigid foam	—
E1640	Standard test method of assignment of *glass transition temperature* by dynamic mechanical analysis	—
D1708	*Tensile properties* of plastics by use of microtensile specimens	6239
D1709-04	Free-falling weighted dart for *impact resistance* of plastic film, sheet	7765-1
D1746	Regular *transparency* of clear sheet, ratio of undiffused transmitted flux to incident flux (specular transmission is a property of transparent plastic sheet to show clearly a relatively distant object)	—
D1790	*Brittleness temperature* of plastics sheeting by impact	8570
D1822	*Tensile-impact energy* to break plastics and electrical insulating materials	8256
D1876	Standard specification *for PEKEKK* resin for surgical implant applications	—
D1894	Static and kinetic *coefficients of friction* of plastic film and sheeting; static coefficient relates to initial force needed to start motion; kinetic coefficient relates to force needed to maintain sliding motion	6601
D1895	*Apparent density*, bulk factor, pourability; ease of handling pellet, powder, granule flow during packaging, bulk loading, through hoppers and feed tubes	—

TABLE 3.2 Selected ASTM and Similar ISO Standards [1] (*Continued*)

ASTM/2000 Standard test methods and specifications		ISO
D1921	*Particle size* (sieve analysis) of plastics materials	4610
D1922	Propagation of *tear resistance* of plastic film and thin sheet by pendulum method; snagging occurs in products such as bags, liners, tarpaulins	6383-2
D1929	*Ignition temperature* of plastics	871
D1938	*Tear propagation resistance* of plastic film and thin sheeting by a single tear method	6383-1
D2240	*Shore hardness*	—
D2344	Short beam *shear*; see D0732	—
D2457	Specular *gloss* for film and solid plastics	—
D2468	Standard specifications for acrylonitrile-butadiene-styrene (*ABS*) Plastic Pipe Fittings, Schedule 40; Committee F-17 on Plastics Piping System	—
D2583	*Barcol hardness*	—
D2661	Standard specification for acrylonitrile-butadiene-styrene (*ABS*) Schedule 40, Plastics Drain, Waste, and Vent (DWV) Pipe and Fittings; Committee F-17 on Plastics Piping Systems	—
D2680	Standard specification for acrylonitrile-butadiene-styrene (*ABS*) and Poly(vinylchloride) Composite Sewer Piping; Committee F-17 on Plastics Piping Systems	—
D2857	*Intrinsic viscosity*; dilute solution viscosity of polymers	307, 1628-1
D2863	Measuring the minimum oxygen concentration to support candlelight combustion of plastics (*oxygen index*)	4589-2
D2990	Tensile, compressive, and flexural *creep* and creep-rupture of plastics	899-1,2
—	General requirement for the competence of calibration and testing laboratories	ISO/IEC 17025
D3028	Kinetic *coefficient of friction* of plastic solids using pendulum moment	—
D3417	*Heat of fusion and crystallization* of polymers by thermal analysis	11357-3
D3418	Peak *crystallization temperature* (DSC)	—
D3518	*Tensile shear* stress	14129
—	Interlaminar shear strength	14130
—	In-plane shear modulus	15310
D3641	Injection molding *test specimens* of thermoplastic molding and extrusion materials	
D3763	High-speed *puncture properties* of plastics using load and displacement sensors; instrumented dart impact; Dynatup	6603-2 7765
D3801	Measuring the comparative *extinguishing characteristics* of solid plastics in vertical position	1210-B

(*Continued*)

TABLE 3.2 Selected ASTM and Similar ISO Standards [1] (*Continued*)

ASTM/2000	Standard test methods and specifications	ISO
D3835	Determination of properties of polymeric materials by means of a capillary *rheometer*, shear sweep	11443
D3846	Double notch *shear* test	—
D3853	Determination of properties of polymeric materials by means of a capillary *rheometer*, thermal stability	11443
D3935	*Polycarbonate* (PC) unfilled and reinforced materials	7391-1 7391-2
D3965	Rigid acrylonitrile-butadiene-styrene (*ABS*) compound for pipe and fittings	7245
D4001	Determine weight (*MW*) average by light scattering	—
D4065-01	Determining and reporting *dynamic mechanical properties*, plastics	6721-1
D4066	*Nylon 6, 66 and 612* injection and extrusion materials	1874-1 1874-2
D4067-03	Standard specifications for reinforced and filled *polyphenylenesulfide* (PPS) injection molding and extrusion materials	—
D4092-01	Standard terminology for *dynamic mechanical measurements* on plastics	6721
D4181	Standard specifications for *acetal* (POM) molding and extrusion materials	DIS9988-1 DIS9988-2
D4226	Falling dart *impact resistance* (Gardner impact); see also D5420, D5628	—
D4329	Weathering QUV; also see D4587, D2565, D4459	4892
D4349	*Poly(phenylene ether)* (PPE) materials	DIS15103-2 DIS15103-1
D4440-01	Rheological measurements of polymer melts using *dynamic mechanical procedures*	6721-10
D4473-01	Test methods for plastics; *dynamic mechanical properties*; cure behavior	—
D4603	*Inherent viscosity*	—
D4673	Acrylonitrile-butadiene-styrene (*ABS*) molding and extrusion materials	2580-1 2580-2
D4804	Determining the *flammability characteristics* of non-rigid solid plastics	9773
D4812	*Impact strength*, Izod, unnotched cantilever beam testing	180
D4986	Horizontal *burning characteristics* of cellular polymeric materials	9772
D5023-01	Measuring the *dynamic mechanical properties* of plastics in flexure using three point bending	6721-3
D5024-01	Test method for plastics; *dynamic mechanical properties*; in compression	—
D5025	A *laboratory burner* used for small-scale burning tests on plastic materials	IEC 695-11-3 and 10093

TABLE 3.2 Selected ASTM and Similar ISO Standards [1] (*Continued*)

ASTM/2000	Standard test methods and specifications	ISO
D5026-01	Measuring the *dynamic mechanical properties* of plastics in tension	6721-5
D5045	Plane-strain *fracture toughness* and strain energy release rate of plastics materials	572
D5048	Measuring the *burning characteristics* and resistance to burn-through of solid plastics using 125-mm flame	10351
D5205	*Poly(ether-imide)* (PEI)	
D5207	Calibration of 20 and 125 mm test flames for *small-scale burning tests* on plastics materials	IEC 695-11-3, 4
D5279-01	Measuring the *dynamic mechanical properties* of plastics in torsion	6721
D5379	Double V-notched *shear* test	—
D5418-01	Test method for plastics; *dynamic mechanical properties*; in flexural dual cantilever beam	—
D5420	Falling dart *impact resistance* (Gardner impact); see also D4226, D5628	—
D6100	*Acetal* stock	—

IEC is International Electrotechnical Commission

Although the term *engineering thermoplastics* may imply load-bearing applications, advances in polymers and compounds, and application-specific grades, bring engineering thermoplastics products and markets far beyond these applications. They are increasingly used for semistructural and nonstructural products in electronics, automotive and transportation, clear products for windows, architectural products, compact disks, lenses, reflectors, and light transmission pipes. Long-term mechanical, thermal, and electrical properties are hallmarks of engineering plastics. Advanced grades retain properties at elevated temperatures and at electrical frequencies up to 10^9 Hz. It is the longer-term retention of properties at higher temperatures and higher electrical frequencies that primarily distinguishes advanced from standard engineering thermoplastics. Also, dielectric constant values of advanced engineering thermoplastics show less change than those of standard engineering thermoplastics at high frequencies.

Dynamic Mechanical Properties

Dynamic mechanical properties (DMP) refer to the mechanical properties of a polymeric material, such as a composite, when a periodic load imposes a strain (deformation) on the material. *Dynamic mechanical analysis* (DMA) is used to determine low cycle fatigue, high cycle fatigue, and

TABLE 3.3 ASTM and ISO Standard Test Methods and Specifications—Engineering Thermoplastics

ASTM		ISO
D0789	Determination of the Relative Viscosity and Moisture Content of Polyamide [ISO 960 Water Content Only]	[960]
D2468	Standard Specifications for Acrylonitrile-Butadiene-Styrene (ABS) Plastic Pipe Fittings, Schedule 40, Committee F-17 on Plastics Piping Systems	—
D2661	Standard Specification for Acrylonitrile-Butadiene-Styrene (ABS), Schedule 40, Plastics Drain, Waste, and Vent (DWV) Pipe and Fittings, Committee F-17 on Plastics Piping Systems	—
D2680	Standard Specifications for Acrylonitrile-Butadiene-Styrene (ABS) and Poly(vinylchloride) Composite Sewer Piping Committee F-17 on Plastics Piping Systems	—
D3935	Polycarbonate (PC) Unfilled and Reinforced Materials	7391-1 7391-2
D3965	Rigid Acrylonitrile-Butadiene-Styrene (ABS) Compound for Pipe and Fitting D3965 and ISO7245 are not equivalent.	7245
D4066	Nylon 6, 66 and 612 Injection Molded and Extruded Materials	1874-1 1874-2
D4181	Acetal (POM) Molding and Extrusion Materials	DIS9988-2
	ISO is replacing the paper-based DIS (Draft International Standard) with a more cost-effective electronic system.	
D4349	Poly(phenylene-ether) PPE Materials	DIS15103-1 DIS15103-2
	ISO 15103-1 and ISO/WD 15103-1: Part 1, PPE specifications. (ISO/WD: ISO Working Draft); ISO 15103-2: Part 2, PPE preparation of test specimens, and determination of properties.	
D5205	Poly(ether-imide) Materials	
D4507	Thermoplastic Polyester Materials	7792-1 7792-2
D4673	Acrylonitrile-Butadiene-Styrene (ABS) Molding and Extrusion Materials	2580-1 2580-2
D5989	Extruded and Monomer Cast Shapes from Nylon	
E595	NASA Space-Rated Composites, e.g., outgassing requirements, zero halogen outgassing, such as Amodel PPA, Ryton PPS, Victrex PEEK PAEK, Siveras LCP	
ASTM Int'l. F1579	Standard Specification for PAEK Polymers for Surgical Implants Developed by ASTM Subcommittee F04.11	
F2026	Standard Specifications for PAEK Polymers for Surgical Implant Applications	

TABLE 3.3 ASTM and ISO Standard Test Methods and Specifications—Engineering Thermoplastics (*Continued*)

ASTM		ISO
F1876	Standard Specification for PEKEKK Resin for Surgical Implant Applications	
F1855-00	Standard Specification for Polyoxymethylene (Acetal) for Medical Applications—Medical Devices, Instrumentation or Components Thereof Developed by ASTM Subcommittee F04.11	

fatigue crack cycle. DMA is used for research, product development, and quality control. It is also used to determine viscoelastic properties, such as elastic modulus (storage modulus G' or E'), viscous modulus (loss modulus G'' or E''), and damping coefficient (mechanical damping tan δ) as a function of time, temperature, or frequency. Storage modulus is the ratio of stress in phase with strain to the amount of strain. Storage modulus is proportional to the resonant frequency of the plastics. Data are plotted as G', G'', or tan δ versus time, temperature, or frequency. Calculations are based on the elastic region where the relationship is linear between stress and strain, and strain returns to zero when an applied load is removed.

A number of materials characterization instrument or testing service companies are available, including Rheologica® Instruments AB (Lund, Sweden), Netzsch Instruments (analyzing and testing headquarters, Selb, Germany; U.S. sales and service, Burlington, Mass.), Datapoint Labs (testing services, Ithaca, N.Y.), and TA Instruments. TA Instruments bought

TABLE 3.4 ASTM Standard Specifications for Engineering Thermoplastics

	ASTM Standard specification	
Resin	Resin	Stock shape
Polycarbonate	D3935	D6098
Nylon	D4066	D5989
PPS	D4067	
Acetal	D4181	D6100
Homopolymer, copolymer	Polyoxymethylene (POM) acetal homopolymer	D4181
	Polyoxymethylene polyacetals	D6778
PPE	D4349	
Polyesters	D4507	D6261
ABS	D4673	
	D5927	
PEI	D5205	
PAEK	—	D6262

TABLE 3.5 Typical ASTM Test Methods—Suppliers' Property Tables

ASTM	
D0149(2)	Dielectric strength, short term
D0150(2)	Dielectric constant, dissipation factor, loss tangent, tan δ
D0256 A	Impact strength, Izod
D0495	Arc resistance
D0570	Water absorption
D0638	Tensile strength, tensile modulus, elastic modulus, elongation at break
D0621	Compressive deformation under load
D0648	DTUL
D0695	Compressive strength, rupture at yield, compressive modulus
D0696	Coefficient of thermal expansion (CTE), coefficient of linear thermal expansion (CLTE)
D0732	Shear strength
D0785	Hardness, Rockwell
D0790	Flexural strength at yield or break, flexural modulus
D0792	Specific gravity, density
D0955	Linear mold shrinkage
D1238	Melt flow rates by extrusion plastometer
D2240	Hardness, Shore
D2583	Hardness, Shore
D3418	T_g amorphous

the assets of the Rheological Division of Rheometric Instruments (Piscataway, N.J.) and consolidated Rheometrics® into TA Instruments business in New Castle, Del. Rheometric Instruments changed its name to Proterion Corporation in 2003, and in 2004 it became part of Wyatt Technology Corporation (Santa Barbara, Calif.), which manufactures molecular characterization instruments such as light scattering instruments.

TA Instruments dynamic mechanical analyzers are used over a temperature range from –150 to 600°C (–238 to 1112°F) to measure deformations for shear, tension, compression, three-point bending, and dual/single cantilever [3]. They include an optical encoder. DMA instrumentation is more sensitive than differential scanning calorimetry for measuring smaller transition regions. The company's DSC instruments measure heat

TABLE 3.6 Other Relevant ASTM and ISO Test Methods

D1505	Test method for density of plastics by density gradient techniques
D3417	Test method for heats of fusion and crystallization of polymers by differential scanning calorimeter (DSC)
D4000	Classification system for specifying plastic materials
ISO-1133	Plastics—determination of melt *mass flow rate* (MFR) and *melt volume* flow *rate* (MVR) of thermoplastics
ISO-1628/1	Plastics–guidelines for the standardization methods for determination of viscosity number and limiting viscosity number of polymers in dilute solution; Part I: general conditions

flows and temperatures for materials' thermal transitions including T_g, crystallization phase changes, melting, product stability, oxidative stability, cure, and cure kinetics [3].

Thermogravimetric analysis (TGA) measures changes in materials' weight over a temperature and time range, to determine composition and heat stability [3].

Engineering thermoplastics possess better dynamic mechanical properties than other thermoplastics. They have current or potential applications for gears, valves, rotating blades, biomechanicals such as prosthetics and orthopedic implants, springs, pumps, thin film membranes, transmission components, and small-amplitude vibration step-loading applications [3].

ASTM D4065-01 (ISO 6721-1), "Standard Practice for Determining and Reporting Dynamic Mechanical Properties of Plastics," (Adoptions: DOD Adopted, Building Codes Adopted) describes tests for torsional, flexible, compressive, or tensile dynamic properties. It includes laboratory procedures for determining the dynamic mechanical properties of plastics subjected to different oscillatory deformations on dynamic *thermomechanical analyzers* (TMAs) or dynamic mechanical analyzers. The methods are used for viscoelastic plastics with an elastic modulus from 0.5 MPa to 100 GPa (73 psi to 1.45×10^7 psi). Data are used for determining viscoelastic properties such as elastic modulus and loss modulus as a function of temperature, frequency, or time; and transition temperatures. Five free-vibration, resonant or nonresonant forced-vibration test methods in ASTM D4065-01 (ISO 6721-1), "Standard Practice for Determining and Reporting Dynamic Mechanical Properties of Plastics," are (1) torsional pendulum, (2) torsional braid analyzer, (3) dynamic mechanical analyzer, (4) viscoelastometer, and (5) mechanical spectrometer. The torsional pendulum data are used to calculate oscillating strain, usually of a rectangular cross section. The ratio of loss modulus to the storage modulus tan δ is measured in compression, tension, flexure, and shear. The torsional braid analyzer test method uses a resin-coated glass fiber braid to determine oscillating strain, with the elastic component and damping component. The dynamic mechanical analyzer, viscoelastometer, and mechanical spectrometer test methods use a rectangular or circular specimen to determine the oscillating strain, elastic component, and damping component.

ASTM D4092-01 (ISO 6721) is entitled "Standard Terminology for Dynamic Mechanical Measurements on Plastics," DoD Adopted. It contains descriptions of the technical terms for dynamic mechanical property measurements on plastics including solids, melts, and solutions. It is also relatable to ISO 472 'Definitions' and certain items in ISO 6721-01, "Plastics—Determination of Dynamic Mechanical Properties, Part 1, General Principles." Other ASTM/ISO standard test methods for dynamic mechanical analyses are

ASTM D4440-01 (ISO 6721-10), "Rheological Measurements of Polymer Melt Using Dynamic Mechanical Procedures"

ASTM D4473-01, "Standard Test Methods for Plastics: Dynamic Mechanical Properties: Cure Behavior"

ASTM D5023-01 (ISO 6721-3), "Standard Test Measuring the Dynamic Mechanical Properties of Plastics in Flexure Using Three Point Bending"

ASTM D5024-01: "Standard Test Methods for Plastics: Dynamic Mechanical Properties: In Compression"

D5026-01 (ISO 6721-5), "Standard Test Method for Measuring Dynamic Mechanical Properties of Plastics in Tension"

ASTM D5279-01 (ISO 6721), "Measuring the Dynamic Mechanical Properties of Plastics in Torsion"

ASTM D5418-01, "Standard Test Method for Plastics: Dynamic Mechanical Properties: In Flexural Dual Cantilever Beam"

ASTM E1640, "Standard Test Method for Assignment of Glass Transition Temperature by Dynamic Mechanical Analysis"

Information on storage modulus, loss modulus, and DMA is found in Chap. 2, "Products and Designs," and Chap. 4, "Processes."

University of Maryland Computer Aided Life Cycle Engineering (CALCE) Electronic Products and Systems Center provides an example of polymeric materials characterization using dynamic mechanical analytical instrumentation [2]. The instruments evaluate dynamic mechanical properties including creep, stress relaxation, modulus, stress-to-strain ratio, and viscosity from –100 to 500°C (–148 to 932°F). Dynamic mechanical analyzers such as Rheometrics Solid Analyzer® (RSA II)™ are used to estimate dynamic mechanical properties. CALCE includes ISTHMUS TFA (thin film analyzer) instrumentation. The MTS Dynamic Testing System TFA involves a computer system to measure electronic laminate creep, stress relaxation, strain, elastic modulus, yield strength, stiffness, dimensional stability, and fatigue over a range of humidities. When an MTS environmental chamber such as model 651.06D-03 is included, the evaluation can characterize a polymeric material response to stress over a wide range of temperatures and loads [2].

TA Instruments ARES® rheometers measure controlled strain and controlled stress by using two technologies: *combined motor and transducer* (CMT) and *separate motor and transducer* (SMT). The company's rheometer instrument controls using Ochestrator™ software include

1. Stress and strain by dynamic (sinusoidal) oscillation at different frequencies, times, and temperatures, and multiwave sweeps

2. Stress and strain by steady (linear) shear at different times and temperatures
3. Creep and stress relaxation
4. Parallel superposition
5. Squeeze flow, pull-off tests, and other linear tests

Data analysis [3] includes

1. Long-term property predictions using time-temperature superpositions
2. Linear viscoelastic functions and interconversions
3. MWD data
4. User-defined variables and models
5. Cut-and-paste graphics
6. Custom reports

The company's *dielectric analyzer* (DEA) measures capacitive and conductive properties over different frequencies, temperatures, and times to determine the permittivity ε', loss factor ε'', dielectric loss tangent tan δ, and ionic conductivity. The DEA measures data at eight decades from 0.003 to 300,000 Hz [3]. Decades and octaves quantify frequency changes.

Decades mean that data are measured at frequency intervals that are 10 times apart. Frequencies at 5 and 50 Hz, 10 and 100 Hz, 25 and 250 Hz are one decade apart; 2000 and 200,000 Hz are two decades apart (2000 to 20,000 is one decade, 20,000 to 200,000 is the second decade). Frequency intervals of octaves are 2 times apart, 5 and 10 Hz are one octave, 1000 and 2000 Hz are one octave [11, 12].

Applied torque

Roark's formulas for torsional stress from a twisting motion can be expressed for beam loading conditions [4], e.g., for a power transmission application. Shear stress developed in a material subjected to a specified torque in a torsion test is estimated by [5]

$$S = \frac{Tr}{J}$$

where S = shear stress developed in a material subjected to torque or torsional shear stress, MPa (psi)
T = torque, N·m (ft·lb)
r = distance from axis of twist to outermost fiber of specimen, cm (in)
J = polar moment of inertia, cm^4 (in^4)

and by

$$S = \frac{T\gamma}{t/J}$$

where S = torsional shear stress
T = torque
γ = factor based on height/thickness ratio
t = thickness
J = polar moment of inertia

The angle of twist for a given applied torque can be estimated by [6]

$$\phi = \frac{TL}{JG}$$

where ϕ = angle of twist, rad (deg)
T = internal torque in the shaft, N·m (ft·lb)
L = length of shaft being twisted, cm (in)
J = polar moment of inertia of shaft, cm^4 (in^4)
G = modulus of rigidity (shear modulus of material), MPa (psi)

When torque is applied, the modulus of elasticity in shear (shear modulus) can be estimated by using Poisson's ratio:

$$G = \frac{E}{2(1+\nu)}$$

where G = modulus of elasticity in shear, shear modulus, modulus of rigidity, MPa (psi)
E = modulus of elasticity of plastics, MPa (psi)
ν = Poisson's ratio

Shear [8]

ASTM and ISO test methods for shear are as follows

ASTM		ISO
D3518	Tensile Shear Stress	14129
	Interlaminar Shear Strength	14130
	In-Plane Shear Modulus	15310
D3846	Double Notch Shear Test	—
D5379	Double V-Notch Shear Test	—

Shear modulus can be expressed with rheological variables [14]:

$$G = \frac{\tau}{\gamma}$$

where G = shear modulus, MPa (psi)
τ = shear stress, MPa (psi)
γ = shear strain, cm/cm (in/in) %

$$\gamma = \frac{D}{H}$$

where D = displacement of cubical specimen, cm (in)
H = height of cubical volume, cm (in)

$$\gamma^* = \text{shear strain rate } = \frac{V}{H}$$

where V = velocity of displacement caused by applied force
H = height of cubical specimen

Sinusoidal time-varying (STV) flow demonstrates differences between elastic and viscous properties, and it demonstrates viscoelastic behavior in more complex time-varying flow [14].

With a beam equation, shear modulus is expressed as [7]

$$G = \frac{F/A}{M/L} = \frac{F/A}{\tan\theta}$$

where F = shear load, N (lb)
A = cross-sectional area of applied shear load, cm^2 (in^2)
M = shear elongation, cm (in)
L = unit length of beam, cm (in)
θ = shear angle (strain), rad (deg)

Shear force is applied tangentially to the surface of a part. Shear stress—the tangential force divided by the applied force area—can be tensile, flexural, and compressive.

Creep

Creep and stress relaxation are the principal causes of failure due to deformation (strain) for long-term service applications, and engineering plastics usually are designed for long-term service. A plastic gear or mechanical fastener such as a nut and bolt, nail, or screw that produces creep and stress relaxation can malfunction. The result can be catastrophic failure of the entire product system. A plastic gear produces dynamic creep, which is caused by a fluctuating applied load or fluctuating temperature. A stationary mechanical fastener produces static creep, which is caused by a constant applied load and typically at constant temperature. At the macromolecular level, creep is the result of a delay in response to load by the macromolecules during gradually increasing strain. When the load is removed, strain gradually reduces (stress relaxation). The two phenomena of creep and stress relaxation are time-dependent and temperature-dependent. These viscoelastic phenomena are depicted with the spring-and-dashpot models in Chap. 2, “Products and Designs.”

Creep is covered in ASTM D2990 (ISO 899-1,2), “Tensile, Compressive and Flexural Creep and Creep-Rupture of Plastics,” and ISO/IEC (International Electrotechnical Commission) 17025, “General Requirements for the Competence of Calibration and Testing Laboratories.” *Creep* is defined in ASTM D2990 as “the progressive deformation of a material at constant load (stress).” Creep tests measure the dimensional changes under constant load over a period of time, plotted at different constant temperatures. Creep rupture tests are used to estimate the required time for rupture under a constant load at different constant temperatures. ASTM D2990 (ISO 899-1,2) recognizes that creep values used in engineering design should be determined under application-specific simulated conditions. Application-specific conditions are obtained with CAD/CAE and prototypes. Creep values are only estimates, and as with other engineering plastics properties for long-term applications, safety factors are incorporated into the engineering data.

Figure 3.1 shows a general creep curve for total strain, in percent (y axis), versus time, in minutes (x axis), at constant load and temperature, in ASTM D2990 [1]. The load can be tension, flexure, compression, or torque. The creep curve has four sections. Starting at (0, 0) for (y, x), the sections are

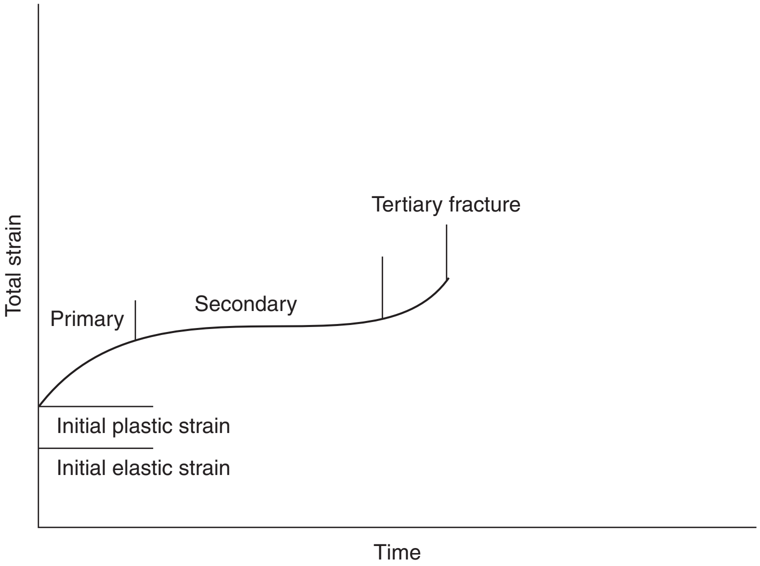

Figure 3.1 Progressive creep strain with time at a given temperature.

1. *Initial application of load*, instantaneous initial strain, elastic and plastic strains, along the y axis at virtually 0 min.
2. *Primary phase*, with elastic and plastic strain combined; creep *rate* (slope of curve) decreases rapidly.
3. *Secondary phase*, which shows further decrease in creep rate (decrease in total strain increase per minute). The secondary phase shows a shallow, virtually linear slope.
4. *Tertiary phase*, when strain rate increases again, leading to fracture, product failure.

ASTM D2990 cautions that this creep curve "is an idealized curve." Presentation of total strain (y axis) and time (x axis) as instantaneous, primary, and secondary stages depends on the time scale (x axis). Not all polymeric materials have a secondary phase; and the tertiary creep phase occurs at high stresses for ductile materials [1].

Clear Engineering Plastics

Transparent (clear) engineering thermoplastics are used increasingly for medical, automotive, and architectural products; windows, skylights, panels; compact disks, fiber-optics sleeves; lenses, reflectors, and light transmission pipes. ASTM D1003 (ISO 14782/13468), "Haze and Luminous Transmittance of Transparent Plastics (Hazemeter or Spectrometer)," describes optical properties of thermoplastics.

Light pipes are used to transmit light from a light source to an outlet interfaced with a clear medium, usually air or water [9]. Light pipes are typically clear, solid, curved or bent plastic rods. The objective with light pipe design is to transmit the maximum amount of light. The distance x between the light pipe and the incident light is based on the design. One way to reduce the number of reflections and light path length is to design a convex entrance. Curved light pipes are designed with a maximum angle of bend—radius of curvature—to avoid or minimize light loss. The maximum radius of curvature for Lexan® polycarbonate, e.g., is 51°. At angles below the maximum radius of curvature, there is light loss; and there is a minimum radius of curvature. To calculate the minimum radius of curvature [9], use

$$\frac{R_{\min}}{t} = \frac{n_p + n_a}{2(n_p - n_a)}$$

where $R_{\min}$ = minimum radius of curvature, deg
t = diameter or thickness of light pipe, mm (in)
n_p = refractive index of light pipe = 1.585 for Lexan polycarbonate
n_a = 1.00 for refractive index of air

When the radius of curvature of a convex surface such as a light pipe or lens is too small, the critical angle is compromised.

Internal reflection at the interface with air or water keeps the light rays within the light pipe. However, just as power loss is important to determine power cable design, minimal light ray loss during light transmission through a light pipe is important for efficient light pipe design.

Refractive index *n* is the ratio of the velocity of light in a vacuum to the velocity of light in a medium, as shown in Table 3.7. It is the degree to which a transparent material bends light.

The higher the refractive index of a given medium, the slower the light rays travel through the medium. Slower light rays travel closer to the normal line in Fig. 3.2, and the angle of refraction is smaller.

The ratio of the refractive index of two clear materials such as plastics and air at their interface is related to the angle of refraction (bending) according to Snell's law. Snell's law equates the sine of the angle of incidence to the sine of the angle of refraction [9]. "Incidence angle is the angle formed by a ray arriving at a surface and the perpendicular to that surface at the point of arrival" [10].

When light travels through a clear plastic to the interface with air, it refracts unless the angle of incidence is greater than the critical angle. At the critical angle the refractive angle is 90° from the line normal to the interface surface. See Fig. 3.2.

1. The normal line is a perpendicular line (y axis) to the interface surface (boundary) at the point where the incident light rays pass through the interface surface. It is the reference line for the angle of incidence and angle of refraction.
2. Light rays refract toward the normal line when the speed of the light rays is slower than that of the incident light rays. "Slower is closer."

TABLE 3.7 Refractive Index Ratios

Medium	Refractive index
Acrylic	1.49–1.51
Polystyrene	1.59
Polycarbonate	1.58–1.60
Polysulfone	1.63
Flint glass	1.57–1.75
Crown glass	1.50–1.62
Water (20°C)	1.333
Air	1.0003
Vacuum	1.00000

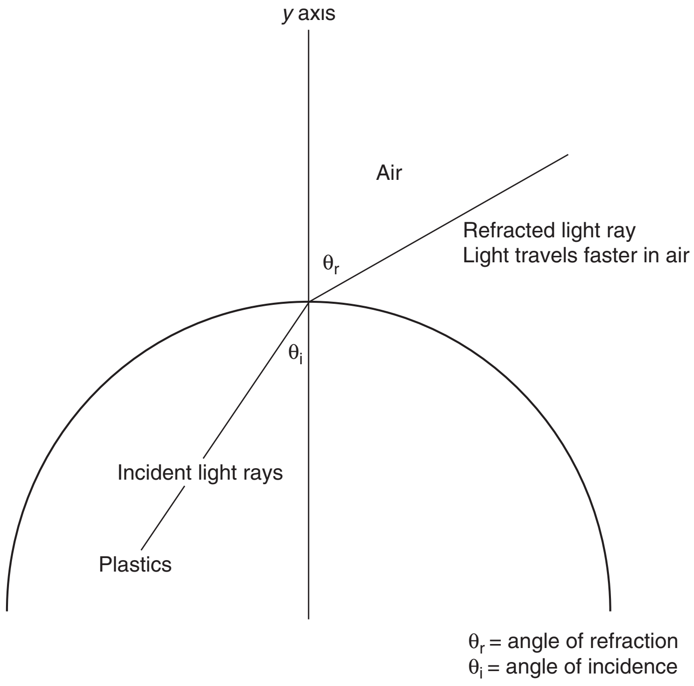

Figure 3.2 Incident light rays and refractive light rays.

3. Light rays refract away from the normal line when the speed of the light rays is faster than that of the incident light rays. “Faster is farther.”
4. The more the light rays refract, the larger the difference between the angle of incidence and the angle of refraction.
5. The critical angle is the angle of incidence that creates an angle of refraction that is 90° from the normal line. At the critical angle, light is not transmitted across the interface.

According to Snell’s law, when the angle of incidence equals the angle of reflection [9],

$$\theta_{\text{incidence}} = \theta_{\text{reflection}}$$

then

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$

where n_1 = index of refraction of medium 1
θ_1 = angle of refraction, rad (deg)
n_2 = index of refraction of medium 2
θ_2 = angle of refraction, rad (deg)

Fresnel's equation is used to estimate the amount of light reflected under ideal conditions [9].

$$R_f = \frac{n_2 \cos\theta_1 - n_1 \cos\theta}{n_2 \cos\theta_1 + n_1 \cos\theta}$$

where R_f = amount of light reflected
n_2 = refractive index of one medium
θ_1 = angle of refraction, rad (deg)
n_1 = refractive index of other medium
$\theta = \theta_{\text{incidence}} = \theta_{\text{reflection}}$, rad (deg)

As light travels through a clear plastic, imperfections and impurities greatly diminish light intensity, which scatters and attenuates exponentially by light absorption. The amount that light intensity diminishes can be estimated by

$$I_x = I_0 e^{-\mu x}$$

where I_x = intensity of light beam at x, cd (fc), lx
I_0 = free air density
μ = plastics attenuation coefficient at x
x = distance light traveled through plastics at I_x, cm (in)
1 candela (cd) = 10.74 lux (lx)

Measure with a lightmeter.

The total attenuation coefficient α_t is used to calculate the amount of light lost when light is transmitted through a plastic light pipe, assuming no light is lost by refraction from the critical angle. Coefficient α_t is the sum of (1) refraction at entrance and exit (of plastic light pipe), (2) material absorption per unit length of light pipe, (3) loss at each reflection, and (4) number of reflections per unit length [9].

Surface imperfections and impurities scatter light which reflects off the interface of the plastic and air (or other medium). The amount of light scattered at each reflection is estimated as loss per reflection. Light loss by reflection is calculated as [9]

$$\Lambda_{\text{reflection}} = e\left(\pi\sigma r^2 \frac{\cos\theta}{\lambda_n}\right)^2$$

where $\Lambda_{\text{reflection}}$ = light loss per reflection
σ = surface roughness, mm (in); height from surface of surface imperfections, measured from the mean
r = thickness of plastics, cm (in)
θ = angle of incidence of light rays *entering* plastics surface from air (medium), rad (deg)
λ_n = wavelength of light source in plastics

Transparent plastic refractive index test methods are described in ASTM D0542 (ISO 489), “Index of Refraction of Transparent Organic Plastics.” Test methods for transmission through clear plastic sheet are described in ASTM D1746, “Regular Transparency of Clear Sheet, Ratio of Undiffused Transmission Flux to Incident Flux.” Specular transmission is a property of transparent plastic sheet to show clearly a relatively distant object. ASTM D1044 is entitled “Resistance of Transparent Plastics to Surface Abrasion.”

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Chapter

4

Processing*

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Processing is step 4, near the end of a finished product's road, but processing considerations have been present since Chap. 2, "Products and Design." Process selection is often made according to a product's configuration or design. When the process is selected, there are important decisions to be made. This chapter provides background for complex and critical decisions when one is selecting processes for engineering plastics and other thermoplastics.

Processing Methods Checklist

Engineering and other plastics

- Injection molding
  - Insert molding
  - Coinjection molding
  - Injection compression molding
  - Gas-assisted injection molding
  - In-mold decorating (IMD) injection molding

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*The chapter author, editors, publisher, and companies referred to are not responsible for the use or accuracy of information in this chapter, such as property data, processing parameters, and applications.

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  - Overmolding
  - Structural foam molding
  - In-mold assembly (IMA) injection molding
  - Reaction injection molding (RIM), structural reaction injection molding (SRIM)
- Compression molding
- Resin transfer molding (RTM)
- Blow molding
  - Extrusion blow molding
  - Injection blow molding
  - Stretch blow molding
- Extrusion—pipe, profiles, tubes, rods
  - Extrusion—sheet and film
  - Coextrusion
  - Extrusion—blown film
  - Extrusion—foam
- Thermoforming; vacuum forming, pressure forming
- Other processes
  - Pultrusion
  - Filament winding
  - Hand layup
  - Spinning
  - Casting
  - Calendering
- Assembly, decorating, finishing
- Coating
  - Powder coating
  - Spray coating, electrospray coating
  - Dip coating
  - Fluidized-bed coating
  - Emulsion, dispersion, suspension coating

Rheology [1]

Rheology is the science of flow and deformation of a fluid. It is a function of load (force) and time. Understanding rheology during melt processing engineering thermoplastics is fundamental for maximum product quality and process economics. Viscoelastic rheology is primarily observed by melt behavior changes as a function of time, temperature, pressure, and viscosity. A resin or compound rheology is influenced by processing parameters, machinery, and equipment design. Melt rheology is probably the single most important consideration when one is designing polymer systems for ease of injection molding.

Time-Temperature Superposition Shift Principle

A cursory description of the time-temperature superposition shift principle is provided with a cartesian graph for a given viscoelastic polymer, with the y axis equal to Young's modulus (as tensile or compression modulus), MPa, and the x axis equal to time, s. Data are plotted at increasing times, for different temperatures. A temperature is selected as the reference temperature, and isotherms for other temperatures are shifted along the x axis (time) to provide a master curve. The master curve shows the dynamic characteristics of the viscoelastic polymer beyond the time and frequency ranges of conventional test measurements.

To calculate the time-temperature superposition shift factor [2], use

$$a_T = \frac{\eta_0 \tau_{\text{test}} / \eta_0 \tau_{\text{ref}}}{T_{\text{ref}} \rho_{\text{ref}} / T_{\text{test}} \rho_{\text{test}}}$$

where a_T = time-temperature superposition shift factor
η_0 = zero shear rate viscosity (steady-state viscosity at zero shear rate)
τ_{test} = relaxation time for tested specimen
τ_{ref} = relaxation time for reference specimen
T_{ref} = reference temperature, K
ρ_{ref} = reference density
T_{test} = test temperature, K
ρ_{test} = test density

$$a_T = \frac{\tau_{\text{test}} T_{\text{test}}}{\tau_{\text{ref}} T_{\text{ref}}}$$

To calculate the time-temperature superposition shift factor by using the WLF (Williams-Landel-Ferry) equation for polymers at temperatures less than 100°C (232°F) above their T_g [2], use

$$\ln a_T = \frac{-C_1 (T - T_{\text{ref}})}{C_2 + (T - T_{\text{ref}})}$$

where a_T = time-temperature superposition shift factor
C_1 = WLF constant for an individual polymer
T = specified temperature
T_{ref} = reference temperature
C_2 = WLF constant for an individual polymer

Ferry published a list of WLF C_1 and C_2 constants when $T_{\text{ref}} = T_g$ in *Viscoelastic Properties of Polymers* (2d ed., Wiley, New York, 1970).

The WLF equation for a_T does not work for polymers at temperatures 100°C (232°F) above their T_g. For these polymers an Arrhenius formula is used.

To calculate the time-temperature superposition shift factor for polymers at temperatures about 100°C (232°F) above their T_g, the following Arrhenius formula is used.

$$\eta = A \exp \frac{\Delta E}{R_g T}$$

where η = viscosity
A = Arrhenius constant
ΔE = activation energy for flow
R_g = gas law constant
T = temperature, K

From this expression, the time-temperature superposition shift factor a_T becomes [2]

$$a_T = \exp\left[\frac{\Delta E}{R_g}\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right]$$

Another route to calculate the shift factor is to equate the natural log of a_T ($\ln a_T$) to free volume f when f is assumed to be linearly dependent on temperature.

Loss Modulus

Viscoelastic behavior can be viewed as three fundamental modulus characteristics: G^* or E^* = complex modulus, G' or E' = storage or dynamic modulus, and G'' or E'' = loss or viscous modulus. The moduli are related by the angle of phase lag δ in stress-to-strain phase lag. They are derived from measurements of the complex modulus and phase angle δ relationships of stress to strain, by dynamic mechanical analysis (DMA) using a Rheometric Solids Analyzer,® RSA,™ supplied by TA Instruments [19]. Further information on loss modulus, storage modulus, and DMA is found in Chap. 2, "Products and Designs," and Chap. 3, "Properties."

To calculate the loss modulus as a function of time [2], use

$$G''_{T_{\text{ref}}} = (G''_{T_{\text{test}}})\frac{T_{\text{ref}}\rho_{\text{ref}}}{T_{\text{test}}\rho_{\text{test}}}$$

where $G''_{T_{\text{ref}}}$ = loss modulus as a linear viscoelastic property at reference temperature
$G''_{T_{\text{ref}}}$ = loss modulus at test temperature
T_{ref} = reference temperature, K

ρ_{ref} = reference density
T_{test} = test temperature, K
ρ_{test} = test density

Shear Rate

Shear rate is the rate at which a layer of melt slides over the layer below. It is observed as velocity. Shear rate applies to nonnewtonian (shear-dependent) macromolecular polymeric melts and solutions. Newtonian fluids, typically small molecules such as H_2O and oil, have constant viscosities and are not shear rate–dependent.

Zero shear rate viscosity (the steady-state viscosity at zero shear rate) is influenced by the type of polymer, MW, MWD, and additives. To calculate the increase of zero shear rate viscosity with increasing MW [3], use

$$\eta_0 = KMa$$

where η_0 = zero shear rate viscosity, s^{-1}
K = empirical constant
M = molecular weight of macropolymer
a = 3.4 at $M >$ critical molecular weight M_c
= 1 at $M <$ critical molecular weight M_c

Shear rate viscosity (shear strain or stress) behavior is fundamental to controlling melt flow rheology. At low strain rate viscosity, the zero strain rate viscosity is directly related to extensional (stretching) strain viscosity by [3]

$$\eta_E = 3\eta_0$$

where η_E = extensional strain viscosity, s^{-1}
η_0 = zero shear rate viscosity, s^{-1}

The effects of shear on viscosity are plotted in three phases (y axis = log viscosity, x axis = log shear rate): I, a newtonian plateau which is the initial phase where the viscosity shows no change with increased shear rate; II, the power law region which shows a rapid drop in viscosity as shear rate increases; and III, the newtonian plateau which is the final phase where the viscosity again shows no change with increased shear rate [3]. Newtonian law works with low shear rate, and the power law works with high shear rate.

At low shear rates, polymeric liquid properties are characterized by two constitutive parameters: zero shear rate viscosity η_0 and recoverable shear compliance J_0^e, which indicates fluid elasticity. At higher shear strain rates, rheological behavior is measured with a viscometer. Extensional strain viscosity, associated with extensional flow, occurs with film extrusion, thermoforming, and blow molding. Observing the melt flow through a capillary is used to measure apparent viscosity, and it offers information on melt flow during various processing conditions [20].

ASTM D3835/2000 test method measures rheological properties of thermoplastic (and thermosetting) melts by using a capillary rheometer [4]. The test method includes measurements of viscosity, shear rate, shear stress, swell ratio, and percent of extrudate swell. Assuming a newtonian fluid, to calculate melt viscosity μ, use

$$\mu = \frac{Fr^4t}{8r^2LI'} \qquad \text{Pa} \cdot \text{s}$$

where F = force on ram, N
r = radius of capillary, m
t = extrusion time, s
L = length of capillary, m
I' = volume extruded, m^3

To calculate shear rate S_r,

$$S_r = \frac{4Q}{\pi r^3} = \frac{4I'}{\pi r^3 t} \qquad \text{s}^{-1}$$

where Q = ram speed (m/s) × barrel cross-sectional area (m^2)
= flow rate (m^3/s)

Die swell ratio and melt shear modulus exhibit melt viscoelasticity.

Rheological behavior can be determined with small-amplitude sinusoidal shear, using the cone-and-plate steady-shear test to determine the linear viscoelastic shear strain. A sinusoidal curve is charted to represent the viscous (loss) modulus (out-of-phase segment) and the elastic (storage) modulus (in-phase segment) [2].

G'' = viscous modulus

G' = elastic modulus

δ = phase angle, rad

$$\frac{G''}{G'} = \tan\delta$$

Viscous and elastic moduli with small-amplitude sinusoidal shear can be determined by using an orthogonal rheometer [2]. Small-amplitude sinusoidal shear, using cone-and-plate or parallel-plate test methods, can determine rheological behavior for normal stresses in shear flow, as well as for shear strain.

To calculate the first normal stress difference for low shear rates, using the cone-and-plate method [2], use

$$N_1 = \frac{2F_z}{\pi R_p^2}$$

where N_1 = first normal stress difference, MPa (psi)
F_z = normal force, N (lb)
R_p = radius, cm (in)

Extrusion

Most of this information is relevant to extruders and injection molding machines. Extrusion is a continual process to make products such as film and sheet, wire covering, pipe, and profiles. Essential components include the hopper, barrel, cylinder, plasticating screw, thrust bearing, breaker plate and screen pack, backpressure regulating valve, die adapter, die, sizing, and haul-off equipment. Heater bands heated by built-in thermocouples are strategically located around the cylinder. A key word for the plasticating screw function is *uniformity*: uniform (homogeneous) melt mix and uniform melt flow through the die. Uniformity is achieved by screw configuration (e.g., flight and zone designs, length, and L/D) and circumferential speed (rpm). Flight design goes a long way to product quality and process economics. Flight design includes flight height, width, clearance and angle, number of flights, and distance between flights. Breaker plate functions include increasing backpressure and changing melt flow from rotational to axial flow prior to melt flow to the die. The screw root diameter increases from the hopper end to the metering zone. Channel depth is increased or decreased according to melt rheology.

Two standard specifications for extruder and injection molding machines are L/D and the helix angle. Length L is the length of the flighted section, which consists of the feed section, transition section, and metering section for metering screws; diameter D is the outside diameter.

To calculate the helix angle [3],

$$\phi = \tan^{-1} \frac{t}{\pi D}$$

where ϕ = helix angle, rad
t = axial distance from center of one flight to center of next flight, mm
D = outside diameter of screw, mm

In addition to metering screws, there are other designs including barrier screws which enhance melting and two-stage screws with five zones, used in vented barrel extruders. The five zones are the feed, transition, first metering, vent, and second metering. Pressure is reduced in the vent zone and increased in the second metering zone. Pump ratio ϑ indicates the capability of the second metering zone Π_2 to pump more resin (compound or composite) than the first metering zone Π_1 delivers [3].

$$\vartheta = \frac{\Pi_2}{\Pi_1}$$

(The two-stage screw is described in "Plasticating Components Technology," Spirex Corporation, Youngstown, Ohio, 1992.)

Melt flow near the screw is forced back into the cylinder. Extruder output can be estimated by subtracting melt pressure flow from drag flow Q_D which conveys melt along the cylinder wall to the die. Melt pressure is highest in the metering zone immediately prior to entering the die, where flow splits into two components: the pressure flow Q_P and a leakage flow Q_L. An order-of-magnitude net output Q of a single-screw extruder is based on the following assumptions [3]:

Melt flow is newtonian.

Extruder is at a steady state.

Extruder is at a constant temperature.

Output is due to only the metering zone.

$$Q_D = AN = \frac{\pi^2 D^2 h \sin\phi \cos\phi}{2} N$$

$$A = \frac{\pi^2 D^2 h \sin\phi \cos\phi}{2}$$

$$Q_P = \frac{B\,\Delta P}{\mu} = \frac{\pi D h^3 \sin^2\phi}{(12L_m)} \frac{\Delta P}{\mu}$$

$$B = \frac{\pi D h^3 \sin^2\phi}{12L_m}$$

$$Q_L = \frac{C\,\Delta P}{\mu} = \frac{\pi D^2 \delta^3 \tan\phi}{(12eL_m)} \frac{\Delta P}{\mu}$$

$$C = \frac{\pi D^2 \delta^3 \tan\phi}{12eL_m}$$

$$Q = \frac{\Delta P}{K\mu}$$

where Q_D, Q_P, Q_L = drag flow, pressure flow, leakage flow, N/h
A = screw geometry constant
N = screw speed, rpm
D = screw diameter, mm
h = channel depth in metering zone, mm
ϕ = helix angle of screw, rad
B = screw geometry constant
L_m = length of metering zone, mm
C = screw geometry constant
ΔP = head pressure, MPa
μ = apparent viscosity in metering zone, s^{-1}
δ = flight clearance, mm
e = flight width, mm
K = die constant

Drag flow is primarily determined by helix angle, barrel, and channel design; pressure flow is determined by helical length, channel design, pressure rise, and melt viscosity. Extruder output, therefore, is a function of all these factors. Assuming newtonian, isothermal melt flow [2],

$$\text{Drag flow} = AN$$

$$A = \frac{n}{2}(\pi D_b W H \cos\theta_b)$$

where A = geometry constant
N = screw speed, rpm
n = number of parallel channels
D_b = inside diameter of barrel, mm
W = width of screw channel, mm
H = channel depth, mm
θ_b = helix angle at barrel surface, rad
Z = helical length, mm
B = geometry constant
ΔP = pressure rise, MPa
μ = melt viscosity, s^{-1}
Q = net output of extruder, N/h

The compression ratio enhances melt mixing and uniform melt delivery. The compression ratio ranges from about 1.5:1 to 4:1. It is generally the ratio of the volume of the channel of the screw at the hopper end to the volume of the channel at the die end. It can be measured in other ways. The feed (hopper) zone channel volume depth is greater than the metering zone. The compression ratio for more viscous resins is lower to avoid overheating. Higher compression ratios are used when large amounts of low bulk density are in the feed.

To calculate the compression ratio [3], use

$$\mathrm{CR} = \frac{V_{\text{feed zone}}}{V_{\text{metering zone}}} \cong \frac{H_{\text{feed zone}}}{H_{\text{metering zone}}}$$

where CR = compression ratio
$V_{\text{feed zone}}$ = feed zone channel volume, mm^3
$V_{\text{metering zone}}$ = metering zone channel volume, mm^3
$H_{\text{feed zone}}$ = feed zone channel depth, mm
$H_{\text{metering zone}}$ = metering zone channel depth, mm

The power to turn an extruder screw is determined in part by the helix design. To calculate the power, first calculate the value of E by the following formula, assuming an isothermal newtonian melt [2].

$$E = \frac{\pi^3 D_b^3 \sin\theta_b}{H}(1 + 3\ \sin^2\theta_b)$$

where E = extruder factor, mm^2
D_b = inside diameter of barrel, mm
θ_b = helix angle at barrel surface, rad
H = channel depth mm

$$P = E\mu N^2 Z + AN\Delta P$$

where P = power required to turn screw
μ = melt viscosity, P
N = screw speed, rpm
Z = helical length, mm
AN = drag flow, N/h
ΔP = pressure rise, MPa

The extruder thrust bearing is a critical component that contributes to product quality and extrusion efficiency. It couples the gearbox to the screw shank and gives support to the screw. It would be expected to last the service life of the extruder, assumed to be 10 years or more. Thrust bearing life expectancy is a function of head pressure and screw speed. Life expectancy B-10 is the number of hours when 10 percent of the bearings fail when tested at a standard pressure and screw speed. When the operating pressure and/or screw speed is greater than the B-10 standard, thrust bearing life is reduced, and an estimated new life expectancy is calculated by [3]

$$\text{B-10} = \text{B-10}_{\text{standard}}\left(\frac{N_{\text{standard}}}{N}\right)\left(\frac{P_{\text{standard}}}{P}\right)K$$

where N = screw speed, rpm
P = pressure, Pa
K = thrust bearing constant

The thrust bearing constant is described in C. Rauwendaal.[1]

Among other machinery and equipment considerations critical to good performance are the land length and gearbox. When the land length is too long, excessive shear can generate; when the land length is too short, insufficient molecular alignment and extrudate swell can occur. The two main properties to look for with a gearbox are strength and torque.

Injection Molding

Injection molding machinery and processes using engineering thermoplastics were introduced at K2004 [18]. Nestal Machinery (Devens, Mass., USA) all-electric 132-ton Elion series molds PC/ABS cellphone shell halves. Arburg Inc. (Newington, Conn., USA) and Engel Canada Inc. (Guelph, Ontario, Canada) introduced machines for injection comolding of nylon and *liquid silicone rubber* (LSR), a thermosetting synthetic rubber. Arburg has an Allrounder 570C injection molding machine and an Engel tiebarless Victory injection molding machine. Engel's Duo Combo CS system combines injection-compression with a rotary stack mold.

Principal injection-molded parts considerations that influence processing conditions, machinery, and mold design include wall thickness, parting line and ejection, appearance, ribs, boss designs, holes and depressions, and corners, radii, and fillets [5].

Computer controls for injection molding monitor the viscosity, temperature, and pressure. Many important injection molding technology advances with computer software come from universities. Cornell Injection Molding Program (CIMP) at Cornell University [6] has about 30 software programs for injection molding such as its TM series, which includes mold-filling analyses and capillary-rheometer viscosity. The University of Massachusetts-Lowell, Plastics Engineering Department [7] software includes AutoCAD, Cadkey, Pro/Engineer, and SolidWorks. The University's CAE program funded by Moldflow is linked to state-of-the-art Ferromatik Milacron injection molding machines, which include all-electric models. Moldflow software is applied to molding processes and manufacturing. Ferromatik Milacron North America (Batavia, Ohio, USA) controls can be "wired" from the plant to other machines and to all departments in the company and globally. The company's XTREEM Control was the first PC-based control to be developed for the plastics processing industry and

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[1] C. Rauwendaal, ed., *Polymer Extrusion*, 2d ed., Hanser Publishers, Munich, Germany, 1990.

plastics processing equipment, according to the company. It provides real-time controls in milliseconds. The company's Moldwatcher complements its XTREEM. The University of Massachusetts-Lowell, Plastics Engineering Department, has HPM, Battenfeld, and other injection molding models.

The University of Massachusetts-Amherst [8] polymer and plastics research facilities include the Silvio O. Conte National Center for Polymer Research and the Polymer Science and Engineering Department with (1) a Center for UMassachusetts/Industry Research on Polymers (CUMIRP) which links industry and government agencies, established by the National Science Foundation, and (2) a Materials Research Science and Engineering Center sponsored by the National Science Foundation.

Virginia Tech has (1) a National Science Foundation, Science and Technology Center for High Performance Polymers, Adhesives, and Composites and (2) a Polymer Materials and Interface Laboratory [9].

Injection molding processes using Stat-Ease Inc. response surface methods for process optimization are developed with *design of experiments* (DOE) and a *multifactor linear constant* (MLC) [10].

Injection molding pressure is determined by the hydraulic pressure, hydraulic cylinder area, and plasticating screw cross-sectional area [3]

$$P_i = P_h\left(\frac{A_h}{A_s}\right)$$

where P_i = injection pressure, MPa (psi)
P_h = hydraulic pressure, MPa (psi)
A_h = area of hydraulic cylinder, mm^3 (in^3)
A_s = cross-sectional area of screw, mm^3 (in^3)

The injection molding clamp force is directly proportional to the projected area of the part, or to the empirical pressure or viscosity factor. Clamp force can be related to melt flow length and part thickness [3] by

$$F_c = f_\eta A$$

where F_c = clamp force, N (tons)
f_η = empirical pressure of viscosity factor
A = projected area of part, cm^2 (in^2)

When actual or estimated peak cavity pressure $P_{\max}$ is used,

$$F_c = P_{\max}A$$

When clamp force is a function of melt flow length and part thickness,

$$F_c = \frac{L}{H}$$

where L = melt flow length, cm (in)
H = part thickness, cm (in)

Injection-molded polycarbonate sheet for car windows requires injection molding thin-wall large panes up to 11 ft^2 with minimum molded-in stress. They can be injection-compression-molded, with overmolded frames, and removed by a press-mounted six-axis articulating robot [11].

The complexity of injection molding equipment is illustrated with the choice of nonreturn valves which prevent flow of melt back to the screw. There are two basic types: ball check, and ring check, and their variations. Valve selection extends further, to include general-purpose three-piece, four-piece, and five-piece valves; free-flow valves; castle valves; smear valves; and spring (poppet) valves [12].

Mold Design

Mold design affects process productivity and product quality. A good example is improvement of a product's mechanical properties, such as impact strength, by locating gates and weld lines away from high-impact areas [5]. The effect of mold design on product and process quality begins with the runners. Fluent Inc. FIDAP fluid dynamics software, a *computational fluid dynamics* (CFD) package, is used for analysis of melt flow through runners[13]; runner design contributes to product quality and process economics [14, 15]. Runner diameter contributes to smooth flow through the gates and into the mold cavity, and the runner diameter directly connected to the mold cavity is typically the same as the wall thickness. The diameter of upstream runners depends on the number of branches. To calculate the diameter of upstream branches [3], use

$$D_{\text{br}} = n^{1/3} D$$

Where D_{br} = diameter of upstream branches, mm (in)
n = number of runner branches
D = diameter of runner connected to cavity, mm (in)

Thermoforming

Principal thermoforming factors contributing to finished-product quality are the use of right temperature settings, and vacuum or pressure uniformity and gradients. Heating can be uniformly or unevenly distributed, according to the part's configuration and wall thicknesses, by convection, radiation, or conduction. The temperature profile is determined by the part's configuration. Thin-gage and heavy-gage thermoforming includes vacuum and pressure forming, predraw stretching, slip forming, and twin sheet forming. The stretch ratio and depth-of-draw ratio also influence product quality and process economics. Stretch ratio is the initial film or sheet gage, divided by wall thickness of the thermoformed product. Depth-of-draw ratio is the maximum depth of the thermoformed part, divided by the minimum part width.

Low-volume production of building panels, automotive body panels, and bumpers is thermoformed from engineering thermoplastics. ABS, polycarbonate, polycarbonate/ABS, polyamide, and polyesters are thermoformed into in-mold decorating films which are robotically placed into an injection molding mold. The substrate is back-molded onto the film.

Blow Molding

Engineering thermoplastic blowmolding developments are gaining, such as the three-dimensional blow-molded automotive coolant ducting, and higher-MW, higher-melt-strength PPS for parison formation [16].

With more blow molding applications being introduced, the blow molding engineering thermoplastics capability becomes more important, and the R^* index is a rating for blow molding processing capability. High R^* indicates that melt flows more easily through the extruder and still maintains a high enough melt strength during parison formation where there is no shear. Shear thinning, which occurs during extrusion blow molding, differs from shear thinning behavior for other melt processes. Shear is generated only when there is a sliding action between a metal surface such as the plasticating screw and the melt flow [5].

Assembly

Assembly methods include in-mold assembly [5] and

1. Welding
2. Press-fits
3. Snap-fits
4. Heat staking
5. Cements and adhesives
6. Mechanical fastening

Welding methods include

1. Spin
2. Inertia
3. Ultrasonic

4. Vibration
5. Hot plate
6. Laser
7. Electromagnetic
8. Hot bar and impulse (for films)
9. Radio frequency
10. Infrared
11. Induction

plus variations of these welding methods and joint designs [17].

Press-fitting a metal shaft into the hollow core of a rigid tube or hub has a variety of assembly applications. Key cautions include

1. Very close tolerance between shaft outer diameter and hub inner diameter, with sufficient but not excessive holding force
2. Long-term stress or loading value, such as 14 MPa for polycarbonate
3. Dimensional strength
4. Maximum allowable hoop stress
5. Diametric interference

There are three types of snap-fits:

1. Cantilever, which is the most common
2. Torsional
3. Annular

Snap-fits are injection-molded into the two components of the assembly. Two general heat staking methods are low profile and high profile. Methods of the two types include spherical, flush, hollow, and knurled. In addition, there are cements and adhesives, and a mechanical fastening assembly. Whatever assembly method is used, the choice is usually made at the design stage.

Trends

Processing is dedicated to two objectives, quality and productivity; and trends improving these objectives are as follows:

1. Flexibility and versatility by using modular retrofitting, hybrid process technologies, voice-activated controls, and artificial intelligence for

"smart" controls that change temperatures and pressures and their gradients automatically. Band heaters "talk" to adjacent band heaters.

2. Increased use of automation and floor or overhead crane-guided robots.
3. Process integration. Vertical integration is gradually being recognized for improved quality and process economics. Injection molders are integrating vertically with in-line compounding and molding. An injection molder can compound, in-mold decorate (IMD), and in-mold assemble (IMA). A processor can integrate horizontally by offering extrusion, injection molding, thermoforming, and blow molding.
4. On-site dedicated injection molding plants located at automotive, appliance, and furniture assembly plants contribute to finished-product quality and lower finished-product costs.

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17. TWI Ltd., operating company of The Welding Institute, Great Abington (near Cambridge), UK. Associate organizations (partial list): Edison Welding Institute, Columbus, Ohio, USA; UK Dodwell Ltd., Taitori-ku Tokyo, Japan; Kumdong Industries Corporation, Pusan, South Korea.
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Part

2

Engineering Plastics

Chapter 5

Polyacetals*

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Introduction

Polyacetals, also referred to as *polyoxymethylenes* (POMs) or polyformaldehydes, are a semicrystalline engineering thermoplastic polymerized as a homopolymer and copolymer. The homopolymer and copolymer have somewhat different molecular structures and performance values. The difference between performance values is narrowing with new formulations (compounds). Polyacetal engineering thermoplastics were introduced to the world in 1956 with the potential of replacing metals, aluminum, brass, and cast zinc, which polyacetals continue to do.

Primary polyacetal resin producers, custom compounders, and distributors are shown in Table 5.1.

The Asahi Kasai Corporation (50%) and DuPont China Holding Company (50%) joint venture produces acetal copolymer at Zhangjiagang, Jiangsu Province, People's Republic of China, to sell jointly in China and separately outside China. Mitsubishi Gas Company produces acetal copolymer in south Korea, Japan, and Thailand. PTM Engineering

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*The chapter author, editors, publisher, and companies referred to are not responsible for the use or accuracy of information in this chapter, such as property data, processing parameters, and applications.

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TABLE 5.1 Primary Polyacetal Resin Producers, Custom Compounders, and Distributors

Company	Material or product
Primary resin producers (also compounding)	
Asahi Kasei Osaka, Japan	Tenac® acetal homopolymer Tenac®C acetal copolymer Lynex®T acetal copolymer conductive grades
BASF Ludwigshafen, Germany Florham Park, N.J., USA	Ultraform® acetal copolymer
DuPont Engineering Plastics Wilmington, Del., USA	Delrin® acetal homopolymer, copolymer
Formosa Plastics Corp. of Taiwan Part of Formosa Group Taipei, Taiwan Livingston, N.J., USA	Formosacon® acetal copolymer
Kolon Industries Toray and Kolon, codevelopers Acetal Copolymers Kwacheon-city, Kyunggi-do Korea (Rep.)	Kolon Kocetal® acetal copolymer High heat stability
KTP (Kisan), joint venture of Toray and Kolon, codevelopers of acetal copolymers Kimchon-City, Gyungsanbuk-Do Korea (Rep.)	Amilus® acetal copolymer, marketed by Toray in North America, Europe High heat stability
Korea Engineering Plastics Seoul, Korea (Rep.)	Kepital® acetal copolymer
LG Chem Seoul, Korea (Rep.)	Lucel®, Lucet® acetal homopolymer, copolymer
Mitsubishi Gas Chemical (Mitsubishi Engineering Plastics) Marunouchi, Chiyoda-ku, Tokyo, Japan	Lupital® acetal copolymer
Polyplastics, joint venture of Ticona and Daicel Chemical Inds. 2-chome, Minato-ku, Tokyo, Japan	Duracon® acetal copolymer
PTM Engineering Plastics (Nantong) Joint venture of Polyplastics, Ticona, Mitsubishi Gas Chemical, and Korea Engineering Plastics Nantong Municipality Jiangsu Province, PROC	Acetal copolymer, production started February 2005
Ticona GmbH (a Celanese AG business) Kelsterbach, Frankfurt, Germany (owned by Blackstone Capital Partners)	Celcon®, Hostaform®, Duracon® acetal copolymer

TABLE 5.1 Primary Polyacetal Resin Producers, Custom Compounders, and Distributors (*Continued*)

Company	Material or product
Custom compounders	
Ashley Polymers Compounder, Distributor Brooklyn, N.Y., USA	Polyacetals, other engineering plastics
Chem Polymers, unit of Teknor Apex Fort Myers, Fla., USA	Formax® acetal copolymer
LNP, a business of GE Adanced Materials Exton, Pa., USA	Thermocomp® polyacetals, other engineering thermoplastics
Network Polymers & Diamond Polymers, subsidiary Akron, Ohio, USA	Kepital® acetal copolymers
PolyOne Cleveland, Avon Lake Ohio, USA	Lubri-Tech® wear-resistant, Stat-Con ESD, EMI shielding, Edgetech® acetal homopolymer, copolymer
RTP Winona, Minn., USA	RTP 800 Series acetal homopolymer, copolymer
Techmer Lehvoss Compounds, Joint Venture of Techmer PM and Lehvoss Lehman & Voss in Germany (Plaslube® was sold by DSM in September 2004) Clinton, Tenn., USA	Plaslube® lubricated engineering plastics including polyacetals
Distributors	
API—Kolon Advanced Plastics Inc. is a U.S. distributor for Kolon Inds.	Kocetal® acetal copolymer
Albis Plastics GmbH Hamburg, Germany Rosenberg, Tex., USA Albis Plastics resin distributing business acquired by Ashland Distribution Co. in spring 2005	Distributor, compounder
China (HK) Chemical & Plastics Co. Ltd., subsidiary of New Universe Holdings, Hong Kong Kowloon, Hong Kong, China	
K-Mac Wyoming Wyoming, Mich., USA	Macetal® acetal homopolymer, copolymer primary resins, sheet, rod, tube

Plastics (Nantong) Co. Ltd. is a joint venture of Polyplastics Co. Ltd. and Ticona GMBH and Mitsubishi Gas Chemical Co. Inc. and Korea Engineering Plastics Co. Ltd. PTM Engineering Plastics (Nantong) is located in Nantong municipality, a part of the Yangtze River Delta economic circle across the Yangtze River including Shanghai. Originally scheduled to go onstream in April 2005, it started up its 60,000 Mtons/yr capacity acetal copolymer plant in February 2005 due to the increasing demand for acetal copolymer in China, which is 150,000 Mtons/yr and gaining more than 10% per year.

Chemistry of Acetal Polymerization

Acetal homopolymers are polymerized from purified anhydrous formaldehyde. Acetal copolymers are copolymerized from cyclic 1,3,5-trioxane cyclic trimer ($C_3H_6O_3$) of formaldehyde, typically with a cyclic ether comonomer such as ethylene oxide [1]. Ethylene glycol is the product of hydrolysis of ethylene oxide.

Formaldehyde is the building block for polyacetal resins. Therefore it is valuable to examine first the attributes of this simplest of all aldehydes. Formaldehyde (CH_2O) is a highly reactive, colorless, flammable, noxious, pungent-smelling gas; yet it provides many diverse benefits to society. It is produced by oxidation of a mixture of methanol vapor and air (oxygen), by passing the mixture over a catalyst such as metal oxide, silver, or copper catalyst. It can be produced by oxidizing natural gas [2]. Its boiling temperature is –21°C (–5.8°F) and melting temperature is –92°C (–139°F) [2]. In a gaseous state, formaldehyde polymerizes to paraformaldehyde solid, used to fumigate rooms [2]. Purified formaldehyde is produced by conversion to cyclohexyl hemiformaldehyde and partial condensation. Formaldehyde gas readily dissolves in water, and it is used commercially in a range from 28% to 56% aqueous solution with 1% to 15% methanol added as a stabilizer to prevent polymerization [3]. The solution is called formalin or formol. Methanol (methyl alcohol) increases formaldehyde solubility and keeps oligomers from growing [3]. In low concentrations, formaldehyde monomer reacts with water and methanol to form long-chain oligomers, poly(oxymethylene glycols) [$HO(CH_2O)_nH$] in aqueous solution, and poly(oxymethylene) hemiformals [$H_3CO(CH_2O)_nH$] in methanol solutions [4]. It is soluble in alcohols, acetones, ethers, and benzene. Because formaldehyde is oxidized by exposure to air (oxygen) to form formic acid, solutions of formaldehyde are kept in tightly sealed containers during storage to prevent oxidation to formic acid.

Most formaldehyde is used to make polymeric resins. It is copolymerized into melamine formaldehyde, urea formaldehyde, and phenol formaldehyde, which are among the earliest commercial thermosetting resins. It is used in the manufacture of pentaerythritol and other polyols, raw materials for polyurethanes and alkyds; disinfectants, antiseptics, fungicides, germicides, and preservatives in medical laboratories and embalming fluids; and deodorizers, dyes, fertilizers, and corrosion inhibitors in the metal industry.

The U.S. Occupational Safety and Health Administration (OSHA), Department of Labor, states that “Formaldehyde is a sensitizing agent that can cause an immune system response upon initial exposure" and cites adverse health conditions associated with formaldehyde. According to OSHA, "The OSHA standard that protects workers exposed to formaldehyde, *Title 29 of the Code of Federal Regulations (CFR) Part 1910.1048* and equivalent regulations in US States, with OSHA approved State Plans, apply to all occupational exposures to formaldehyde gas, its solutions and materials that release formaldehyde."

Synthesis of polyacetal resins

Formaldehyde is a strong electrophile, allowing acetal to polymerize by nucleophilic, anionic, or cationic addition of an alcohol to ketene carbonyl groups. Relatively weak bases such as pyridine initiate anionic addition polymerization; cationic addition polymerization is catalyzed by strong acids. When the cyclic trimer trioxane is used as a copolymer to polymerize acetal copolymers, Lewis acids such as boron trifluoride promote copolymerization. A more fundamental description is polymerization of an aldehyde or ketone + alcohol + an acid or base catalyst to form hemiacetal, which further converts to acetal. The hemiacetal reaction is reversible to aldehyde and alcohol.

$$\text{Hemiacetal} + \text{alcohol} + \text{catalyst} \Leftrightarrow \text{acetal} + \text{water}$$

Chain growth polymerization produces linear polyacetal macromolecules. Polyacetal resin is a clear, flammable, volatile, highly crystalline liquid with the repeating units

$$—(\mathrm{CH_2}—\mathrm{O})_x— \qquad —[—(\mathrm{CH_2}—\mathrm{O})_a— \backslash\backslash\backslash —(\mathrm{CH_2CH_2O})_b—]_y—$$

Acetal homopolymer Acetal copolymer

Acetal homopolymer has a T_m of about 175°C (347°F) and specific gravity of 1.41 g/cc; acetal copolymer has a T_m of about 165°C (329°F) and specific gravity of 1.42 [5]. Acetal polymers are synthesized entirely from formaldehyde directly, as noted earlier, or by copolymerization of the formaldehyde cyclic trimer (cyclic oligomer) trioxane and cyclic ethers.

Commercial polymerization of acetal homopolymer starts with anhydrous formaldehyde monomer from formaldehyde solution. Water is evaporated from the aqueous solution, forming paraformaldehyde, polyoxymethylene, and hemiformal, which are purified and thermally decomposed to form anhydrous formaldehyde [6]. Methanol and formic acid are removed, either by freeze-trapping at a temperature just above the boiling temperature of formaldehyde or by washing with a nonvolatile polyol [6]. The anhydrous formaldehyde is fed into a reactor containing the inert hydrocarbon solvent, initiator, and dispersant, where the formaldehyde is slightly soluble [5, 6]. Polyacetal is the simplest polyether molecule. Acetal homopolymer is composed of repeating oxymethylene linkages (—OCH_2—). Amine initiator (or other initiators) and chain-transfer agent are added into the reactor. Transfer agent and chain termination agents control MW; and polymerization is terminated by stopping the formaldehyde monomer flow [6]. During the exothermic reaction, solvent evaporates, pulling the reaction to end-capped polyacetal, which precipitates and is removed [5]. Precipitated solid acetal homopolymer, separated by filtration and centrifuging, is slurried with sodium acetate and acetic anhydride catalysts. By this process, the chain produced from ketones or aldehydes plus alcohols is end-capped with acetyl groups —(—O—C—O—). Chain ends are stabilized with acetic anhydride and then refluxed to form the acetyl groups [6]. The acetal homopolymer is washed and dried.

When the acetal copolymer is produced, trioxane is first produced by acidification of aqueous formaldehyde and distillation. The cyclic trimer 1,3,5-trioxane, (Fig. 5.1) which is formed, is crystallized or extracted and removed from the distillate [6]. Further fractional distillation purifies the cyclic trimer, which is copolymerized with a cyclic ether [6]. Trioxane is produced by distillation in an aqueous solution in the presence of *p*-toluene sulfuric acid catalyst. Trioxane is also known as 1,3,5-trioxane, 1,3,5-trioxacyclohexane, metaformaldehyde, *s*-trioxane, *s*-trixane, sym-trioxane, trioxymethylene, triformal, aldeform, and other names [22]. It is a colorless, toxic, highly flammable crystalline solid with a chloroformlike odor. Although trioxane is stable, over time it can gradually sublime to toxic formaldehyde gas. Besides the interest in it as a copolymer in acetal copolymer and its use in organic chemical syntheses, trioxane is used in a number of very different applications, such as a disinfectant and solid fuel bars for activities like camping [alternative to sterno (alcohol) canned fuel and esbit tablets].

Structure of the trioxane molecule is as follows:

Methanol → Formaldehyde → Additives, stabilizers →
→ Reinforcements → Acetal homopolymer
Methanol → Formaldehyde → Trioxane comonomer →

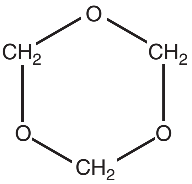

Figure 5.1 1,3,5-trioxane. (*From BASF.*)

Cyclic ether comonomer → Additives, stabilizers →
Reinforcements → Acetal copolymer

There are a variety of different process plant designs used by polyacetal producers [1, 6]. Polyacetal resins are typically compound-extruded with property enhancers (additives) added during extrusion. The extrudate is water-quenched and pelletized. A state-of-the-art process can in-line extrude and injection-mold, using robotics and automation. Otherwise, the pelletized polyacetal is stored.

Research at the University of Colorado investigates the behavior of the six-member acetal ring. Research includes study of five- and six-member acetal ring structures—cyclic acetals—such as cyclic acetal (meth)acrylate, ethyl cyclic acetal acrylate, cyclic acetal carbamate (OCN) acrylate, cyclic acetal carbamate (OCN) methacrylate, and polymerizations [7]. Copolymerization of the trioxane comonomer, the cyclic trimer of formaldehyde, and cyclic ether comonomer yields acetal copolymers. Boron trifluoride dibutyl etherate [$BF_3(Bu)_2O$] or other cationic initiators plus 2% ethylene oxide to form a Bronsted acid start the copolymerization. Early research at Celanese [23] found that *p*-chlorophenyldiazonium hexafluorophosphate and *p*-chlorophenyldiazonium hexafluoroarsenate showed superior performance as catalysts compared to $BF_3(Bu)_2O$ for cationic polymerization and copolymerization of trioxane. Acetal copolymerization is achieved by ring-opening the six-member ring trioxane [5]. In a commercial process, molten trioxane + the second comonomer + initiator + chain transfer agent (optional) copolymerizes in bulk to produce acetal copolymer [5].When comonomers such as trioxane, dioxolane, and ethylene glycol are used, a stable end cap forms [5].

Other acetals are polymerized from aldehydes plus alcohols. Polyvinylacetal, polymerized from an aldheyde plus polyvinylalcohol, is used to make coatings, films, adhesives, and lacquer.

Products and Design

Products

Polyacetal products are listed in Table 5.2.

Also included are a variety of kitchenware and household consumer products such as stain-resistant cutting boards and soap dispensers. Polyacetal products can be molded into precision components.

Polyacetals are used increasingly for electronic, appliance, automotive, industrial, plumbing, construction, pneumatic, and consumer products. They are used for plumbing applications in hot water above 82.2°C (180°F) and in hot air applications above 107°C (225°F). The copolymer has higher continuous-use temperatures in both water and air, and 30% carbon fiber-reinforced polyacetals are molded into bearings, cams, and gears.

TABLE 5.2 Polyacetal Products

Actuators
Aerosol valves
AVD (audio video data) cassette components

Bearings, e.g., ball bearings, ring bearings
Body trim clips (automotive)
Bushings

Cams
Casters
Clips
Coffeemaker housings
Coffee spigots
Conveyor belt links, slats, slides, ways
Couplings to connect tubing

Disposable lighter bodies
Door handle components
Dowel pins

Electrical insulators

Fan blades and shrouds
Fasteners
Filter bodies
Fuel cell components, e.g., fuel delivery pumps and valves, piping
Fuel system components
  Carburetor floats
  Fuel pump components and valves
  Gas tank caps
  Gas tank floats
  Piping

Garden and lawn sprinkler housings
Gears

Handheld IT devices, e.g., cell phones
  On/off buttons, battery access
Headrest guides
Heater and air conditioner components
Hooks

Impellers
Interference fits

Keypads
Kitchenware, mixing bowls, food processor parts

Linkages for machinery
Lock mechanisms
Luggage rack hardware
Lugs

Machinery components for agricultural, textile goods
Machinery linkages and couplings
Milk pumps

Nuts

Paint sprayer housings
Pen cases, barrels
Plumbing components: fittings, pump impellers, shutoff and mixing valves, valve stems, tees, elbows, couplings, water filter housings, irrigation system parts; faucet cartridges, toilet flush valves, ball cocks, showerheads

TABLE 5.2 Polyacetal Products (*Continued*)

Pulley wheels

Radiator caps
Refrigerator bin and shelf parts
Rollers

Seat belt components, e.g., buckles, retractor covers, release buttons
Seat levers
Self-tapping screws
Sensor housings
Shaver cartridges, handles
Ski boot bindings
Slide guides for bureau and desk drawers
Snap-fit components
Soft-touch applications
Spacers
Speaker grills
Spring levers
Sprockets
Steering column components
Sun visor brackets
Switches, electrical

Tea kettles, electric
Telephone components
Tennis racket handles
Trim clips
Turn signal handles, cruise control handles
Toys

Valves, hydraulic, pneumatic, e.g., rollover gas shutoff valves

Washers
Water jugs
Window brackets, cranks, guide strips, support brackets
Windshield wiper blade holders, bezels, pivots
Windsurfing board frames

Zippers

Improved paint adhesion on an acetal homopolymer substrate is supplied by DuPont Engineering Polymers. The substrate is composed of 90 to 99.5% Delrin® and 0.5 to 10% of another semicrystalline or amorphous thermoplastic. Typically, polyacetal does not readily adhere to other plastics. The painted polyacetal composition has good physical and mechanical property retention according to the company. In 2003 the company introduced DuPont™ Delrin® Decorating Solutions for painted and metallized (electroplated) homopolymers which consist of Delrin® ES Etching Solution, coatings, and application technology. Delrin® ES technology prepares the molded product surface for coating or metallizing. Shipley Company, a subsidiary of Rohm and Haas Company, has licensed the manufacturing process for Delrin® Etch etching solution from DuPont [8]. The DuPont painting and plating technology includes specially developed Delrin® grades, Delrin® ES, Cromax®, Centari® 6000, and Aqua Decosoft®.

The company's structural bonding technology combines two resin melts in the mold, such as acetal homopolymer and HDPE, on either side of a thin nonwoven microporous fabric veil which serves as a tie layer. The polyacetal and HDPE penetrate the veil. It is used for molding a fuel tank component and is being developed for soft-touch applications.

DuPont Delrin® 560HD resists hot diesel fuel better than standard grades according to the company. The 560HD meets the requirements of newer low-emissions technology which pressurizes the diesel fuel and raises its temperature. The homopolymer has minimum swelling when it is immersed in automotive fuels; a good combination of stiffness, toughness, and strength; and low fuel vapor permeation. DuPont introduced homopolymer Delrin® 460E, 1260E; and Delrin® copolymer with lower *volatile organic compounds* (VOCs) and odor.

DuPont Engineering Polymer's self-lubricating Delrin® KM reinforced with chopped Kelvin® aramid fiber for beverage bottle conveyor belts has extra high abrasion resistance and durability [11].

Ticona Celcon® (sold in the Americas) and Duracon® (sold in Asia) and Hostaform® (sold in Europe) acetal copolymer resins and compounds have been introduced for the increasing use of laser-markable, UV, and conductive products.

Ticona Hostaform® acetal copolymer was overmolded with *styrene-ethylene/butylene-styrene* (SEBS) *thermoplastic elastomer* (TPE), which had an adhesive strength at the interface between polyacetal and TPE better than the tear strength of the TPE [10].

BASF Performance Products' Ultraform® acetal copolymer applications have been extended to household and kitchenware such as coffeemaker housings because of the copolymer's moldability and resistance to the acids, essential oils, fats, and more than 700 different aromatic chemicals to which the copolymer is exposed [9].

New acetal homopolymer and copolymer compounds are supplied by PennFibre Plastics. Homopolymer compounds are for decorating applications, painting, and printing on injection-molded products. PennFibre Plastics, a division of Ensinger, supplies high-temperature extruded, cast, and pressed semifinished and finished stock shapes, including engineering thermoplastic sheet, strips, coil, plates, rods, disks, heavy and thin wall tubes, plain punched parts, rings, washers, bushings, insulators, standoffs, and custom shapes. Rolls range from 0.025 to 0.625 cm (0.01 to 0.250 in) thick and 125 cm (50 in) wide and strip down to 0.625 cm for stamping. These include fabric backing for gluing and laminate finish types. Copolymer glass-fiber-reinforced composites have been introduced with higher strength-to-weight ratios and a wider range of mechanical properties. The company's portfolio of engineering thermoplastic compounds includes Polypenco® polyacetals, Tecaform®AH polyacetal copolymer, and Tecaform®polyacetal homopolymer. Also in Ensinger's stable are Tecamid and Tecast polyamides, Tecanat® polycabonate, Tecaran™ ABS and Tecanyl® modified PPE, TPI, PAEK, PPS, PEI, and PSU.

Compounder RTP Company adds perfluoropolyether (PFPE) modifier, an internal lubricant system, to increase the wear resistance of polyacetal and nylon. Typically, less than 1% PFPE loading is adequate, and in some polyacetal wear-resistant applications, less than 1% PFPE performs similar to 15 to 20% PTFE, according to RTP. According to the company, other advantages of PFPE are that it (1) eliminates plate-out associated with PTFE; (2) improves fatigue resistance, especially for gears; (3) improves processing by enhancing melt flow, which increases throughput; and (4) serves as an internal mold release agent. The PFPE modifier meets USP Plastics Class VI requirements, and it is NAMSA-tested for use in medical devices and tubing. Besides gears and clean-room applications, PFPE modified polyacetal compounds are used for automotive weatherstripping, airbag doors, seals, and bushings [13].

When 2% silicone is added to acetal copolymer, as an internal lubricant, the compound has good rigidity and toughness, creep resistance, low coefficient of friction, and resistance to most solvents; but it also has disadvantages associated with unmodified acetal copolymer, high mold shrinkage, and poor resistance to UV radiation [14]. Typical thermal properties for 2% silicone lubricated acetal copolymer include T_m of 190 to 210°C (374 to 410°F), maximum service temperature of 90°C (194°F), deflection temperature under load (DTUL)/1.82 MPa of 110°C (230°F), mold temperature of 60 to 120°C (140 to 248°F); and flammability UL_{94} HB. Typical applications include gears, bearings and bearing bushings, sprockets, conveyor belt components, drive chains, snap-fit parts, pulley wheels, and spring studs [14].

Acetal homopolymer with PTFE lubricant shows good solvent resistance typical of standard-grade homopolymer, good hydrolytic stability, and lower coefficient of friction than unmodified grades. Disadvantages include poor resistance to UV radiation, acids, and bases; and lower stiffness, toughness, and strength properties compared with unmodified acetal homopolymer [12]. Thermal properties include a T_m of 210 to 230°C (410 to 446°F), maximum service temperature of 90°C (194°F), DTUL/1.82 MPa of 118°C (244°F), mold temperature of 70 to 110°C (158 to 230°F); and flammability UL_{94} HB [12].

TiO_2-filled, UV-resistant polyacetal compounds are used for outdoor consumer products such as ski boot bindings, tennis racket handles, windsurfing board frames, and toys.

On a different front, Quadrant Engineering Plastics Products manufactures plastic stock shapes—plate, sheet, rod, and tube [15]. The company's Ertacetal® colored extruded polyacetal stock shapes advance precolored polyacetal applications. Advantages include color consistency and accuracy, brand recognition, reduced lead time for delivery to customers, and simplified color coding according to the company [15]. Color coding has several benefits; it allows multiple-component assemblies to be accurately changed out or replaced, which can avoid the possibility of mistakes in assembly; saves time; facilitates inspection of assemblies; and improves safety [15]. The precolored stock shapes meet FDA regulation 21 CFR Section 177.2470(e)(1),(2). They are supplied in the three primary colors (red, yellow, and blue) as well as in orange, green, brown, and gray, beyond black and white [15]. Polyacetals are supplied in all standard colors, custom colors, and natural, which is a translucent white. When processors use color concentrates from colorant suppliers other than the polyacetal supplier, they should check compatibility with their resin supplier. The stock shapes have all the attributes of polyacetals, which include low coefficient of friction, abrasion resistance, hardness, stiffness, and solvent resistance [15].

Design

Software for product and process design is available to any company, with prices aimed at processors, independent design firms, and the entire plastics industry; and polyacetal resin companies are contributing to this movement. Ticona's P-GEAR (Plastic Gear Evaluation And Research) tester software optimizes gear designs based on service temperatures, moisture pickup, and other ambient environmental conditions. The software is used specifically to evaluate plastics for gears in various service environments, according to the company [10]. P-GEAR predicts gear performance more accurately, and this results in faster design time according to Ticona [10].

Polyacetal design can use design software referred to in Chap. 2 of this handbook. These programs are CAD, CAE, FEA, and FEM (finite element modeling), MES (manufacturing execution systems), "Superflow" CAD-like program, ABAQUS Standard®, DesignXplorer VT, ANSYS Paramesh™, I-DEAS, Unigraphic Solutions, CAPTIA, Pro/Engineer, and the NISA family of FEA software. Moldflow Plastics Insight® MPI 5.0 software includes three-dimensional simulation for part and mold design and analysis for thin-wall designs and warpage.

Design for polyacetal resins follows conventional methods, generally based on short-term properties with a safety factor. There are certain design considerations that are more important with polyacetal resins than with some other engineering thermoplastics. These considerations are largely due to the high degree of crystallinity of acetal polymeric macromolecules. Polyacetals are notch-sensitive as a result of their high *degree of crystallinity* (DC). Radii and fillets at wall corners, ribs, and bosses should be generous (not too generous) to avoid internal stress concentrations during cooling in the mold. Wall thickness can be from about 0.5 mm (0.02 in) minimum up to 5 mm (0.2 in). Polyacetal resins freeze rapidly during mold cooling, and the polymers are stiff and strong, allowing thin walls. The cost advantages of thin walls with polyacetal resins are faster cycles and less resin consumption than for polymers that require thicker walls. Thin-wall molding, with judicious processing, can avoid or at least minimize voids and sink marks. High DC causes greater mold shrinkage during cooling than other engineering thermoplastics with less DC; and mold shrinkage, based on millimeters per millimeter (mm/mm) or inches per inch (in/in) or percent of melt volume, is not exactly the same in thick walls and thin. Uneven mold shrinkage will cause internal stresses during molding, which leads to warpage and product malfunction or failure. Mold shrinkage is very complex, primarily due to the cooling rate of the melt in the mold cavity. Thicker walls cool slower than thin walls, and thicker walls have greater mold shrinkage than do thin walls. Mold shrinkage is affected by packing, the compound recipe, fiber reinforcements, fillers, and additives. Postmolding shrinkage can continue due to the ambient environment, especially elevated temperature and humidity. The opportunity to thin-wall mold polyacetal resins brings with it a critical requirement to strive for uniform wall thickness in the part, or design gradual tapering from thick wall to thin wall, and avoid abrupt transition between wall thickness differences. The draft angle for any thermoplastic significantly affects ease of demolding. For polyacetal resins, a minimum draft angle of 0.5°, preferably 1°, has been suggested.

Properties

Polyacetals are distinguished from other engineering thermoplastics by the combined properties listed in Table 5.3.

Typical resins, compounds, and composites are listed in Table 5.4.

ASTM standard specifications are ASTM D-4181 and DIS 99881,2, "Standard Specification for Acetals (POM) Molding and Extrusion Materials." DIS is Draft International Standard, which provides a more cost-effective electronic system; D-6100 is "Acetal Stock" and D-1855-00 is "Standard Specification for Polyoxymethylene (Acetal) for Medical Applications—Medical Devices, Instrumentation or Components Thereof," developed by ASTM Subcommittee F04.11.

Advances in compounding formulations and reinforcing technologies narrow the differences in properties between acetal homopolymers and copolymers. Toughness, for example, is increased by adding an elastomer. Glass fiber reinforcement increases polyacetal tensile strength, modulus, and hardness, and reduces CTE, creep resistance, and mold shrinkage.

TABLE 5.3 Typical Properties of Polyacetals

Abrasion and wear resistance
Low coefficient of friction
Low moisture absorption
Stiffness, rigidity (flexural modulus)
Hardness
Dimensional stability
Creep resistance
Stress crack resistance
Impact-resistant
Dynamic fatigue-resistant
Fuel (gasoline, diesel, oxygenated) resistance
Water resistance
Solvent, chemical resistance to oil, grease, dilute acid, alkalies, detergents (not phenols). Attacked by acids, bases in solution
Property retention at elevated temperatures
Relatively low smoke (particulate) emissions
High T_m
High gloss
FDA, NSF, USDA, EU compliant grades
FDA-compliant grades for repeated food contact to 121°C (250°F)
Excellent machinability of rod and slab with conventional brass turning lathes, cutting tools

Acetal homopolymer and copolymer property values are relatively different for many properties, as shown in Table 5.5. Both polyacetals possess hardness, toughness, stiffness, abrasion, and wear resistance and resistance to many of the same chemicals, and they compete for many of the same applications. These properties are largely due to the high degree of crystallinity of polyacetals. Acetal homopolymers generally have slightly better mechanical properties; the copolymer shows better oxidative and thermal stability. Unmodified acetal homopolymers generally show higher

TABLE 5.4 Typical Resins, Compounds, and Composites

Unreinforced
Impact-modified, unreinforced
Glass-fiber-reinforced, 10%, 20%, 25%, 30%
Glass-bead-reinforced and filled
Carbon-fiber-reinforced, 10%, 20%, 30%
Graphite-fiber-reinforced, 10%, 20%, 30%
Aramid-fiber-reinforced
Stainless-steel-reinforced, 7%, 10%
Mineral-reinforced (chemically coupled) and filled, e.g., 10% $CaCO_3$
Glass-fiber- and mineral-reinforced
PTFE (Teflon®) including powder, 5%, 10%, 15%, 20% lubricated
Silicone-filled, 2%
PTFE (18%) + silicone (2%)-filled
TiO_2-filled
Recycled

TABLE 5.5 Acetal Homopolymer and Copolymer Property Values*

Property	Homopolymer	Copolymer
Specific gravity, g/cc	1.41	1.41
Tensile strength, MPa (psi) 0.32 cm (0.125 in)	72 (10,500)	65 (9460)
Tensile modulus, GPa (psi)	3.0 (436,500)	2.5 (365,000)
Flexural strength, MPa (psi) 0.32 cm (0.125 in)	105 (15,275)	89† (13,000)
Flexural stress† at 5% strain		
Flexural modulus, GPa (psi) 0.32 cm (0.125 in)	3.0 (436,500)	2.6 (375,000)
Elongation at break, % 0.32 cm (0.125 in)	50	60
Shear strength, MPa (psi)	34 (5000)	53 (7700)
Impact strength, Izod notched, J/m (ft·lb/in)	90 (1.7)	80 (1.5)
Hardness, Rockwell M scale	95	85
Taber abrasion, mg/1000 cycles 1000-g load CS-17 wheel	12	14
DTUL/1.82 MPa (264 psi) °C (°F)	145 (293)	120 (248)
DTUL/0.45 MPa (66 psi) °C (°F)	180 (356)	160 (320)
Melt flow index, *g*/10 min	22	9
Water absorption, %		
Equilibrium at immersion	0.7	0.7
24-h room temperature	0.2	0.2
Flammability UL_{94}	HB	HB
Limiting oxygen index, %	18	16
UV radiation resistance	Poor	Poor
Other radiation resistance	Poor	Poor
Dielectric constant, 10^3 Hz	3.5	4.0
Dielectric strength, kV/mm (V/mil)	23	21
Volume resistivity, Ω·cm	10^{16}	10^{15}
Surface resistivity, Ω/sq	10^{17}	10^{15}
Dissipation factor (tan ∂), 10^3 Hz	0.0045	0.009+
Mold shrinkage, % Flow/transverse	2.0	

*Average typical properties (unmodified grades) at room temperature unless indicated otherwise.

†Values are generally based on ASTM D20 test methods, which usually show a range.

hardness, stiffness (rigidity), fatigue resistance, tensile strength, flexural strength, and creep resistance and lower percent of elongation. Higher-MW homopolymers can have higher toughness and percent of elongation. Modified acetal homopolymer compounds are formulated for resistance to hydrolysis at 82.2°C (180°F), similar to acetal copolymer hydrolysis resistance. Both polyacetals can be used for potable water applications at 82.2°C (180°F), and for repeated food contact at 121°C (250°F). Copolymers, having long-term heat stability, are used for continuous hot water exposure applications. Introduction of an ethylene link to produce acetal copolymers increases thermal stability and toughness elongation. Unmodified homopolymers and copolymer, are not resistant to UV and other forms of radiation, or to concentrated acids such as sulfuric acid (H_2SO_4) and hydrochloric acid (HCl).

Acetal copolymer resins have better long-term thermal stability, but heat stabilizers can be compounded into homopolymers to increase heat stability. Acetal copolymers have a UL electrical rating for 100°C (212°F) service, making the copolymers candidates for long-term electrical application service.

Polyacetal resin and compound suppliers recommend that customers switching between the acetal homopolymer and copolymer consult the producer, because there can be differences in processing and selective property considerations. Designers are involved in any polyacetal resin or compound switch, for property and mold shrinkage differences.

Copolymers have lower centerline porosity in extruded products, which enhances color uniformity and structural integrity, minimizes leakage of gases and liquids, and reduces or eliminates areas for bacterial growth [16]. With extrusion, porosity is caused by shrinkage during cooling when the skin cools faster than the core, resulting in porosity [16].

Chemical resistance (unmodified grades)

Polyacetals are resistant to aldehydes, ketones, alcohols, esters, fuels, lube oils, and hydraulic fluids. Both are attacked by oxidizing agents and strong acids, and both lose property levels when exposed to phenols and aniline at elevated temperatures over a long time (Table 5.6).

TABLE 5.6 Chemical Resistance of Polyacetals

	Homopolymer	Copolymer
Concentrated acids	Poor	Poor
Dilute acids	Good	Good
Alkalies	Good	Good
Aromatic hydrocarbons	Good	Good
Halogenated hydrocarbons	Fair	Fair
Halogens	Poor	Poor
Alcohols	Good	Good
Ketones	Good	Good
Aldehydes	Good	Good
Esters	Good	Good
Oils, grease	Good	Good

TABLE 5.7 Viscosity and Melt Flow Index of Polyacetals

Typical grades
General-purpose
High MW
High, medium, low viscosity
Low viscosity for injection molding
Higher viscosity for extrusion and high toughness
High, medium, low flow (MFI)
Wear and friction resistance
UV, light-stabilized, black, TIO_2
Low-warp (20%, 30% mineral)
Low plate-out
Conductive, ESD, EMI/RFI
Laser-markable
Medical grades
Enhanced crystallization

Polyacetals can be classified by viscosity or *melt flow index* (MFI). See Table 5.7. Higher viscosities are used for extrusion and blow-molded; higher-melt-strength, low-MFI terpolymers are thermoformed.

Polyacetal high-flow grades are fast-cycle injection-molded into thin-wall and complex parts in multicavity molds. High-viscosity grades are extruded into profiles, rods, slab, shapes, tube, and sheeting. Their higher melt strength makes these grades useful for thermoforming and parison forming for blow molding. High-viscosity polyacetal composites with higher toughness, rigidity, and creep resistance are molded into heavy-duty gears. Acetal terpolymer resins with higher melt strength for blow-molded parison forming are produced by Ticona.

Formosa Plastics Corp. of Taiwan supplies Formosacon® acetal copolymers in four principal grades: Formosacon® FM 024 extrusion, FM 270 high-flow, FM 450 super-high-flow, and FM 090 standard.

Processes

Polyacetals are typically injection-molded, extruded, blow-molded, compression-molded, rotation-molded, and thermoformed. Primary resin producers and compounders abound with information on conventional processing of their polyacetals. Different polyacetal resin, compound, and composite sources and grades have varying ranges for injection-molding parameters. Typical ranges for injection-molding temperatures, mold temperatures, and injection pressures are higher for acetal homopolymers. See Table 5.8.

In this chapter, we look at processes that are especially interesting for the coming years.

TABLE 5.8 Injection-Molding Parameters of Polyacetals

	Homopolymer	Copolymer
Injection-molding temperatures (barrel)	195–245°C (383–473°F)	165–195°C (329–383°F)
Mold temperature	60–120°C (140–248°F)	70–90°C (158–194°F)
Injection pressure	70–140 MPa (10,185–20,370 psi)	50–115 MPa (7275–16,730 psi)

Rotational molding Celcon®acetal copolymer brings the copolymer advantages to rotomolded shapes, including extremely low gasoline and alcohol permeation. Low permeation is essential to meet evaporative emissions requirements such as the Environmental Protection Agency (EPA) and California Air Resources Board (CARB) *zero-emissions vehicles* (ZEVs) and near ZEV. Acetal copolymer has thermal stability to 105°C (221°F), dimensional stability, strength, and stiffness and long-term resistance to chemicals, fatigue, and abrasion. The rotational molding technology is aimed at fuel delivery systems for small engines such as *outboard* (OB), *recreational vehicle* (RV), golf cart, and power motors. Research is ongoing on rotomolding acetal copolymer/HDPE and other multilayer systems. These developments at Ticona open two new avenues for polyacetals: (1) new rotational molding applications and (2) expansion of the use of polyacetal resins for small engine fuel delivery systems.

Injection molding and extruding of *foam (cellular) polyacetal resins* requires special attention [19]. Processing parameters, machinery, and equipment recommendations are critical because deviation from recommended processing conditions and the use of blowing agents will result in rejects. Processing and equipment considerations include the melt temperature, shot size, fill rate, injection pressure, backpressure, holding pressure, cushion, venting, cooling rate, closed mold time, screw speed, mold temperature, gate type and locations and size, and runner type and size [19]. A shutoff nozzle is necessary. Other factors include letdown ratio and percent, blowing agent level, and design factors such as percent of density reduction, wall thickness, and weld lines (if any). By using RTP Company FCX 27301 foam concentrate for polyacetal resins, the foam activation temperature is 149 to 177°C (300 to 350°F) [19]. By comparison, the foam concentrate activation temperature generally is 238 to 252°C (460 to 485°F) for other engineering thermoplastics, polycarbonate and polycarbonate alloys, PBT, PET, and polyamides (except polyamide 11 and 12) [19]. Injection-molding clamp force is about 1 to 4 tons/in^2 [19]. The surface of cellular parts has swirls and flow lines, but this attribute can be turned into an advantage for consumer products by allowing unique decorative effects. Cellular products include housings, bezels, shrouds, seat belt buckles, tennis racket handles, consumer products such as toys and kitchenwares, profiles, and stock shapes—rods, tubes, sheet, plates, and cones. Cellular polyacetal parts produced with foam concentrates can have up to 20% lower weight than solid parts; and for consumer applications the sink marks are eliminated.

Polyacetals are *overmolded, insert-molded, and coextruded* by using new adhesion technology. Overmolding, a multicomponent molding process, extends product performance properties and applications. Celcon® and Hostaform® acetal copolymer two-step overmolding was codeveloped by Ticona and Kraiburg TPE, using adhesion modified Thermolast® K *styrene block copolymers* (SBCs) such as the styrene-ethylene-butylene-styrene (SEBS). It can be used for nonslip, energy-absorbing, sound-dampening; molded seals; and complex molded-in-place gaskets for fluid handling systems, according to Celanese [21]. Advantages of overmolding and insert molding polyacetals and other engineering thermoplastics are that (1) this reduces assembly steps, assembly time, and assembly costs; (2) there is design versatility such as combining surface appearance (e.g., textured surfaces) with functionality; (3) this produces multifunctional products; (4) it produces integrated parts and benefits of parts unitizing such as seamless, leakproof construction; (5) it allows *in-mold decorating* (IMD) and *in-mold assembly* (IMA); and (6) it produces soft-touch products.

Thermoforming acetal terpolymers, which have high melt strength and low MFI, provide the following advantages: (1) shorter lead times for tooling and processing typically than for injection molding; (2) lower cost and faster production of prototypes; (3) greater cost efficiency for lower-volume housings and other enclosures than injection molding; and (4) textured, colored, and printed surfaces for decorated thermoformed parts and in-mold decorating films.

Delrin® FS (Forming Solutions), the first polyacetal for thermoforming, was jointly announced by DuPont Engineering Polymers and Ensinger/PennFibre Plastics in June 2003 [8]. Delrin® FS was run on Adolph Illig Maschinenbau Model UA-100 4G sheet processing machines, using 3-mm sheet on a Porsche tool 24 in long, 12 in wide, and 6 in deep. Delrin® FS is supplied as coil and sheet. The transforming temperature is 215 to 235°C (419 to 455°F). The lower and upper heat ranges are set to 500 and 700°C (932 and 1292°F). Heat cycle for 3-mm sheet is 70 s; mold temperature is 100°C (212°F). There is homogeneous heating of the sheet, with little heat sag; and overall shrinkage is 1.6 to 2.3% according to the company [8]. The acetal homopolymer has uniform processing parameters, and it handles topographical decorating and printing and sublimation printing. The process targets equipment and decorated housings, panels, trays, handles, conveyor chutes, medical/dental equipment, biochemical research products, and other products that the polyacetal properties satisfy. A range of colored decorative effects allows the designer to combine functionality with consumer appeal, using in-mold decorating, painting (IMD), foil stamping, and other techniques, according to DuPont. The company developed etching technology and special paints to accommodate Delrin® Forming Solutions [8]. Ensinger/Penn Fiber Plastics supplies thermoformable sheet as coil stock and precut sheet for FS technology [8].

Powder metal injection molding (MIM) is a mass-production, versatile method to mold complex metal and ceramic shapes [17]. A 50 to 70% (volume) metal or ceramic powder is mixed into a polyacetal resin at high shear, and the resulting suspension is injection-molded [17]. Powder metal injection molding requires polyacetal binder, which is added to the metal powder by high-shear mixing. The polyacetal binder serves as a carrier during injection molding of complex metal and ceramic shapes. Molten suspension is injected into the mold cavity and sets. Postmolding requires two steps: removing the polyacetal binder and sintering the metal or ceramic shape with special furnaces, such as the BASF catalytic EBO 120 furnaces for catalytic debinding [17]. This furnace uses the patented Advanced Temperature Control System (ATC) with the following advantages: (1) It is fully automatic with highest safety standards; (2) there is reduction of nitric acid time, resulting in lower part cost; (3) equipment control determines the end of debinding; (4) there is online signal input and evaluation (ATC); (5) a costly empirical series of evaluations is eliminated; and (6) emissions are reduced [17]. The EBO 120 furnace has additional advantages such as touch panel with SIMATIC control, automatic control of sweep gas flow depending on nitric acid mass flow, and two-stage propane flare [17].

Recent efforts are directed to improving removal (catalytic debinding) of the polyacetal binder, especially reducing debinding time [17]. A two-step process has required an initial 24 h to debond plus another 16 to 24 h for sintering. Modified polyacetal allows a one-step debinding and sintering process in a total of 24 h [18]. Catalytic debinding begins at the molded product surface, gradually penetrating to the center of the part. Total debinding time primarily depends on the size and shape of the molded part, furnace loading, and amount of acid used [17]. Polyacetal binder decomposes mostly to formaldehyde in the presence of nitric acid vapor by an interfacial reaction at the vapor/solid boundary which penetrates through the polyacetal molding, leaving the metal powder form [17].

The rate of depolymerizing polyacetal to formaldehyde is the subject of much research, because the rate of depolymerizing is a critical factor in MIM costs, and there is not that much proven information on it. Removal of binder is determined by various factors, namely, binder removal temperature, about 120°C (248°F); catalyst; linear or random degradation of polyacetal resin; fineness of powder; mold part shape and size; and catalytic debinding furnace. The catalytic furnace developed for debinding has automated controls for the debinding time required and debinding completion time [17]. Automation reduces the debinding cost and time and simplifies the process [17]. Contamination from residual binder due to carbonization during sintering is eliminated [17]. Heated-chamber sintering furnace walls are heated up to 180°C (359°F) to prevent condensation which occurs on cold chamber walls [17].

By using GERO-Hochtemperaturoefen (high-temperature) equipment, following catalytic debinding, load stacks are placed into the PDS 120 sintering furnace followed by residual debinding and sintering of "brown pieces." Low-alloy steels such as carbonyl iron and $42CrMo_4$, tool steels such as $100Cr_6$, stainless steels such as 316L and 17-4PH, and titanium and titanium alloys are sintered in the PDS 120 sintering furnace [17]. According to GERO, the company's PDS 120 sintering furnace has the following benefits compared with conventional sintering equipment:

1. N_2, H_2, or Ar partial-pressure operation for effective residual debinding
2. Heat exchanger and circulation of process gas that provide cycle times less than 12 h (cold/cold)
3. Special rotary vane pump for vacuum applications
4. $T_{\max}$ up to 1450°C (2642°F)
5. Hot wall furnace with a metallic heater
6. Low carbon content, perfect part surface
7. Very little finishing needed, allowing applications such as watch components, glasses, and other jewelry parts

Hot air staking is the method of choice for assembling polyacetal pneumatic valves for seat-height adjuster systems in commercial vehicles [20]. Phasa Developments Type 30/10 plastic hot air staking machine was finally selected over ultrasonic welding because staking was found to provide consistent assembling and high throughput, independent of operator skill level [20]. Further, hot staking was determined to be quieter and cleaner than ultrasonic welding. Hot air staking is used by KV Ltd. (Milton-Keyes, UK), which designs, develops, and manufactures pneumatic and fluid control systems [20].

The polyacetal pneumatic valves replaced more expensive metal valves which were either machined or cast. The polyacetal pneumatic valve meets several operating requirements, including reliable performance for several years (in trucks that must endure the harsh environment of road-to-vehicle vibration), design life of 100,000 operating cycles, and cost-effectiveness [20]. Hot staking assembly satisfied two operational requirements of the in-place pneumatic valves: using the vehicle's air supply and installing a microswitch to bring in an external air supply as needed [20]. Consequently,

TABLE 5.9 Companies Developing Polyacetal Processes

- API-Kolon, Lake Zurich, Ill., USA
  - Advanced Plastics Inc., Bensenville, Ill., USA (sales liaison office)
- Adolph Illig Mascinenbau, Heilbronn, Germany
- Albis Plastics, Hamburg, Germany
  - Resin distribution business acquired by Ashland Distributors Company, Dublin (Columbus), Ohio, USA (FRP thermoset distributor)
- Asahi Kasei, Osaka, Japan
- Ashley Polymers, Brooklyn, N.Y., USA
- BASF, Ludwigshafen, Germany
- Chevron Phillips Chemical Company LP, The Woodlands, Tex., USA
  - Chevron Phillips Chemical Company LP, Plastics Technical Center, Bartlesville, Okla., USA
- China (HK) Chemicals & Plastics, Hong Kong, People's Republic of China
- Colder Products Company, St. Paul, Minn., USA (mold couplings)
- Daicel Chemical Industries, Ltd., Osaka, Japan
  - Daicel (USA) Inc., Fort Lee, N.J., USA
- DuPont Engineering Polymers, Wilmington, Del., USA
- Ensiger, Nufringen, Germany
  - PennFiber Plastics Inc., a division of Ensinger, Bensalem, Pa., USA
- Formosa Plastics, Taipei, Taiwan
- GE Advanced Materials, Pittsfield, Mass., USA
  - GE Advanced Materials—Noryl®—Selkirk, N.Y., USA
  - GE Advanced Materials, Mount Vernon, Ind., USA
- GERO Hochtemperaturoefen GmbH, Neuhausen, Germany
- Kolon Industries, Kyunggi, Korea (Rep.)
- K-Mac, Wyoming, Mich., USA
- KTP, Kimchon City, Gyungsanbuk-do, Korea (Rep.)
- KV Ltd., Milton-Keyes, UK
- LG Chem Ltd., Seoul, Korea (Rep.)
  - LG Chem America Inc. (Detroit), Southfield, Mich., USA
  - LG Chemical of America Inc., Englewood, N.J., USA
  - LG Chem Ltd., Tech. Center, Daejeon, Korea (Rep.)
- LNP, a business 0f GE Advanced Materials, Exton, Pa., USA
- Mitsubishi Gas Chemicals, Tokyo, Japan
- Mitsui Chemicals Inc., R & D Center, Chiba, Japan
  - Mitsui Chemicals America Inc., Purchase, N.Y., USA
- Phasa Developments, Harlow, Essex, UK
- PolyOne, Cleveland, Ohio, USA
- Polyplastics, Tokyo, Japan
- PTM Engineering Plastics (Nantong) Company Ltd., Nantong Municipality, Jiangsu Province, People's Republic of China
- Quadrant Engineering Plastics Products Inc., Reading, Pa., USA
- RTP, Winona, Minn., USA
- Solvay SA, Brussels, Belgium
  - Solvay Advanced Polymers LLC, Alpharetta, Ga., USA
- Shipley Company LLC, Shipley Europe Ltd., Coventry, UK
  - Subsidiary of Rohm and Haas Company
- Techmer Lehvoss Compounds LLC, Clinton, Tenn., USA
  - Known as Lehman & Voss in Germany, Hamburg, Germany
- Teknor Apex, Pawtucket, R.I., USA
  - Chem Polymers business unit, Fort Myers, Fla., USA
- Thai Polyacetal Ltd., Map Ta Phut Rayong, Thailand
  - Joint venture of Mitsubishi Group (Mitsubishi Gas Ind'l) and TOA Group
- Ticona GmbH/Celanese AG, Frankfurt, Kelsterbach, Germany
  - Celanese AG, Kronberg, Germany
- Toray Industries Inc., Minato-ku, Nagoya, Japan
  - Toray Resins Company, Troy, Mich., USA

assembly is not just the in-plant joining of two halves of the valve; it requires a complex, sophisticated automatic assembly cycle for which engineering thermoplastics is ideally suited. Briefly, hot air at 350°C (662°F) is aimed accurately onto a series of molded pins that precisely position the valve components before final in-place assembly [20]. The pins are brought to a plastic state; then cold-forming tools re-form and solidify the pins to clamp the valve components together permanently, vibration-free and tamper-proof [20].

Companies active in developing processes for polyacetals are listed in Table 5.9.

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Chapter 6

Acrylonitrile-Butadiene-Styrene (ABS) Resin

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Introduction

ABS resins are thermoplastic resins composed of three kinds of monomers—acrylonitrile, butadiene, and styrene. They were created as resins with the harmony of hardness and softness by improving the brittleness, which is the disadvantage of polystyrenes, through addition of a rubber component while maintaining hardness and fluidity, which are the advantages of polystyrenes. See Fig. 6.1.

ABS resins were developed in the form of graft-type ABS by several manufacturing companies, including Borg-Warner (presently, General Electric), Monsanto, and JSR, and introduction of blend-type ABS resins by the U.S. Rubber Industry of America in 1948. The preparation of ABS by graft polymerization was repeatedly developed after its introduction in 1956, and now it is used as one of the major methods for preparing rubber-toughened thermoplastic resins.

As is well known, ABS resins are one type of excellent resin having all the desirable properties, including impact resistance, processability, gloss property, good mechanical properties, and high heat distortion temperature. Therefore, ABS resins have been used in very broad fields of application and particularly in many aspects of daily life. At present, the amount used has gradually increased.

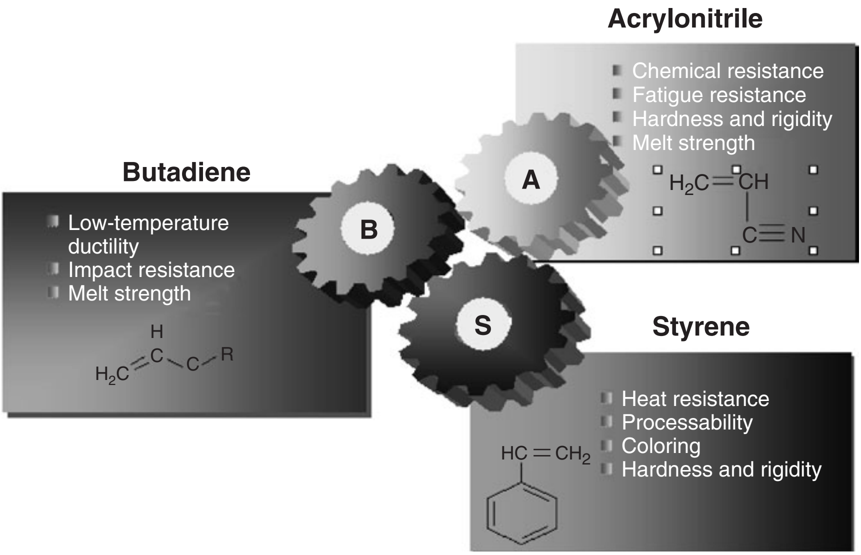


Figure 6.1 ABS terpolymer and its functionality.

However, in practice, since it is also difficult to prepare ABS resins with various harmonized properties, many studies have been made during the past 50 years and more, and currently various studies are underway with the aim to improve both the properties and the manufacturing processes in the industrial and academic fields.

The characteristic properties of ABS resins are strongly affected by molecular characteristics of the *styrene/acrylonitrile* (SAN) copolymer forming the elastomeric phase and the matrix.

The methods for preparing grafted ABS are largely classified into three types, where mass and emulsion polymerization and mass suspension methods have been widely used.

Among those methods, in general, the emulsion polymerization method has been mainly used. In the case of the SAN copolymer, it has been prepared by either emulsion polymerization or bulk polymerization.

ABS resins are generally prepared in the compositional ratio of 21 to 27% acrylonitrile, 12 to 25% butadiene, and 54 to 63% styrene on average, where styrene gives good processability and stiffness to the final ABS, butadiene improves the impact strength, and acrylonitrile improves the chemical resistance.

The increase in the molecular weight of SAN copolymer causes a decrease in fluidity, an increase in impact strength, and creep inhibition; it also results in an increase of resistance against surface-active substances and of tensile strength. The narrow *molecular weight distribution* (MWD) causes an increase in tensile strength, shrinkage reduction, improved dimensional stability, and an increase in creep resistance, whereas the broad MWD improves the flow properties and mold filling but also increases the heat and pressure sensitivity of the melt. The increase in the compositional ratio of the elastomer causes an increase in melt viscosity, heat deformation resistance, and aging resistance and a decrease in stiffness, as well as an increase in impact strength. Such a multiphase system is affected by the interface condition between the rubber and thermoplastic matrix.

The final ABS resins completed by compounding grafted ABS and SAN copolymer have been prepared by subdividing into general-purpose ABS, flame-retardant ABS, extrusion ABS, heat-resistant ABS, transparent ABS, weatherable ABS, etc., depending on the raw materials and additives as applied.

Recently, the application of such ABS resins has been extended to one engineering plastic formed through constitution of the composite alloy with other resins, for example, ABS/PVC, ABS/polycarbonate, ABS/PA, ABS/poly(methyl methacrylate), etc. The representative plastic companies producing such various kinds of ABS resins and ABS alloy products include GE Plastic and Dow Chemical in the United States, Lanxess and BASF in Germany, Chimei in Taiwan, LG Chem. in Korea, etc.

In this present chapter, we review the process for preparing ABS resins, the final products, the main uses, etc., to help promote understanding about general ABS resins.

ABS Polymerization Process

ABS comprises the dispersed phase of styrene/acrylonitrile copolymer grafted on polybutadiene rubber and the continuous phase of styrene/acrylonitrile copolymer. The use of SAN grafted on polybutadiene rubber provides high impact strength, processability, chemical resistance, staining property, etc., as the characteristics peculiar to ABS resins.

The properties of ABS resins can be controlled by changing the composition and molecular weight of SAN, the particle size and size distribution of polybutadiene rubber, the grafted ratio, etc. In using ABS resins, the products having various properties can be manufactured by altering the basic structure and the composition. Specifically it is possible to manufacture the products having various uses, including heat-resistant products, transparent products, and flame-retardant products.

The basic property of ABS resins is impact resistance. In connection with this, various theories relating to the impact property have been established. The rubber particles disperse impact energy through efficient generation and annihilation of craze. By such crazing, the energy is annihilated with deformation of rubber particles to create the cavitation of rubber particles. This phenomenon can be confirmed through *transmission electron*

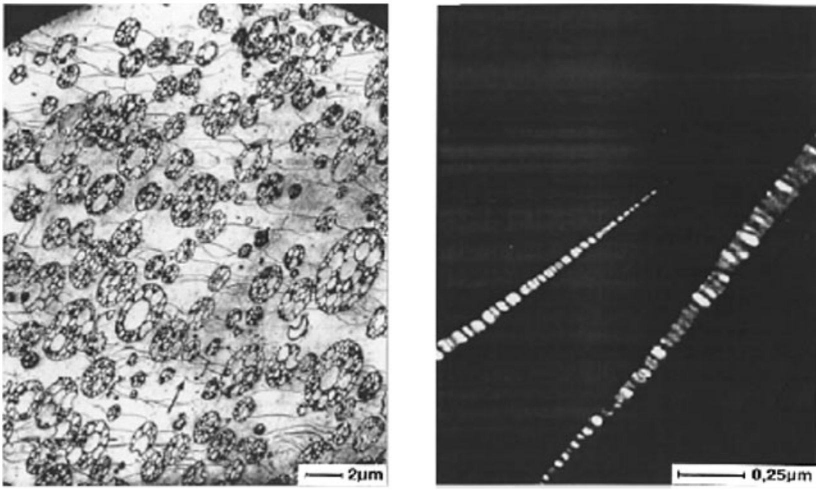


Figure 6.2 TEM of crazes in ABS.

microscopy (TEM). (See Fig. 6.2.) The major fracture mechanism of HIPS is craze with the optimum particle size in the range of 2 to 6 μm, whereas in the case of ABS resins the mechanism is shear yielding that is maximized with very small particles (0.1 μm).

The procedures for manufacturing ABS resins can be largely classified into the mass polymerization process and the emulsion polymerization process. In the case of the mass polymerization process, the size and structure of particles can be controlled through change in viscosity of continuous and discontinuous phases, change in stirring speed, change in molecular weight, and change in added amount of polybutadiene rubber. The typical particle size is about 1 to 10 μm.

The high impact resistance of ABS resins is generally obtained with the particle size below 1 μm, which can be readily obtained by the emulsion polymerization process. Therefore, currently ABS resins are mostly produced by the emulsion polymerization process.

The emulsion polymerization produces ABS resins having rubber particles below 1 μm, from which characteristic features of high gloss and surface distinction result, whereas by mass polymerization the resins having large particles are prepared, and, therefore, low-gloss products are obtained and rubber efficiency is increased.

Emulsion polymerization process

In the emulsion process, ABS resins are obtained by addition of the initiator, the molecular weight regulator, the emulsifier, etc., to polybutadiene rubber latex, followed by graft polymerization of styrene/acrylonitrile copolymer.

Water is present in the continuous phase and plays a role of reaction heat transfer material. The reactants are present in the discontinuous phase. As the reaction proceeds, particles of ABS resins are produced in water, and thus the high reaction heat peculiar to ABS polymerization can be readily removed by water.

Polybutadiene rubber latex is prepared according to trans-1,4, cis-1,4 addition free-radical emulsion polymerization of butadiene. In this reaction, an initiator such as KPS or NaPS can be used.

Oil-soluble initiators such as cumene hydroperoxide are generally used as the initiator for ABS polymerization. The emulsifier plays a role to facilitate the formation of discontinuous phase from the reactants, and the typical example includes rosin, fatty SLS, oleate, etc. See Fig. 6.3. The emulsifier is composed of a hydrophilic portion and a hydrophobic portion, and it plays a role in forming the interface between water and the reactants and in stabilizing the emulsion. The molecular weight regulator is typically TDDM, and it plays a role to prepare ABS resin having the desired molecular weight by stopping the polymerization without influencing the polymerization rate. Upon completion of polymerization, polymer particles are obtained by adding acids or salts to remove the stability of emulsion and then are washed and dried to obtain the final ABS resin.

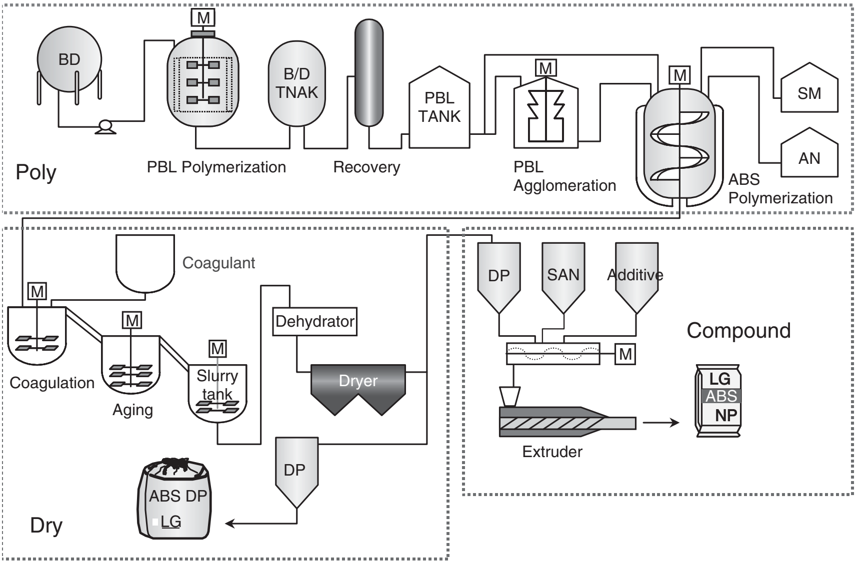


Figure 6.3 Emulsion polymerization process of ABS.

Preparation of polybutadiene latex

The reaction is conducted by introducing the butadiene monomer, emulsifier, initiator, and chain transfer agent into the batch reactor and then elevating the temperature while stirring the reaction mixture. The ratio of butadiene to water is generally about 1:1. The emulsifier is added in the ratio of about 1 to 5 parts with respect to 100 parts of butadiene monomer, and it is used in the form of the salt of rosin or fatty soap. After the grafting reaction, the emulsifier, which can have the agglomerating property for acid or salt, is used.

As the reaction initiator, water-soluble initiators such as KPS or oil-soluble initiators using a redox system can be used. The use of oil-soluble initiator can provide high reaction rate at relatively low temperature compared to the use of water-soluble initiator.

The particle size can be controlled by the ratio between monomer and water as used, reaction temperature, etc. The chain transfer agent is used to control the cross-linking density of polybutadiene rubber, which greatly influences the properties of the final ABS polymer. In general, the cross-linking density is controlled to be at least 60%. After completion of the reaction, unreacted butadiene monomer is recovered and reused in the polymerization reaction.

Although in preparing polybutadiene latex the desired particle size can be achieved through polymerization, particles having the desired size may be prepared by polymerization of small-size particles followed by latex agglomeration. The chemical agglomeration uses an acid or an acid oligomer, and the physical agglomeration utilizes a homogenizer or a freezer. For most cases, the chemical agglomeration is utilized. Such a method is more advantageous than direct polymerization with respect to production efficiency, and it is used by many manufacturing companies. It can produce various kinds of polybutadiene latex, even in small equipment.

Preparation of ABS latex

Generally, ABS resins are produced in the form of a bimodal type comprised of two kinds of particle sizes for better surface and impact resistance properties. In this case, either (1) the graft polymerization is also accomplished in the concurrent presence of two kinds of polybutadiene latex having different particle sizes, or (2) respective polybutadiene latexes, after the graft polymerization is accomplished, may be mixed in a certain ratio to prepare the product. The particle size is generally in the range of 0.1 to 0.4 μm.

Polybutadiene latex comprising large and small particles is introduced in a graft polymerization reactor. Styrene and acrylonitrile monomers are added in a certain quantity to the reactor, and the molecular weight regulator, initiator, activator, and emulsifier as required for the reaction are added. Then the reaction progresses at elevated temperature. The emulsifier that can be used in this reaction is identical to that used in preparation of polybutadiene latex, and the oil-soluble initiator using the redox system is utilized as the initiator in this reaction.

The ratio between polybutadiene latex and styrene and acrylonitrile monomers is controlled according to the purpose of use, and is generally in the ratio of 1:1 by weight. The ratio between styrene and acrylonitrile monomers is controlled according to the purpose of use, and is generally in the ratio of 7:3 by weight. The used amounts of molecular weight regulator, initiator, and activator determine the molecular weight of the final ABS resin. Thus, when they are used in a small amount, the phenomenon of lowering the polymerization conversion rate may occur.

The amount of styrene/acrylonitrile copolymer to be grafted onto polybutadiene latex is increased as the particle size of the polybutadiene latex is increased, but is decreased as the cross-linking density is increased. According to such change in grafting rate the properties of the final ABS resins are also changed. The kinds of initiator also greatly influence the grafting rate. The water-soluble initiator such as KPS allows grafting of styrene/acrylonitrile copolymer on the outside, rather than the inside, of polybutadiene latex, whereas the oil-soluble initiator allows grafting of styrene/acrylonitrile copolymer on the inside, rather than the outside, of polybutadiene latex. The reaction time is usually 4 to 6 h, and upon completion of the reaction the resulting product is transported to the coagulation and drying steps.

Coagulation and recovery

After the reaction is completed, the solution containing a certain amount of antioxidant is added to the resulting ABS latex, to prevent the oxidation of ABS during the coagulation and drying steps. A phenolic-based antioxidant can be mainly used, but a phosphate-based antioxidant may also be used. The amount of antioxidant generally used is about 1 part by weight with respect to 100 parts of ABS resins by weight. The ABS latex to which the antioxidant is added is transported to the coagulation chamber at high temperature.

As a coagulator for the coagulation step, the dilution of acids or the dilution of $CaCl_2$, etc., may be used. The particle size distribution of coagulated ABS powder is very important, and therefore, it is kept at the desired level by the added amount of coagulator, coagulating temperature, residence time in the coagulation chamber, stirring condition, etc. The particle size is decreased as the coagulating temperature is lowered. In addition, as the stirring speed (rpm) is increased, the particle size is decreased and the particle distribution is also narrowed. Long residence time contributes to an enlargement of particle size. However, too long a residence time may induce a discoloration of ABS resin.

The coagulated ABS slurry is centrifuged to remove water and then washed to remove the impurities. The removed water is purified through the filtering apparatus and then recycled. The water content after drying is kept below 2%. The fluidized-bed type of dryer is generally used.

Mass polymerization process

According to the mass process, polybutadiene rubber is dissolved in the mixed solution of styrene and acrylonitrile monomers, and then the reaction proceeds to prepare the ABS resin. For polybutadiene rubber, the method for grinding and then adding the rubber is utilized. Contrary to the emulsion process, the particles of polybutadiene rubber are not present before the reaction, and therefore, the shape and distribution of particles appear to be different from those of the emulsion process. The molecular weight of polybutadiene rubber to be used is about 200,000, with the cis-1,4 ratio being about 40%. The amount of polybutadiene rubber used should be kept to 20% due to the problem related to a viscosity of polymerization solution.

The radical prepolymerization occurs in the oil-in-oil emulsion state. As the reaction proceeds, the copolymer of styrene and acrylonitrile is produced, and when the ratio between the produced copolymer and polybutadiene rubber reaches 1:1, the phase inversion occurs. Thereafter, styrene/acrylonitrile copolymer is present in the continuous phase, and polybutadiene rubber is present in the dispersed phase. In general, the phase inversion is terminated when the polymerization conversion rate reaches about 15%. The particle size is varied depending on the change in stirring rate, the viscosity ratio between the rubber phase and the monomer phase, and the interfacial tension.

The grafting rate is affected by the initiator types, the kinds of molecular weight regulators, and a difference in solubility of two monomers in the rubber phase and the matrix phase. Due to such difference in solubility, the grafting rate is lowered and any difference in the composition between rubber and the matrix is created.

After the prepolymerization step, as the reaction proceeds, the molecular weight and molecular weight distribution are controlled by the temperature, the kinds and added amounts of the initiator, the content of the solvent, the added amounts of the molecular weight regulator, etc. To prevent a cracking of the particles, it may be necessary to increase the crosslinking density of rubber. In such a case, the reaction temperature and time can be controlled to obtain the desired properties.

The molecular weight of the final product is usually around 100,000, and the size of rubber particles is about 1.0 to 2.5 μm. Various particle size distributions of rubber can be obtained by using two kinds of prepolymers.

Preparation of mass polymerization ABS

The greatest difference between the ABS mass process and the HIPS mass process is the presence or absence of acrylonitrile monomer, but in the two processes there are many other similar points. See Fig. 6.4. Any other differences between the two processes involve the method for removing reaction heat, the radial and vertical mixing extent, the numbers of reactors, etc. The reaction heat can be removed by means of boiling and reflux cooling, heat-transfer surface, addition of low-temperature monomer and solvent, etc.

The radial mixing plays a role in preventing the deviation of temperature and concentration in the reactors. Such deviation forms the layer on the surface of the reactor wall, to adversely influence the removal of reaction heat, and eventually influences the quality of products.

The polymerization reaction is initiated by dissolving polybutadiene rubber in monomer. As mentioned above, rubber is ground and then added. Together with this, a small amount of the solvent is introduced. In general, ethyl benzene is used and introduced in the ratio below 5% for the purpose of lowering the viscosity. This solution is introduced into the high-temperature reactor to move the reaction forward. The reaction heat is removed through the reactor jacket. In the phase inversion step, stirring at a high shear rate is essential. At this step, the size and distribution of rubber particles are determined. When the phase inversion is completed, the reaction is continued in the matrix phase, and the monomer present in rubber is reacted in the occlusion state. In

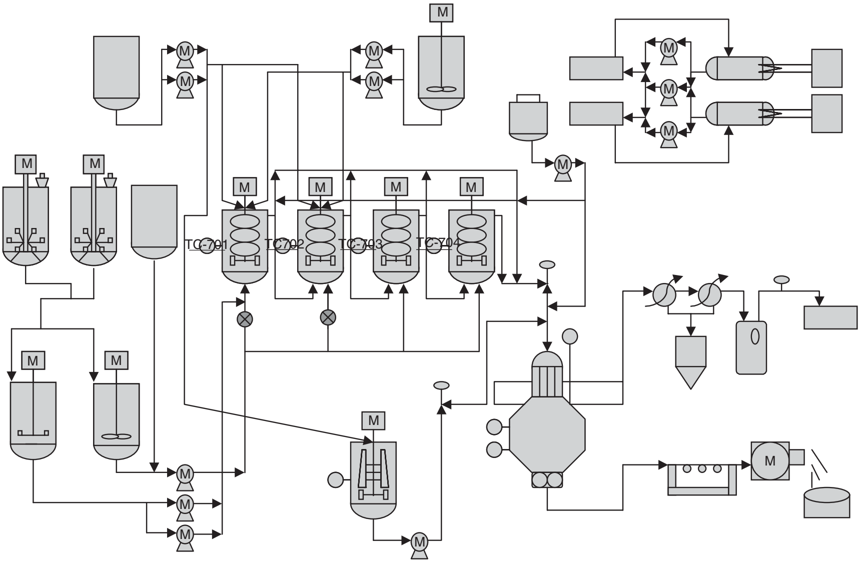


Figure 6.4 Mass polymerization process of ABS.

this step, stirring is conducted at a low shear rate so that the monomer can be retained within rubber.

After the reaction is completed, the resulting product is transported to the devolatilization step. In this step, residues including residual monomers are removed by using water or methanol. Such materials have the solubility for polymer solutions and play a role in preventing the foaming phenomenon by lowering the partial pressure of monomer. The methods for removing residual monomers include falling strand devolatilization, extrusion devolatilization, film evaporation, etc. The last two methods are superior in view of their effect, but have the disadvantage of high cost.

Flame-Retardant ABS

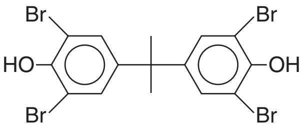
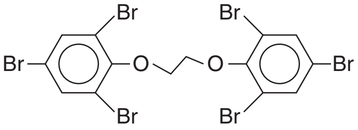
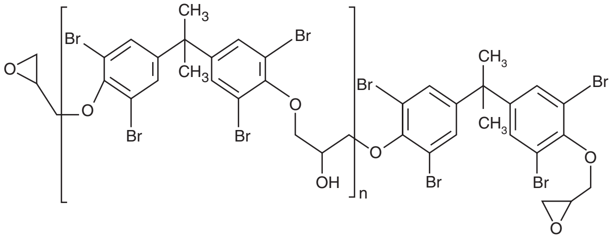
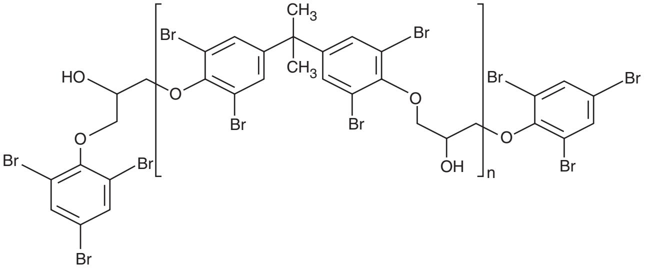
Flame-retardant ABS has excellent properties and processability and therefore has been most widely used as the parts of office automation (OA) equipment including copiers and printers and various kinds of electric and electronic equipment as well as computer monitor housings. Further, since recently safety has been emphasized, the application field and use of flame-retardant resin have been expanded, and the requirements in the market have been diversified according to the environmental problems. In this section, we review the overall present situation and future prospects of flame-retardant ABS resins.

The flame-retardant ABS resin is prepared by addition of flame retardant, impact modifier, lubricant, and stabilizer. As the flame retardant, halogen-based organic compounds containing bromine, chlorine, etc., are mainly used. Although phosphorus-based flame retardant may be used, its use is limited to only low levels of flame-retardant products (V-2). Therefore, in the following we focus on halogen-based flame retardant, as flame-retardant ABS generally uses halogen-based flame retardant.

As the flame retardant, organic halogen compounds having a bromine (Br) content of at least 50% are mainly used, and they can be added to the level of at least 5 to 20 parts by weight per 100 parts of resin (phr) depending on the flame-retardant rating of the final product and the flame-retarding efficiency of flame retardant, to readily obtain UL-94 V-2 to V-0. Since the flame retardant in flame-retardant resin determines the flame-retardant property, and furthermore, influences the properties and characteristics of the resin itself, it is important to select the flame retardant according to the desired characteristic properties required for the final product. The kinds and properties of flame retardants used in flame-retardant ABS are shown in Table 6.1.

Tetra-bromo bisphenol-A is the most widely used flame retardant for flame-retardant ABS, since it is relatively inexpensive and has excellent flame resistance, in comparison to other flame retardants. Although it has the advantage of excellent fluidity, it is required to use a suitable

TABLE 6.1 Kinds and Properties of Flame Retardants

Chemical name	Chemical structure	Br content (%)	Melting point(°C)	Remarks
Tetra-bromo bisphenol-A		59	180	Excellent fluidity Weak thermal stability
1,2-Bis(tribromophenyl) ethane		68	225	Excellent fluidity Good weather resistance
Brominated epoxy oligomer	 	49–53	100–120	Excellent weather resistance Excellent heat resistance

stabilizer and to use an impact reinforcing agent such as *chlorinated polyethylene* (CPE) to compensate for impact strength, because of the weak thermal stability and impact strength.

1,2-Bis(tribromophenyl) ethane has the advantages of good impact strength and excellent fluidity and thermal stability in preparing flame-retardant ABS. In using this flame retardant for a long time, it is difficult to apply to a resin having black or dark color. The reason is because this flame retardant migrates to the surface of a finished product.

Use of brominated epoxy oligomer is gradually increasing due to its excellent weather resistance and heat resistance, and it is suitable for preparing the heat-resistant flame-retardant ABS resin, since it is possible to prepare high heat resistance products according to their molecular weights.

As the flame-retardant auxiliary, antimony trioxide (Sb_2O_3) is primarily used, and it is added at the level of about 30% of the flame retardant to obtain a synergistic effect. The synergistic effect of the halogen-antimony flame-retardant system is very effective for improvement of the flame resistance and therefore has been applied to most of the halogen flame retardants and has been generalized. See Table 6.2.

Halogen released from combustion is reacted with antimony trioxide to produce antimony trihalide having a high boiling point, which can be retained in the state of a noncombustible gas due to its high boiling point to exhibit a synergistic flame-retarding effect by blocking oxygen and stabilizing a radical chain reaction.

To compensate for the lowering of impact strength caused by addition of the flame retardant, auxiliary chlorinated polyethylene, having a good compatibility with ABS resin and an excellent impact reinforcing effect, is primarily used as the impact modifier. It is generally added at the level of 3 to 5%, and one having a chlorine content of about 35% is most widely used.

A suitable amount of the amide and metal salt-based internal and external lubricants is used to improve the processability of resin, and the antioxidant, stabilizer, and ultraviolet stabilizer are used to prevent thermal degradation of resin in processing and lowering of thermal stability caused by the flame retardant, and to improve weather resistance.

TABLE 6.2 Synergistic Flame-Retardant Mechanism with Halogen—Antimony

$Sb_2O_3 + 6HX \rightarrow 2SbX_3 + 3H_2O$ (when HX is much produced)
$Sb_2O_3 + 2HX \rightarrow 2SbOX + H_2O$ (when HX is less produced)

SbOX reaction mechanism:

Step 1: $5SbOX \rightarrow Sb_4O_5X_2\,(s) + SbX_3(g)$
Step 2: $4Sb_4O_5X_2 \rightarrow 5Sb_3O_4X + SbX_3(g)$
Step 3: $Sb_3O_4X \rightarrow Sb_2O_3 + SbX_3(g)$
Step 4: $Sb_2O_3(s) \rightarrow Sb_2O_3\,(l)$ (where X = Br, Cl)

TABLE 6.3 Properties and Characteristics of Flame-Retardant ABS

	Unit	ASTM test method	Flame-retardant TBBA	Flame-retardant BEO	Flame-retardant FF-680
Mechanical					
Tensile strength (5 mm/min)	kg_f/cm^2	D638	420	430	400
Elongation at break	%	D638	28	26	18
Flexural strength (1.3 mm/min)	kg_f/cm^2	D790	685	700	670
Flexural modulus	kg_f	D790	23,500	24,500	21,000
Izod impact (notched, 23°C)	cm/cm	D256	29	22	25
Rockwell hardness	R-scale	D785	104	102	104
Thermal					
Heat deflection temperature ($18.5\ kg_f/cm^2$)	°C	D648	82	86	78
Flowability					
Melt index (220°C, 10 kg)	g/10 min	D1238	50	38	48
Flame rating					
UL-94 (1/16 in)			V-0	V-0	V-0

NOTE: TBBA is tetra-bromo-bisphenol A, BEO is brominated epoxy oligomer, and FF-680 is 1,2-bis(tribromophenyl) ethane.

Since flame-retardant ABS has excellent properties and processability (Table 6.3), the application field has been expanded to the parts of various kinds of electric and electronic equipment as well as computer monitor housings. As safety is emphasized, the flame-retardant standard has been strengthened, and the environmental problem is an issue, as the harmful effect of halogen-based flame retardant has been criticized. Therefore, for flame-retardant ABS it is necessary to abide by the uses and regulations according to the safety and environmental issues in each country.

The movement to regulate flame retardants was led by the Green Party in Germany in the middle of the 1980s, and it then came to be noticed by the public through participation of other European countries. Accordingly, as the risk assessment depending on the kinds of flame retardants is established, the regulation of some flame retardants has been envisioned. Recently, even in the United States, which has held on to a generous policy for flame retardants, the movement to regulate some flame retardants has arisen, centering on California. However, since the flame retardant used for flame-retardant ABS has been classified as a relatively safe material, its use has not been regulated up to now. Self-imposed control has been practiced by establishing the ecolabel mainly in European countries. See Table 6.4.

The flame-retardant ABS resins are mainly used in the parts and housings of various kinds of electric and electronic products that require the flame-retardant property. Specific applications have been made in various fields including *cathode-ray tube* (CRT) and LCD monitor housings, TV

TABLE 6.4 Ecolabels in Europe

TCO	Blue angel	Nordic swan	EU flower
			
Sweden	Germany	Nordic countries	EU

housings, copy machines, printers, audio, VCR, DVD, wall sockets, battery chargers, adapters, plastic doors, etc.

For the flame-retardant ABS resins, the product must be developed to have the properties required according to the application use. As products are gradually getting larger and the design and molding of ultrathin films have been made possible through development of the part design and molding technology, and improvement of processing capability, etc., it is necessary to improve the properties and processability of resins. Furthermore, to expand the application it is necessary to develop a suitable product in line with developments in primary industrial applications. These include development of (functional) products having heat resistance, flame-retardant properties, antistatic functionalities, etc., and development of the halogen-free flame retardant products having a high future growth potential. See Table 6.5.

TABLE 6.5 Future Work

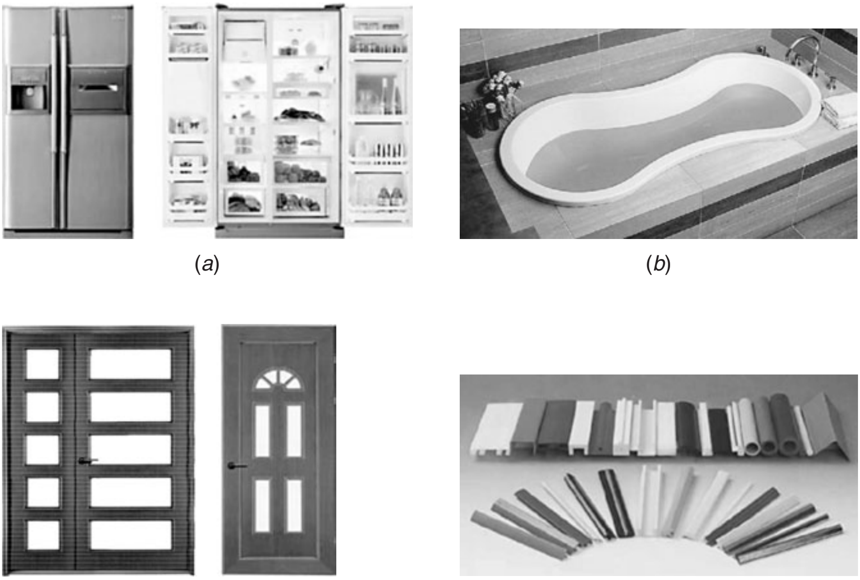
Development direction	Approach direction
High toughness/high flow	▪ ABS rubber morphology and matrix rheology control
High heat resistance	▪ Polymeric flame retardant ▪ Heat-resistant resin blend
Development of halogen-free products	▪ High-performance phosphorus ▪ Modified inorganic flame retardant ▪ Higher thermally stable intumescent system ▪ Nanoparticle application Enhance char formation Lower heat release rate ▪ New alloy system

Extrusion ABS

The extrusion ABS resin is processed through a sheet or profile extrusion. Although the resin in the form of a sheet may be used itself, depending on the application, it is processed as the final product through thermoforming, which is applied to refrigerator inner door cabinets, bathtubs, door covers, etc., or is applied to sashes, pipes, etc., through the continuous profile extrusion, as shown in Figure 6.5 and Table 6.6.

For the case of extrusion ABS, when there is any change of throughput in the continuous process, such as sheet extrusion, profile extrusion, etc., inferior conditions such as surface inferiority or thickness deviation can be created. Therefore, the extrusion stability (less deviation of melt flow depending on temperature, less additives) is regarded as the major important characteristic, as shown in Table 6.7.

Although the extrusion ABS may be used as the final product in the profile form, such as sheet, film, or pipe, in most cases it is generally molding-processed as the final product through sheet extrusion followed by a thermoforming process. The typical example is the refrigerator inner door cabinet product. In thermoforming processing, deformation and thickness variation may be raised, and to minimize such problems, the extrusion ABS is mainly characterized by an excellent thermoformability.



(*a*) (*b*)

(*c*) (*d*)

Figure 6.5 Extrusion ABS applications: (*a*) refrigerator inner door cabinet, (*b*) bathtub, (*c*) door covers, and (*d*) pipes and sashes.

TABLE 6.6 Properties of Various Extrusion-Grade ABS Resins

Properties	ASTM measurement method	LG extrusion ABS (general-purpose)	LG extrusion ABS (CFC resistance)	LG extrusion ABS (HCFC resistance)	LG extrusion ABS (high impact)
Tensile strength, kg/cm^2	D638	460	440	420	410
Tensile elongation at break, %	D638 (50 mm)	30	35	30	30
Flexural strength, kg/cm^2	D790 (15 mm/min)	760	730	680	670
Flexural modulus, kg/cm^2	D790 (15 mm/min)	26,000	24,000	22,000	21,000
Impact strength, kg·cm/cm	D256 (23°C, 1/8 in)	31	40	48	52
Melt flow rate, g/10 min	D1238 (220°C, 10 kg)	7.2	4.5	4.5	5.0
Flammability	UL-94	HB	HB	HB	HB

As the index of thermoformability, the hot tensile test is used, and the larger area of the stress-strain curve exhibits an excellent thermoformability property. The thermoformability is dependent on rubber content, acrylonitrile content, and molecular weight, as shown in Fig. 6.6. When the molecular weight is low, the sheet extrusion is readily accomplished due to a low torque, but the deep drawing is impossible in the thermoforming procedure due to a low level of melt strength at high temperature. Therefore, different from the injection-molding ABS, the extrusion ABS is characterized by a high molecular weight.

Recently, the method used for improving the thermoformability while maintaining the sheet extrusion stability has added some high-molecular-weight additives, as shown in Fig. 6.7.

TABLE 6.7 Comparison between Extrusion ABS and Injection-Molding ABS

Items	Extrusion ABS	Injection ABS
Processing properties	Extrusion stability Thermoformability Thermal stability Chemical resistance	Fluidity Appearance
Melt viscosity	High	Low
Properties	Stiffness Toughness Low-temperature ductility	Stiffness
Additives	Less	Processing aids

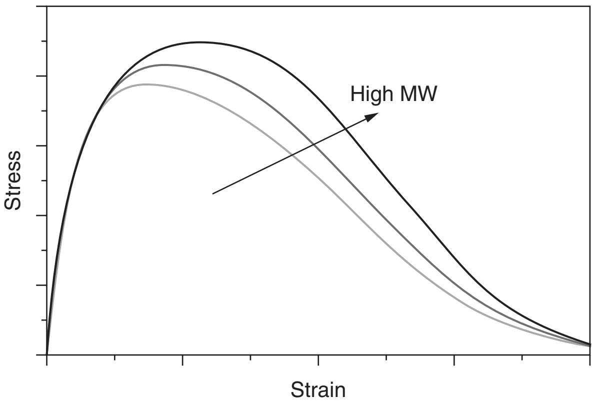


Figure 6.6 Hot tensile profile according to molecular weight (150°C, 15-min annealing).

For a refrigerator inner door cabinet, the most widely used product among extrusion ABS resins, cracks may occur due to chemical attack by the foaming agent (cyclopentane, HCFC-141b, HFC-245fa, etc.) of polyurethane foam used as the insulation material after a vacuum thermoforming process. The ABS demands a superior chemical resistance property. The polyurethane foaming agents used in a refrigerator are shown in Table 6.8.

Chemical cracking due to the refrigerator foaming agent can be prevented by controlling the rubber content, acrylonitrile content, and molecular weight of styrene-acrylonitrile copolymer, or adding a chemical resistance modifier to provide better chemical resistance to ABS resin.

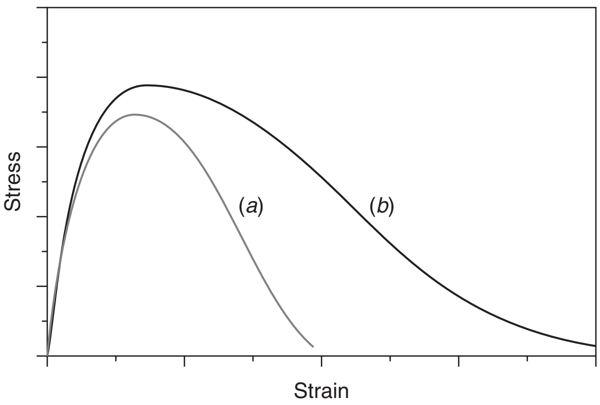


Figure 6.7 Hot tensile profiles (150°C) for extrusion ABS: (*a*) without high-MW additives; (*b*) with high-MW extrusion ABS.

TABLE 6.8 Properties of Foaming Agents*

	HFC-245fa	R-11	HCFC-141b	Cyclopentane
Molecular weight	134.0	137.4	116.9	70.0
Boiling point, °C	15.3	23.8	32.2	49.3
Specific gravity, g/cc at 20°C	1.32	1.49	1.24	0.74
Vapor pressure, kPa at 20°C	122	88.0	69.0	34.0
Vapor thermal conductivity, kcal/mh°C at 44°C	0.012	0.008	0.010	0.011
Flame limit, vol%	None	None	7.6–17.7	1.4–9.4
Ignition point, °C	None	None	None	–37
Lift time in atmosphere, yr	8.4	50	9.4	A few days
GWP (R-11 = 1)	0.21	1.0	0.12	<0.001

*Utech 96 Paper 55, p. 355.

The sheet extruder consists of extruder, cooling and takeoff rolls, and cutting unit, as shown in Fig. 6.8, and the general processing conditions are shown in Table 6.9.

The thermoforming process is the method for annealing a sheet of thermoplastic resin to manufacture the final product by vacuum or air pressure, as shown in Fig. 6.9. It has these advantages: The cost of equipment is inexpensive, the processing of multilayer sheets can be readily achieved, and the production of thin products is possible. The disadvantages of this process are that the procedure for preparing sheets is necessary, the selection of available plastic material is limited, and manufacturing with accurate dimensions is difficult.

Transparent ABS

Transparent ABS is a quaternary copolymer composed of butadiene, styrene, acrylonitrile, and methyl methacrylate. It is composed of a core-shell structure, where the core component uses butadiene rubber or

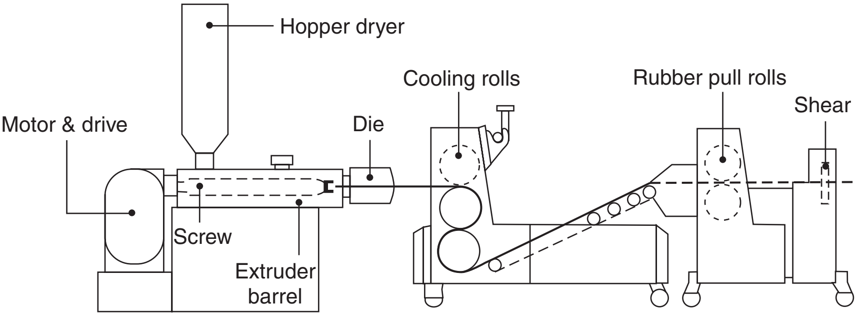


Figure 6.8 Sheet extrusion process.

TABLE 6.9 **Condition of Sheet Extrusion Process**

Items	Conditions
Extruder barrel temperature	200–230°C
Die temperature	210–240°C
Resin melt temperature	220–250°C
Roll temperature	70–90°C

styrene-butadiene rubber and the shell component is comprised of a random copolymer of styrene, acrylonitrile, and methyl methacrylate. This resin is a macromolecular substance having all the properties of four kinds of components constituting the resin, i.e., processability derived from styrene, chemical resistance and excellent physical properties derived from acrylonitrile, impact resistance derived from butadiene, and optical property derived from methyl methacrylate. It is structurally similar to ABS, but uses methyl methacrylate, in addition to styrene and acrylonitrile used for ABS, as the shell component to be consistent with the refractive index of rubber used as the core, thereby providing a transparency.

The refractive index of the respective component is 1.516 to 1.518 for polybutadiene, about 1.49 for poly(methyl methacrylate), 1.592 for polystyrene, and about 1.52 for polyacrylonitrile. The *refractive index* (RI) of the grafting copolymer can be calculated according to

$$\mathrm{RI} = \mathrm{Wt}_A \cdot \mathrm{RI}_A + \mathrm{Wt}_S \cdot \mathrm{RI}_S + \mathrm{Wt}_M \cdot \mathrm{RI}_M$$

Where Wt_A = weight percent of acrylonitrile
RI_A = refractive index (1.52) of polyacrylonitrile
Wt_S = weight percent of styrene
RI_S = refractive index (1.592) of polystyrene
Wt_M = weight percent of methyl methacrylate
RI_M = refractive index (1.49) of poly(methyl methacrylate)

The composition of each respective component can be calculated so that the refractive index of the grafting copolymer as calculated from the above

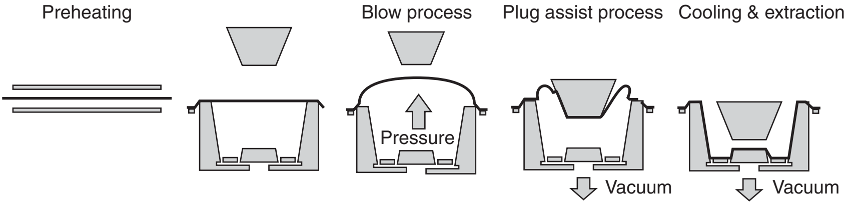


Figure 6.9 Vacuum forming process.

equation can be consistent with the refractive index of the rubber used as the core. Although the composition is varied depending on the kinds of rubber used as the core and the mechanical properties required for the final product, it is usually in the ratio of methyl methacrylate/acrylonitrile/butadiene/styrene = 30~60/0~10/10~20/20~40%. Transparent ABS has been produced by major ABS resin makers all over the world, including Toray, Denka, BASF, Chimei, and LG Chem., and the compositions and manufacturing methods differ according to the makers. Although the names may be differently designated, e.g., as transparent-(M)ABS, transparent HIPS, transparent MBS, etc., depending on the characteristic features, they are commonly called transparent ABS because there is no great difference in the overall basic properties.

ABS resin has excellent physical properties including impact strength as well as excellent processability. Transparent ABS is structurally similar to such ABS resin and therefore maintains the balance between mechanical properties and processability properties. Of course, although there is a small change in properties by providing the transparency, it maintains the balanced properties in comparison to other transparent resins.

Table 6.10 shows the general properties of transparent ABS. Since the characteristics differ according to the makers and the grades, only the most representative properties are listed. In addition, to show how the properties of the present transparent ABS are different from those of other transparent resins, the properties of the different kinds of transparent resins are also described.

One of the important properties in selection of the resins is the impact strength. As can be shown from Table 6.10, poly(methyl methacrylate) resin has excellent modulus and optical properties, but has the disadvantage that it may readily break due to a significantly low impact strength. To compensate for such a disadvantage, impact-resistant poly(methyl methacrylate) has been prepared using acrylate rubber. However, its impact strength is still below 5.

TABLE 6.10 Properties of Transparent Resins

	ASTM test	Unit	Transparent ABS	PMMA (general-purpose)	PMMA (impact resistance)	PC
Izod impact	D256	kg·cm/cm	15	1	4	> 30
Tensile strength	D638	kg/cm^2	430	720	570	870
Tensile elongation	D638	%	50	10	40	6
Flexural strength	D790	kg/cm^2	670	1300	1100	1400
Flexural modulus	D790	kg/cm^2	20,500	33,000	24,000	35,000
Processing temp.		°C	210	200	220	300
Total transmittance	D1003	%	90	93	91	89
Haze	D1003	%	2.0	0.5	1.0	1.0

Although there is some difference by grade, notched Izod impact strength of transparent ABS is about 10 to 20 kg·cm/cm, which is much higher than that of poly(methyl methacrylate). In the case of polycarbonate, the impact strength is excellent—at least 30 kg·cm/cm to at most greater than 60 kg·cm/cm. In addition, other physical properties, i.e., tensile strength and flexural strength, are also very high. However, since polycarbonate has poor processability in spite of excellent impact, tensile, and flexural strength, its application field is limited. There is a difficulty in using polycarbonate products for injection products having a complicated structure or large injection products. Different from other transparent resins, transparent ABS is a resin comprising the rubber phase, having T_g below –40°C. Therefore, transparent ABS exhibits ductile properties provided by the rubber phase and has relatively low rigidity, tensile strength, flexural strength, etc. In comparison to other transparent resins, the tensile strength is in the range of 350 to 550 kg/cm^2, and flexural strength is in the range of 500 to 850 kg/cm^2. Thus, as the rubber content is increased, tensile strength and flexural strength are decreased.

One of the most important advantages of transparent ABS is easy processability. Since transparent ABS has a processing temperature of about 210° and therefore can be readily processed by the general extrusion and injection, it has been used in various application fields. However, transparent ABS has the disadvantage that its optical properties are inferior to those of poly(methyl methacrylate) or polycarbonate because they are composed of a single component, and therefore have excellent optical properties. In transparent ABS, since the transparency is provided by controlling the refractive index of the matrix phase to be consistent with the refractive index of the rubber phase, there is a limit to the transparency. Since the refractive index is altered by monomers swelled on the rubber phase, it is difficult to make the refractive index of the matrix phase completely correspond to that of the rubber phase, resulting in a high haze. Although the haze value is being lowered as the technology is developed, transparent ABSs have mostly a haze value in the range of 1.5 to 2.5.

Before the year 2000, the transparent ABS business was not on a large scale, and no intense competition was present in the market. However, as it has been recognized that the transparent ABS is raising more concerns than other ABS resins, the number of companies that concentrate on the transparent ABS business have increased. To comply with such commercial situations and consumer demand, the transparent ABS makers concentrate their effort on the development of various grade products. The initial market of transparent ABS concentrates on the high-rigid-grade products having a notched Izod impact strength of about 10 kg·cm/cm, and the high-impact-strength grade products having an impact strength of 15 to 20 kg·cm/cm have been developed. Much functionality is added to introduce various products including flame-retardant grade, antistatic grade, *environmental stress chemical resistance* (ESCR) grade, and extrusion grade into the market. Such various grade products have been prepared by methods for changing the constitutional ratio of the transparent ABS resin, or for controlling the kinds of rubbers, particle size, gel content, and the composition ratio between resin and rubber, for controlling the grafting ratio or molecular weight of resin, and for changing the additives. Since it is necessary to vary the properties while maintaining the transparency, the variation range is relatively limited in comparison to other ABSs (Table 6.11). For example, in the case of the transparent ABS with flame-retardant functionality most commercially available grades are at the level of UL V-2. The reason is that the flame retardant lowers the transparency of ABS, and so the kinds and amount are limited. The antistatic-grade product includes product having a surface resistance of about $10^{11}\Omega$. Contrary to the general transparent ABS having a resistance value of about $10^{16}\Omega$, antistatic-grade surface resistance is lowered by using the antistatic agent. It can be used for semiconductor carriers, etc. The ESCR grade product is reinforced by controlling the molecular weight and gel content. In general, while the transparent ABS is characterized by weakness against chemicals in comparison to the general ABS, the ESCR grade is reinforced.

The transparent ABS is prepared by different methods by the makers, but is generally prepared by emulsion polymerization and bulk polymerization. Specifically, for transparent ABS, the grafting copolymer having a core-shell structure is prepared by emulsion polymerization; the ternary copolymer comprised of styrene, acrylonitrile, and methyl methacrylate is prepared by bulk polymerization; and then the two kinds of copolymers are mixed. The process is substantially identical to the process for preparing the general ABS, except that the composition is different. The grafting copolymerization is practiced by introducing the emulsifier, initiator, activator, and monomer into emulsified polybutadiene rubber; then the resulting copolymer thus prepared is passed

TABLE 6.11 Properties of Various Transparent ABSs

Grades (LG product)			General-purpose	High impact	ESCR	Antistatic
ASTM test		Unit	(TR-558A)	(TR-557)	(TR-552)	(TR-300)
Izod impact	D256	kg·cm/cm	11	15	25	10
Tensile strength	D638	kg/cm^2	500	430	390	430
Tensile elongation	D638	%	50	50	50	55
Flexural strength	D790	kg/cm^2	800	670	600	700
Flexural modulus	D790	kg/cm^2	23,800	20,500	17,700	22,000
Haze	D1003	%	1.5	2.0	2.4	5.0
Total transmittance	D1003	%	91	90	90	88
Flame class (UL certification)			HB	HB	HB	V–2

through a series of coagulation, dehydration, and drying procedures to obtain the product in powder form. The resulting powder is compounded together with styrene-acrylonitrile-methyl methacrylate terpolymer as prepared by bulk polymerization to produce the desired final product. Although the final product can be generally prepared by mixing powders having high rubber content, as prepared from the emulsion polymerization, with styrene-acrylonitrile-methyl methacrylate terpolymer, the transparent ABS powder having low rubber content may be prepared and then used by singly passing through the extrusion and injection procedures. In addition to the monomers used for polymerization generally including styrene, acrylonitrile, and methyl methacrylate, such monomers as α-methyl styrene and butyl acrylate can be used for providing the functionality.

Other products having properties similar to those of the transparent ABS, transparent HIPS, transparent MBS, etc., can be included. Since such similar products have the properties and qualities similar to those of the transparent ABS, the names used may be the same, but the manufacturing methods and compositions differ somewhat.

Although the transparent HIPS and the transparent MBS have no differences in their compositions, the difference in their names is caused by a difference in the manufacturing process. The transparent MBS is prepared by copolymerizing styrene and methyl methacrylate with emulsified poly(styrene-butadiene) rubber to prepare the grafting copolymer, which is then compounded with methyl methacrylate-styrene copolymer as prepared by bulk polymerization. Contrary to this, the transparent HIPS resin is prepared by introducing monomers (styrene, methyl methacrylate) and the solvent into solid poly(styrene-butadiene) rubber in bulk polymerization. The grafting reaction of rubber is continuously raised, and after polymerization, solvent and residual monomer are removed from the reaction mixture to obtain the desired resin. In this case, when the polymerization is practiced only by the bulk polymerization, the viscosity inside the reactor is increased such that the rubber content cannot be increased, and therefore, the product having high impact strength cannot be produced. To overcome such a disadvantage, the method may also be practiced in the manner of the bulk suspension reaction wherein bulk polymerization is practiced at the early stage of the reaction and then in the remaining stage the reaction is converted to the suspension reaction during the grafting process after phase transition.

As can be seen from Table 6.12, the transparent ABS uses polybutadiene rubber, whereas transparent HIPS or transparent MBS uses poly(styrene-butadiene) copolymer. Although such a difference in the rubber used does not have a great influence on properties, it creates a difference in the refractive index, which in turn creates a difference in the composition of the shell. The refractive index of poly(styrene-butadiene)

TABLE 6.12 Rubber-Toughened Transparent Resins

	Process	Refractive index	Rubber
Transparent ABS	Emulsion, bulk	1.51–1.52	Butadiene
Transparent HIPS	Bulk, bulk suspension	1.53–1.56	Styrene-butadiene
Transparent MBS	Emulsion, bulk	1.53–1.56	Styrene-butadiene

rubber is higher than that of polybutadiene rubber. Therefore, the transparent HIPS or transparent MBS uses much more styrene, having a high refractive index in comparison to the transparent ABS. Further, a difference in the T_g values of the rubbers creates a difference in impact resistance at low temperature. For the transparent ABS using polybutadiene rubber, the impact resistance at low temperature (measured at –30°C) is excellent, about 3 to 5 kg·cm/cm.

The transparent resin used commercially includes poly(methyl methacrylate) resin, polystyrene resin, SAN resin, polycarbonate resin, etc. Since these resins have both merits and demerits, their use is limited. Although polystyrene and SAN have very low impact strength, they are often used as the inexpensive transparent resin that does not demand certain impact strength, such as for toys, stationery, etc., due to their low price. Poly(methyl methacrylate) resin has very low impact strength, as does polystyrene resin or SAN, but can be used as the optical material for lenses, glass, CDs, etc., due to its excellent optical properties. Although polycarbonate has excellent transparency and excellent optical properties, and can be used for any purpose in view of these properties, its practical use is limited due to its high cost and poor processability.

The transparent ABS has the properties to the intermediate extent between said resins in mechanical, optical, and processability; therefore, it has been used for substantially various purposes. Specifically, it has been used for various fields including housings for electric home appliances such as washing machines and cleaners; OA supplies such as copiers, facsimiles, etc.; stationery such as ball pens; toy and medical appliances; and the like. Further, the use of transparent ABS has been expanded to the market of existing transparent resin. The toy market, which has used inexpensive SAN or polystyrene resin, has been converted to the transparent ABS or other materials as the uses of SAN and polystyrene are limited due to regulation under the consumer's protection law, such as the *product liability* (PL) law. The conversion of the materials to the transparent ABS can be shown similarly in the field of *polyvinyl chloride* (PVC) materials. As the use of transparent PVC resin, which has been employed for semiconductor carriers, etc., has been limited due to the environmental regulation, the conversion of this PVC resin to other materials has been researched. Transparent ABS, which has excellent processability and maintains the required impact resistance, has been regarded as the suitable alternative. According to development of the use under various regulations and consumer protection laws and further development of various grades of the products by transparent ABS makers, it is anticipated that the transparent ABS market will be continuously expanded for the next few years.

Heat-Resistant ABS

The heat-resistant polymer generally is also called a high heat temperature polymer or a thermally stable polymer, and it means the engineering plastic that can be processed or applied at high temperature. See Fig. 6.10.

As one of such heat-resistant polymers, heat-resistant ABS is a plastic having excellent processability and mechanical properties, and it is the product that can particularly be applied to the field requiring high heat resistance among the applications where coloring properties and gloss are demanded. As the major use, it is broadly applied to electric and electronic products and daily miscellaneous goods; further, it can be extensively applied to the interior and exterior materials of automobiles.

Although the heat-resistant ABS generally includes high heat grades having a heat resistance of 90 to 95°C and very high heat grades having a heat resistance of 100 to 105°C, heat-resistant ABS product having a heat resistance of 110 to 115°C has been commercialized for the special application requiring a superhigh heat resistance.

Contrary to the general-purpose ABS comprised of grafted ABS and styrene-co-acrylonitrile blend, heat-resistant ABS constitutes the final products by blending various kinds of styrenic matrix for providing heat resistance properties, that is, α-methyl styrene-co-acrylonitrile, α-methyl

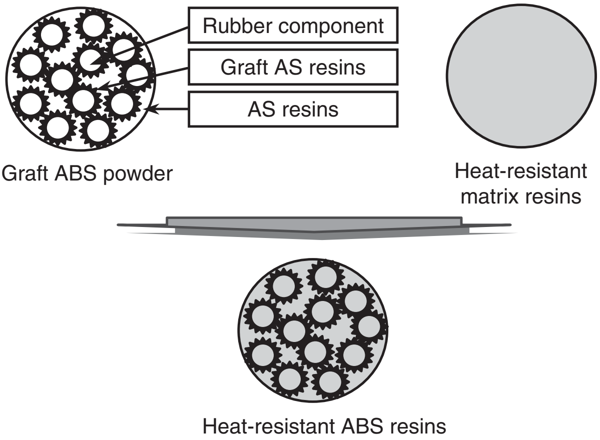


Figure 6.10 Composition of heat-resistant ABS.

styrene-co-methyl methacrylate styrene-co-maleic anhydride, SMA-MMA, phenyl maleimide, etc., with grafted ABS. See Table 6.13. Among these AMS-based SAN is primarily used to produce heat-resistant ABS. The method used for manufacturing AMS-based SAN is generally the emulsion polymerization method or the bulk polymerization method. The emulsion polymerization method can readily control styrene/acrylonitrile content and molecular weight, but includes a large amount of the reaction additives for polymerization, which may cause problems. SAN produced by the bulk polymerization method has excellent producibility, but it is relatively hard to control acrylonitrile and molecular weight in practice.

In the 1950s Borg-Warner, which first commercialized ABS, introduced the product having well-balanced mechanical and heat resistance properties by developing the ABS final product utilizing α-methyl styrene-co-acrylonitrile copolymer.

In the 1970s, different from the method for producing heat-resistant ABS by generally applying AMS-based SAN, the method for improving heat resistance properties and further providing excellent impact strength by applying styrene-co-maleic anhydride was reported by DOW Chemical.

In the 1980s, in the method for improving heat resistance properties and further providing melt flowability and surface properties, the AMS component, instead of styrene, is grafted onto the grafted ABS, which is then compounded with SAN. This is in contrast to the method for preparing heat-resistant ABS product by applying heat-resistant SAN.

Further, Monsanto developed the technology to prepare heat-resistant ABS having excellent mechanical properties and reinforced weatherability by introducing the terpolymer of styrene–maleic anhydride–methyl methacrylate into ABS to produce heat-resistant ABS, which has excellent heat resistance properties.

TABLE 6.13 Composition of Heat-Resistant Matrix

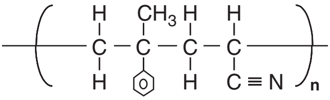
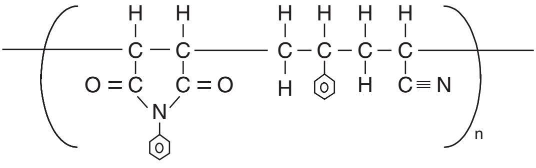
	Component
Copolymer of α-methyl syrene-acrylonitrile	
Terpolymer of PMI-styrene-acrylonitrile	

TABLE 6.14 Properties of Heat-Resistant ABS

Properties	ASTM measurement method	LG high HR ABS	LG very high HR ABS	LG super HR ABS	LG super HR ABS
Heat distortion temp., °C	D648 (18.5 kg/cm^2, 1/4 in)	96 (unannealed)	100 (unannealed)	107 (unannealed)	112 (unannealed)
Vicat softening temp., °C	D1525 (5 kg, 50°C/h)	103	107	116	118
Tensile strength, kg/cm^2	D638	500	480	500	500
Tensile elongation at break, %	D638 (50 mm)	25	20	25	20
Flexural strength, kg/cm^2	D790 (15 mm/min)	810	780	790	850
Flexural modulus, kg/cm^2	D790 (15 mm/min)	25,000	24,000	24,900	25,500
Impact strength, kg·cm/cm	D256 (23°C,1/8 in)	23	20	15	15
Melt flow rate, g/10 min	D1238 (220°C, 10 kg)	9	7	3	2
Flammability	UL-94 (1/8 in)	HB	HB	HB	HB

Recently, a great variety of superhigh *heat-resistant* (HR) ABS products utilize the imide-based matrix, which can provide improved heat resistance properties in comparison to AMS-based systems. See Table 6.14. Since the heat-resistant efficiency of the imide-based matrix is far superior to that of the AMS-based system, the production of heat-resistant ABS, which attains the desired extent of heat resistance and also can control the remaining properties, has been mainly accomplished by addition of a small amount of imide-based matrix.

However, the fact is that in comparison to ABS with AMS-based matrix only, ABS with imide-based matrix has superior heat resistance properties but has relatively poor fluidity and mechanical properties and therefore can only be used in a limited fashion. To overcome such problems, research in compatibility and thermodynamic studies of the ternary blend comprised of grafted ABS, SAN, and imide-based matrix is ongoing.

Weatherable ABS

The plastics are readily discolored primarily by ultraviolet rays. Although there is a difference in the extent depending on the kinds of plastics, the plastics incur deterioration or discoloration upon receiving high-energy light such as UV rays. The UV has high energy to make the material chemically unstable, and such an unstable state is readily combined with oxygen in the air to deteriorate the material, during which various chemical compounds are produced that cause discoloration of the material.

General ABS has excellent moldability and mechanical properties, but has poor weatherability due to the double bond of the butadiene rubber component used as the impact reinforcing agent. The double bond requires less energy to cleave one chain, in comparison to the single bond, and therefore is easy to discolor by oxidation. Therefore, in the environment directly receiving UV rays, such as outdoors, ABS resin sees a change in the appearance and color of the resin and exhibits a rapid deterioration of mechanical properties.

To prepare the resin having balanced properties by providing weatherability while maintaining several excellent properties of ABS resin, methods including addition of the ultraviolet stabilizer, painting, and metal plating may be adopted. However, it is not the essential improvement. Here, various resins have been developed wherein the butadiene component is removed as the cause of deterioration and, instead, the rubber containing no unsaturated bond is replaced.

The representative resin includes ASA resin using acryl rubber instead of butadiene rubber and AES resin using EPDM rubber. Those resins are for use outdoors without postprocessing such as painting and metal plating and have been reported to have comparable properties, moldability, and weatherability.

However, there are slight differences according to the manufacturing processes. In general, ASA is made by preparing acrylic rubber latex and then grafting SAN with emulsion polymerization; AES is prepared by two methods. One method is to dissolve EPDM rubber in a polar solvent and then graft SAN thereon to prepare AES. The second method works by reacting EPDM rubber with SAN during the extrusion procedure to prepare AES.

In comparison to AES prepared in the polymerization, AES prepared by grafting SAN in the extrusion procedure may reduce the manufacturing cost by simplification of the procedures, but has the disadvantages that (1) it is somewhat inferior in view of the properties and weatherability, and (2) the use of polar solvent makes the procedure complicated and induces environmental problems. Particularly, due to low gloss of AES, it can be limited to applications in the electric and electronics fields and therefore cannot be widely used in comparison to ASA resin.

Therefore, at present the demand for ASA as the weatherable resin is great all over the world. Moreover, recently ultraweatherable ASA resins having heat resistance and surface properties, processability, and weatherability are being developed.

ASA resin

ASA resin is a terpolymer formed by graft polymerization of acrylonitrile and styrene onto acryl rubber, and it is opaque. By adjusting the composition of acrylonitrile, acryl rubber, and styrene and the grafting ratio, a resin having high impact strength and excellent fluidity in molding can be prepared.

In comparison to ABS resin, ASA resin has somewhat greater specific gravity, somewhat less tensile strength, and somewhat greater elongation. The other properties of ASA are comparable to those of ABS.

For weatherability it has been reported that after outdoor exposure of ASA resin, there is extremely little deterioration of the mechanical properties such as impact and elongation, and there is substantially no change in appearance. ASA resin can endure the conditions of outdoor use for a long time in comparison to the general-purpose resin.

In addition, ASA resin has excellent molding processability and is molded under the same molding conditions as is ABS resin. Particularly, since the fluidity of ASA resin is superior to that of a high rigid ABS resin, the large product with small thickness is more easily processed with ASA resin than with ABS resin. Further, since ASA resin has excellent elongation, it is suitable for processing parts requiring deep design.

ASA resin has been sold as the flame-retardant grade and finer glass-reinforced grade, which can be used in broad applications. ASA resin has seen use in substantially the same application fields as ABS resin, and particularly has been developed mainly for the outdoor product which demands the weatherability:

1. Fields related to electricity: switch case, housing (washing machine, refrigerator, ventilator, pump, room cooler, etc.), fluorescent lamp, mercury lamp cover, antenna cover, door horn, metacover
2. Fields related to automobiles: headlight body, radiator grill, limp body, parts of farming machines
3. Others: industrial articles, bolts, signal boards, parts of fire extinguishers

AES resin

AES resin has excellent heat resistance, impact resistance, and weatherability, as do other weatherable resins. For example, after standing at 88°C for 14 h, the strength of AES resin according to the Izod impacting method is lowered only by 5 to 8%, whereas the strength of ABS resin is greatly lowered by about 30 to 40%. In addition, under the same conditions the falling weight impact strength of AES resin shows excellent maintenance in comparison to ABS resin. Further, the capacity of AES resin having oxidation resistance, yellowing resistance, etc., is sufficiently superior to that of ABS resin.

In general, although EPDM rubber is more expensive than polybutadiene rubber, the amount of EPDM rubber used in AES resin is as low as about 60% of the content of polybutadiene used in ABS resin, and therefore, the price of AES resin as a whole may be somewhat competitive. In addition, since the moldability of AES resin is somewhat better than that of ABS resin, AES resin can be regarded as having high possibility of use if the environmental problem as mentioned above can be solved.

ACS resin

Since ACS resin contains chlorine, it has excellent properties including flame-retardant and antistatic properties as well as weatherability. It has the pale yellow, translucent or white opaque, glossy appearance, and the properties of the resin are substantially similar to those of ABS resin, with the impact strength being somewhat high. Since the weatherability of ACS resin is excellent, as the falling weight impact maintenance of about 60% after 2 years of outdoor exposure and the elongation maintenance of about 50% even after 1000 h illustrate, this resin can be used for 6 to 7 years or more if some stabilizer is added.

Particularly, it has been shown that the flame-retardant property of ACS resin is sufficiently good for use in the hot-wire ignition and high-voltage arc ignition test. In addition, the fact that general plastic resin has excellent electric insulating properties and hygroscopic resistance generally creates the disadvantage that the resin is easy to charge. To the contrary, ACS resin has a great advantage in that it is difficult to charge and there is substantially no surface contamination with dust.

The processing of ACS resin uses the same molding conditions as for ABS resin, HIPS, etc. However, since ACS resin contains chlorine, and it is easy to cause thermal decomposition at high temperature, careful attention must be paid. Therefore, in the injection-molding process, the cylinder temperature is set not to exceed 220 to 230°C, and long-term retention in it must be avoided. In addition, in the extrusion-molding process there is a necessity for strictly establishing the die temperature at 190 to 220°C. Secondary processing such as adhesion, hot stamping, and painting can be practiced in the same manner as for ABS resin. In conclusion, the effect of ACS resin can be maximized when this resin is used for the product that simultaneously demands both flame resistance and weatherability.

LG ASA

ASA resin exhibits somewhat low impact strength and significantly deteriorated staining properties compared to ABS resin. Therefore, ASA resin has limited use. However, the product has far superior weatherability while maintaining the advantages of ABS resins, as they are recently developed by multilayer structure technology.

Chapter 7

Polybutylene Terephthalate (PBT)

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Introduction

Polybutylene terephthalate (PBT) resin is a semicrystalline thermoplastics polyester derived from 1,4-butanediol with either terephthalic acid or dimethyl terephthalate (see Fig. 7.1). The commercial production of PBT compound for engineering plastic applications was started in the United States by Celanese in 1970 and grew rapidly as it found utility in various applications, most commonly in the automotive, electrical, and electronics industries. As engineering thermoplastic polyesters, polyethylene terephthalate (PET) compounds are also produced. Because of rapid crystallization and easy processing, PBT compounds are more popular engineering thermoplastics than other polyesters. The main difference between PBT and other commercial polyesters is its fast crystallization characteristics. This ability to crystallize very fast allows fast cycle times during injection molding, and complete crystallization during molding leads to high productivity [1].

PBT is noted for its high heat resistance, stiffness and hardness, excellent electrical properties, and good resistance to environmental influences. PBT resins are high-performance engineering thermoplastics that can be used in a variety of applications, most commonly in functional components and structural parts that are formed by injection molding. In addition to unfilled neat PBT grades, impact-modified, glass-reinforced, mineral-filled, flame-retardant grades and blends based on PBT are

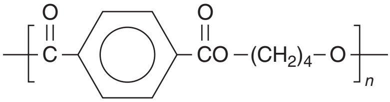

Figure 7.1 The chemical structure of polybutylene terephthalate.

commercially available. PBT can be tailored to various applications by blending it with other components (PBT/PC, PBT/PET, PBT/ABS).

Table 7.1 shows a list of suppliers of PBT compounds with their trade names. The thermoplastic resins cover a range, such as PBT, PC, polyamide, polyacetal, and modified PPO. They can be classified in accordance with their crystalline state: semicrystalline (PBT, polyamide, and polyacetal) and amorphous (PC and modified PPO). Semicrystalline thermoplastic shows balanced physical properties as well as heat and chemical resistance. Among the semicrystalline engineering polymers, polyacetals exhibit the highest crystallinity, and this structure shows high stiffness, good creep resistance, and a low friction coefficient. While polyacetal has balanced mechanical properties, it shows lower melting point and flammable moiety compared to PBT and polyamides. The main difference between polyamide and PBT is the moisture absorption rate. The higher moisture absorption rate of polyamide is unfavorable to some applications that require high dimensional stability. For low moisture absorption, PBT resin has a more consistent property that shows little change in dimensional, physical, and electrical properties as a function of environmental factors. In Table 7.2, some important properties for various semicrystalline engineering plastics are summarized.

Chemistry of PBT

PBT polymer is commercially produced by polycondensation reaction between 1,4-butanediol and *terephthalic acid* (TPA) or 1,4-butanediol and

TABLE 7.1 Manufacturers and Trade Names of PBT Resins

Manufacturer	Trade name
BASF	Ultradur
Bayer	Pocan
DSM	Arnite
DuPont	Crastin
GE Advanced Materials	Valox
LG Chem, Ltd.	Lupox
Mitsubishi EP	Novadur
Ticona	Celanex
Toray	Toray PBT
WinTech Polymer	Duranex

TABLE 7.2 Properties of PBT Compared with Other Semicrystalline Engineering Thermoplastics

Property	Unit	PBT* (neat)	PBT[†] (GF 30%)	Nylon 6[‡] (neat)	Nylon 6[§] (GF 33%)	POM[¶] (neat)
Specific gravity	—	1.31	1.52	1.13	1.30	1.41
Tensile strength	MPa	54	120	80	190	61
Elongation at break	%	100	3	130	3	65
Flexural strength	MPa	83	175	110	275	89
Flexural modulus	MPa	2250	7650	2700	9000	2550
Izod impact strength (notched)	J/m	35	75	50	130	70
HDT (1.82 MPa)	°C	57	210	60	210	110
HDT (0.45 MPa)	°C	154	215	170	220	160
Melting point	°C	225	225	225	225	165
Water absorption	%	0.08	0.07	1.7	1.1	0.2

* Lupox HV-1010 LG Chem, Ltd.
[†] Lupox GP-2300 LG Chem, Ltd.
[‡] Lumid GP-1200A LG Chem, Ltd.
[§] Lumid GP-2330A LG Chem, Ltd.
[¶] Lucel N109-LD LG Chem, Ltd.
SOURCE: Engineering Plastics Technical Brochure, LG Chem [21].

dimethyl terephthalate (DMT) in the presence of esterification catalyst [2, 3]. The monomers are produced by a number of different commercial processes. Terephthalic acid, dimethyl terephthalate, and 1,4-butanediol are commercially obtained from petrochemical feedstocks such as *para*-xylene and acetylene.

Polymerization

The polymerization of PBT requires a two-step reaction process (see Fig. 7.2). The first stage is an esterification reaction of 1,4-butanediol with TPA or transesterification reaction of 1,4-butanediol with DMT, forming *bis-hydroxybutyl terephthalate* (BHBT). When only one terephthalate unit exists per molecule, the BHBT is formed. But in reality, the transesterification stage produces not only BHBT, but also a number of oligomers containing two or more terephthalate units. Depending on the molar ratio of 1,4-butanediol to DMT or TPA charged into the first reaction, the relative amounts of BHBT and its oligomers may be altered. A lower ratio will generate an excessive amount of oligomer, while a higher ratio of 1,4-butandiol will result in a reaction product with BHBT dominating mixtures (see Fig. 7.3).

The transesterification reaction by-product—water when TPA is used or methanol when DMT is used—is removed during reaction. The second stage is a polycondensation step, in which the prepolymer BHBT formed in the first stage undergoes further polymerization in the melt phase. The two reaction stages can be easily differentiated by the by-product types:

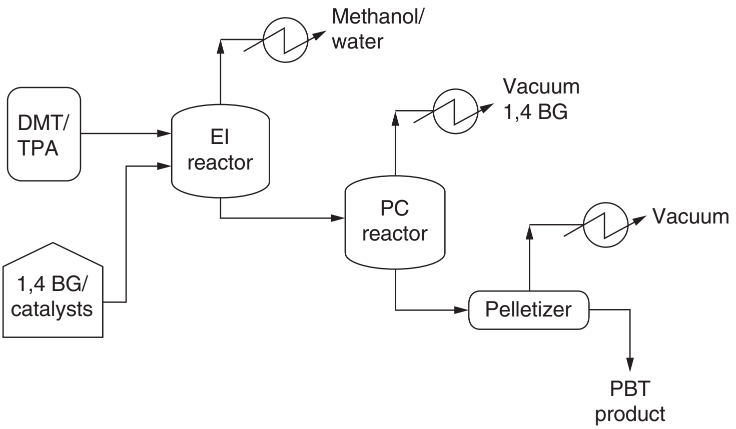

Figure 7.2 Schematic of a polybutylene terephthalate manufacturing flowchart.

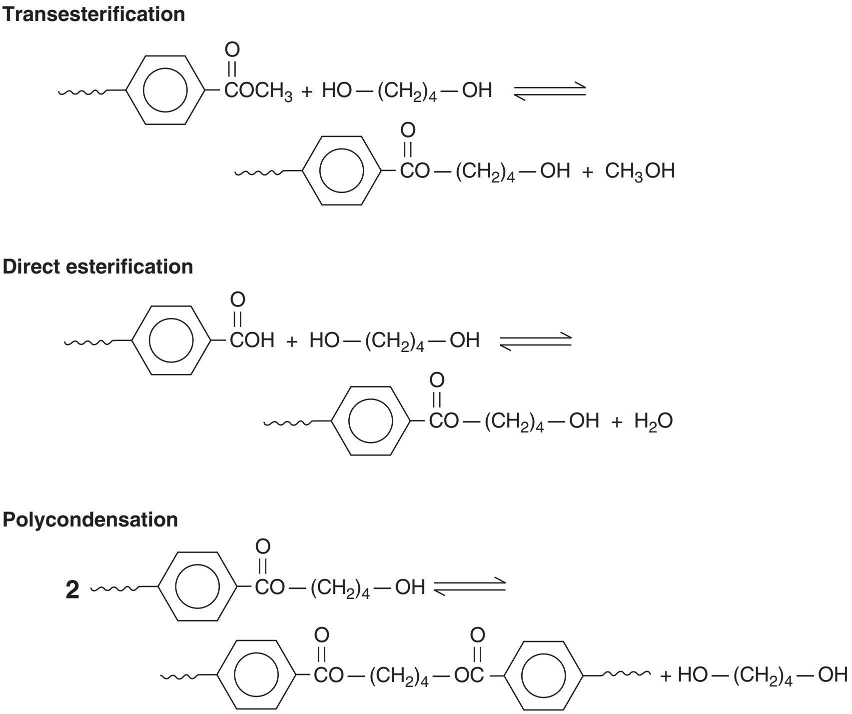

Figure 7.3 Synthesis of PBT via esterification and polycondensation reactions.

methanol or water during transesterification reaction, with 1,4-butanediol during second polycondensation stages. The catalyst is usually applied during reaction; the preferred catalysts are organotitanium or organotin compounds. The most commonly used catalysts for PBT are tetra alkyl titanates. The by-product 1,4-butanediol is removed from the melt by mixing the melt and by using vacuum. Through the elimination of excess 1,4-butanediol, a number-average molecular weight of up to 30,000 g/mol is attainable. Owing to the high temperatures during the second stage, oxidative thermal decomposition and yellowing occur. These decomposition reactions place the upper limit on the molecular weight that can be realized by the normal melt condensation reaction. High-molecular-weight PBT grades for extrusion applications are typically produced by further polycondensation in an additional solid-state process at temperatures 15 to 40°C below the melting temperature of PBT and under vacuum or in an inert gas atmosphere (see Fig. 7.4). The solid-state reaction is carried out separately, generally minimizing the degradation and discoloration of high- molecular-weight PBT [4, 5].

Commercial process

For commercial PBT polymerization, both batch process and continuous process can be used. When a variety of different grades of PBT are needed, a batch process is preferred; however, for large commercial production of PBT of more than 20,000 metric ton capacities, a continuous process is more economical.

Due to different residence times needed for the reaction steps, the industrial batch processes are typically run in multiple reactors. Usually two reactors are involved, an *ester interchange* (EI) reactor designed to extract methanol or water and a *polycondensation* (PC) reactor designed to drive the polymerization and build molecular weight by removing excess 1,4-butanediol as well as volatile by-products. During EI reaction the

Melt polymerization

Direct/Transesterification

$\text{TPA} + 2\ \text{Butanediol} = \text{BHBT} + 2\text{H}_2\text{O}$

$\text{DMT} + 2\ \text{Butanediol} = \text{BHBT} + 2\text{CH}_3\text{OH}$

Polycondensation

$\text{BHBT} + \text{BHBT} = \text{PBT}_2 + \text{Butanediol}$

$\text{PBT}_n + \text{PBT}_m = \text{PBT}_{n+m} + \text{Butanediol}$

Solid-state polymerization

$\text{PBT}_n + \text{PBT}_m = \text{PBT}_{n+m} + \text{Butanediol}$

Figure 7.4 Reaction equations for the polymerization of PBT.

temperature is increased to about 210°C, and the pressure is controlled at about ambient conditions. The esterification by-product—water or methanol—is removed via a process column during reaction, while 1,4-butanediol is refluxed. In the PC stage polycondensation is the equilibrium reaction, to shift the chemical equilibrium to the polymerization side. The by-product 1,4-butanediol is removed via vacuum. The final molecular weight of PBT can be controlled by either setting the reaction time to a predetermined value or by stopping the reaction at a fixed melt viscosity level. After the PI reaction, the reactor vessel is emptied by inert gas pressure or mechanical gear pump, and the final PBT strands are cooled by water and cut into granules. During the batch process, by controlling the reaction time, monomer types and contents, additives, and reaction conditions, a variety of different molecular weights and specific grades of PBT are easily attainable.

Continuous processes involve a series of continuous reactors followed by finishing reactors. In most commercial processes, the melt-phase reactions are performed by three to five (or even more) continuous reactors—the one or two esterification reactors, one or two polycondensation reactors, and high-viscosity finishing reactors. The series of reactors are used to gradually extract by-product such as *tetrahydrofuran* (THF), methanol, and water. Pressure is also gradually reduced with a series of reactors as the polycondensation reaction goes further and 1,4-butanediol is removed from the reactor. In finishing reactors, the volatile by-products and excess 1,4-butanediol are removed under vacuum. The final PBT polymer is discharged from the finisher by pumping, water-cooled, and pelletized to a size. The melt polymerization process can be used to make a variety of molecular weight PBT grades. The higher-molecular-weight grades are generally made by using the solid-state process under inert gas or vacuum, or are produced by melt polymerization equipped with special mixing devices designed for high-melt-viscosity agitation during removal of by-products. In the commercial process, additional solid-state polymerization may be carried out in three ways, which are under vacuum, under a stream of inert gas, and in a fluidized bed under inert gas.

PBT is produced from both terephthalic acid and dimethyl terephthalate with 1,4-butanediol. Most commercial PBT grades are initially developed with DMT because the TPA process generates a larger amount of tetrahydrofuran by-product and DMT is easier to purify than the TPA. Also, the higher solubility of the DMT allows a handling convenience and faster reaction rates in the transesterification stage with lower boiling point of methanol rather than water. The DMT process produces lower amounts of THF, a by-product formed by the irreversible acid-catalyzed dehydration of 1,4-butanediol, compared to the TPA process. However, in the commercial continuous process, more and more processes have shifted to TPA as the feedstock. In the newly developed TPA process, THF by-product formation is largely diminished to approximately 13 mol %, compared to 6 mol % in the DMT process. The TPA process has economic benefits of lower raw material cost of TPA compared to DMT. The process is commercially feasible because THF by-product is easier to separate from water (TPA process) than from methanol (DMT process), and energy consumption and investment costs are lower for the TPA process. Some manufacturers make a variety of different molecular weight resin grades by melt polymerization. But other suppliers, especially those with continuous plant, make a couple of low-molecular-weight and high-molecular-weight grades, and during the following compounding, a range of molecular weight grades are made by combining different ratios of these low- and high-molecular-weight PBT grades. In the commercial continuous process, combination of low- and high-viscosity resins for the intermediate-viscosity grades has more practical benefits compared to making all viscosity range grades in the polymerization reactor.

Properties of PBT and PBT Blends

By adding reinforcing agents and impact modifiers, the inherent low creep, dimensional stability, and good electrical properties of PBT polyester can be enhanced to provide a range of grades with high strength, stiffness, and toughness [6]. Alloying with other polymers and adoption of the proper reinforcement technology can also improve the dimensional stability and surface appearance of PBT. By making technical modifications, a wide range of PBT grades are available that can be adapted to a variety of industrial applications.

Reinforcement of PBT

The properties of PBT resins can be improved by reinforcements, resulting in higher modulus, strength, and heat deflection temperature under load. The properties of reinforced PBT grades are affected by factors such as the types and content of reinforcement and the average size and distribution of fillers. The reinforcing fillers are selected based on desired performance and part cost. The most important reinforcing fillers added to PBT resins are surface-treated short glass fibers. Reinforcing with short glass fiber gives PBT with improved stiffness and higher heat deflection temperature. Figure 7.5 illustrates the temperature dependence of modulus of PBT reinforcement and heat deflection temperature. Besides glass fibers, glass flake, milled glass, and other mineral fillers are used for reinforcement.

The flexural modulus and strength of PBT can be significantly increased through reinforcement with short glass fibers. Surface-treated glass fibers with a diameter of 9 to 14 μm and length of 3 to 6 mm are generally introduced to the PBT during melt mixing. During the melt

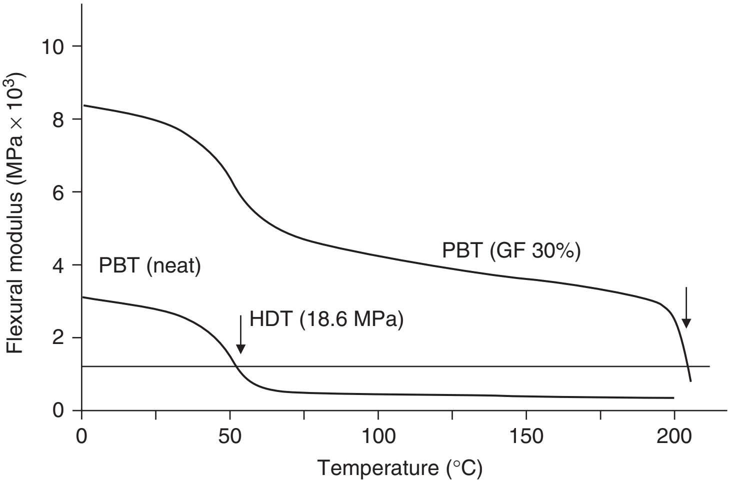

Figure 7.5 Heat deflection temperature and modulus for PBT.

compounding and molding process, glass fiber breakage occurs and results in an average size of 0.2 to 0.4 mm in the molded product. The properties of short glass-fiber-reinforced grades show a much higher flexural modulus and tensile strength but lower elongation at breakage compared to the unfilled PBT. The reinforcements of glass fiber have some drawbacks such as reduced flow, poor surface appearance, and increase of part densities. The overall shrinkage values of glass-fiber-reinforced grades will be decreased [7]. Usually, reinforced glass fibers are not randomly oriented in a molded sample and so result in some directional part anisotropy. The part shrinkage values are different in the flow and perpendicular directions, with the highest orientation in the flow direction, which can lead to warpage problems.

Dimensional stability and anisotropy are the main reasons why mineral filler or glass fiber/mineral hybrid reinforced PBT grades have been developed. Common mineral fillers are talc, mica, silica, clay, wollastonite, glass sphere, glass flake, and milled glass fiber. Mineral fillers are added to PBT to improve stiffness and dimensional stability and to reduce shrinkage. Mineral reinforcements increase the flexural modulus and strength but are inferior to fiber-reinforced compounds. Mineral fillers reduce thermal shrinkage values as a function of loading amount and are added to enhance dimensional stability. Combinations of glass fiber and plate-shaped mineral fillers, hybrid reinforced grades, are often used to balance warpage characteristics and mechanical properties. These properties are in between those of glass-fiber-reinforced and mineral-reinforced grades. Table 7.3 shows summary of physical properties for typical types of reinforced PBT resins.

TABLE 7.3 Effect of Reinforcement on Properties of PBT

Property	Unit	Neat* (0 wt%)	GF[†] (15 wt%)	GF[‡] (30 wt%)	MF[§] (25 wt%)	GF/MF[¶] (40 wt%)
Specific gravity	—	1.31	1.41	1.52	1.54	1.60
Tensile strength	MPa	54	95	120	55	95
Elongation at break	%	100	4	3	4	7
Flexural strength	MPa	83	145	175	95	150
Flexural modulus	MPa	2250	4900	7650	5100	7800
Izod impact strength (notched)	J/m	35	60	75	30	75
HDT (1.82 MPa)	°C	57	200	210	110	195
HDT (0.45 MPa)	°C	154	210	215	200	210
Mold shrinkage	%	1.2–2.1	0.4–1.1	0.3–1.0	0.5–1.2	0.3–0.6

* Lupox HV-1010 LG Chem, Ltd.
[†] Lupox GP-2150 LG Chem, Ltd.
[‡] Lupox GP-2300 LG Chem, Ltd.
[§] Lupox SG-3250 LG Chem, Ltd.
[¶] Lupox LW-5402 LG Chem, Ltd.
SOURCE: Lupox PBT brochure and data sheets [20].

Polymer blending

Polymer blending is a method in which desired properties can be obtained from at least two polymer components. The main reason for PBT blending with other polymer is the development of new materials with improved performance and cost efficiency to meet actual applications. The most common commercial method for producing PBT blend is a melt compounding process, due to its simplicity and cost efficiency. The PBT blending can extend the material range with tailored properties and make possible new market applications without heavy investment related to development and manufacturing of new polymers. PBT itself is relatively tough and ductile in the unnotched state but shows a brittle fracture behavior with notches or surface defects. The improvement of impact strength can be achieved by combination of various rubber impact modifiers. PBT is also blended with amorphous polymers, to increase dimensional stability and overcome some drawbacks of PBT.

The PBT blend with PC was originally developed to combine the high temperature and chemical resistance of semicrystalline PBT with the mechanical property and dimensional stability of amorphous PC resins. PBT/PC blends, often in combination with impart modifier, such as LUPOX TE brand by LGC and many grades from other chemical companies including GE, Bayer, and BASF, are used in automotive applications such as bumper systems and exterior parts. PBT blends with amorphous polymers such as PC, ABS, and ASA reduce mold shrinkage and improve dimensional stability but give a reduction in chemical resistance and high-temperature property. In the case of glass-fiber-reinforced

TABLE 7.4 Typical Properties of PBT and Blend Resins

Property	Unit	PBT/PC	PBT/PC	PBT/ABS	
		PBT*	alloy[†]	alloy[‡]	alloy[§]
Specific gravity	—	1.31	1.22	1.21	1.07
Tensile strength	MPa	54	45	55	49
Elongation at break	%	60	100	100	30
Flexural strength	MPa	83	75	80	90
Flexural modulus	MPa	2250	1950	2050	3230
Izod impact strength (notched)	J/m	30	650	600	170
HDT (1.82 MPa)	°C	57	95	100	85
HDT (0.45 MPa)	°C	154	110	115	95
Mold shrinkage	%	1.2–2.1	0.7–1.0	0.7–0.9	0.5–0.8

* Lupox GP-2000 LG Chem, Ltd.
[†] Lupox TE-5011 LG Chem, Ltd.
[‡] Lupox TE-5000G LG Chem, Ltd.
[§] Lumax HF-5008 LG Chem, Ltd.
SOURCE: Lupox PBT brochure and data sheets [20].

blends, the amorphous resin components reduce warpage of PBT. The primary purpose in blending PBT with amorphous ABS is to combine the good chemical resistance and mechanical properties of PBT and the high impact strength and dimensional stability of ABS. These blends may have the possibility of replacement of more expensive PC/ABS blends in automotive and electronic applications. Typical properties of PBT blends are summarized in Table 7.4.

Blends of PBT and PET are also commercially available, mostly as glass fiber and/or mineral filler reinforced grades. Since PET has a much lower crystallization rate than PBT, the molded products from these blends show improved surface characteristics. The other advantages of PBT/PET blends compared to general-purpose reinforced PBT include higher stiffness and temperature performance with good cost performance. It is known that exchange reactions take place between PBT and PC during high-temperature melt processing [8–13]. Transesterification reaction is influenced by many factors including residual catalyst and content of end carboxyl groups of PBT. The reaction rate also increases with temperature and residence time during the molding process. In general, addition of certain stabilizers is used to suppress the transesterification reactions. Table 7.5 summarizes some PBT blends with other polymers.

Chemical resistance

Chemical resistance of thermoplastics is dependent on a number of parameters, including temperature, time, residual mold stress, and external stress to which the part is subjected in given use conditions. Generally,

TABLE 7.5 Summary of PBT Blend Systems

Types	PBT blend	Property
Crystalline	PBT/PET	Surface gloss, trans reaction
Amorphous	PBT/PC	Impact strength, dimensional stability, toughness, trans reaction
	PBT/ABS	Low warpage, impact strength
	PBT/PPE	Heat resistance, dimensional stability
	PBT/PS	Dimensional stability
Impact modifier	PBT/TPU	Impact strength, chemical resistance
	PBT/elastomer	Low-temperature impact strength

parts molded with semicrystalline polymers will be more chemically resistant than amorphous polymers. The semicrystalline character and the chemical structure of PBT ensure a good resistance to many chemical substances. PBT thermoplastics are characterized by their excellent resistance to organic solvents such as aliphatic hydrocarbons, petroleum, alcohols, oils, ether, detergents, and chlorinated hydrocarbons at room temperature. The material is also resistant to weak acid, weak base, water, and most aqueous salt solutions. However, PBT is not resistant to strong acids and bases, phenols, or strong oxidizing acids. Above the glass transition temperature of PBT, the polymer becomes more sensitive to the effects of aromatic hydrocarbons and ketones. However, PBT is resistant to a typical automotive fluid like petroleum, greases, engine and transformer oils, or brake fluid, even at high temperatures. Table 7.6 shows an overview of the resistance against various chemicals. Product design, processing methods and equipment, and other parameters may affect the actual chemical resistance of a molded part. The true chemical resistance of specific applications should be tested in each specific use condition before commercial production.

Hydrolysis resistance

Under some conditions, the interaction of PBT with water can cause hydrolytic degradation and give loss of molecular weight. With loss of molecular weight, the PBT thermoplastics will lose properties and become brittle. The combination of high temperatures and high moisture content affects the properties of PBT to a serious degree. The hydrolytic degradation can also be accelerated by acidic or basic conditions. The number of free carboxylic end groups in the PBT molecule also influences the hydrolytic resistance [14, 15]. There are two major classes of water exposure: One is the presence of moisture in a molten state during melt processing, and the other is exposure of a molded part to water during its actual use. During melt processing at high temperature, moisture will react very quickly with

TABLE 7.6 Chemical Resistance of PBT

Chemical	Concentration (%)	23°C	60°C	80°C
Acetic acid	5	O	P	X
Acetic acid	—	O	P	X
Brake fluid	—	O	O	—
Cresol	—	X	X	X
Diesel oil	—	O	O	O
Ethanol	—	O	P	X
Ethyl acetate	—	O	X	—
Freon 11	—	O	—	—
Glycerol	—	O	O	P
Heptane	—	O	O	O
Hexane	—	O	O	O
Hydraulic oil	—	O	O	—
Lubricant	—	O	O	O
Methanol	—	O	P	—
Mineral oils	—	O	O	O
Motor oils	—	O	O	P
NaOH	10	X	X	X
Octane	—	O	O	O
Olive oil	—	O	O	O
Paraffin oil	—	O	O	O
Petroleum	—	O	O	O
Petrol, regular	—	O	O	O
Phenol	—	X	X	X
Seawater	—	O	O	X
Silicone oils	—	O	O	O
NaCl	10	O	O	X
H_2SO_4	5	O	O	X
H_2SO_4	25	O	P	X
Toluene	—	O	P	X
Vegetable oils	—	O	O	O
Xylene	—	O	X	X

O: resistant, no or slight weight change; P: partially resistant, extended use of the chemical may cause crack or craze; X: unstable, remarkable decrease in mechanical properties.

SOURCE: Lupox PBT brochure and data sheets [20].

the polyester chain, thus lowering the molecular weight of the PBT. Above the melting point of the PBT, the hydrolysis reaction proceeds very rapidly, even within a few seconds. If undried PBT with enough moisture content is exposed to melt processing conditions, molecular weight or viscosity will drop and properties will be lost to some degree. However, there is not enough water present at this high temperature to give catastrophic degradation, but by losing PBT molecular weight in processing wet resin, one is sacrificing some of the ultimate part performance. This shows the needs to melt-process PBT at very low moisture levels. Moisture content below 0.03% prior to melt processing is generally recommended for PBT.

In cold water below the glass transition temperature of PBT, little reaction is observed and the molded part will not be affected by water exposure. Long-term exposure of molded solid PBT parts to hot water will give some degree of hydrolytic decomposition. The resistance to hot water can be extended through the use of various technologies to suppress hydrolysis. The hydrolysis resistant modified PBT grades will give some degree of extended life to molding parts exposed to high-temperature and high-humidity atmospheres compared to a standard PBT. For some applications it might be necessary to use those grades of PBT that have been specially stabilized against hydrolysis. Those grades normally have only a small amount of carboxylic end groups and are technically modified to make them resistant to hydrolysis.

Flammability

PBT has a limiting oxygen index of about 20 to 23% and is fairly combustible. It is classified as *horizontal burning* (HB) according to UL-94. Flame resistance is a primary requirement for electrical and electronics applications. For applications that require flame resistance, flammability degree is usually achieved by compounding a flame-retardant material that will generate flame-retarding ingredients on burning. Usually flame-retardant PBT grades consist of a halogen-containing organic compound and some inorganic synergists. It is well known that addition of antimony compounds, such as antimony trioxide, gives a strong synergy when used with halogen-containing compounds [16, 17]. Bromine is widely used as the primary flame-retardant ingredient and antimony trioxide as a synergist. Most flame-retardant PBT grades contain from 10 to 25% of flame-retardant ingredient mixtures and have a ULV-0 rating at 0.8-mm or 1.6-mm thickness. Small molecule bromine ingredients such as polybrominated diphenyl (PBD), *polybrominated diphenyl ether* (PBDE), and ethylene bis-tetrabromophthalimide are efficient sources of halogen but may result in blooming during molding and high-temperature use conditions. Polymeric flame retardants such as brominated epoxy, brominated polycarbonates, and brominated poystyrenes are widely used for PBT as non blooming or “non-bleed-out” flame retardants.

There is also concern about the environmental regulations of halogenated *flame-retardant* (FR) additives with respect to recycling and the possibility of release of toxic ingredients on burning. These issues resulted in a growing interest in halogen-free flame-retardant PBT grades [18]. However, halogen-free flame-retardant systems for thermoplastics have their disadvantages. Inorganic flame retardants must be used at high loading levels, which influence the product’s physical properties. Nitrogen-based systems, such as melamine cyanurate, have limited effectiveness in thermoplastics; melamine cyanurate is not effective by itself in PBT.

TABLE 7.7 Properties of Flame-Retardant Glass-Fiber-Reinforced PBT

Property	Unit	Halogen FR* (GF 30%)	Nonhalogen† (GF 30%)	Nonhalogen‡ (GF 30%)
Specific gravity	—	1.62	1.60	1.70
Tensile strength	MPa	130	120	110
Elongation at break	%	3	3	3
Flexural strength	MPa	190	180	170
Flexural modulus	MPa	8500	9500	1100
Izod impact strength (notched)	J/m	80	70	60
HDT (1.82 MPa)	°C	210	210	200
HDT (0.45 MPa)	°C	215	215	210
Flammability	UL-94	V-0	V-0	V-0

* Lupox GP-2306F, LG Chem, Ltd.
† Lupox GN-2306F (with red P), LG Chem, Ltd.
‡ Lupox GN-2308F (without red P), LG Chem, Ltd.
SOURCE: Lupox PBT brochure and data sheets [20].

Flame-retardant systems that combine nitrogen and phosphorus, such as ammonium polyphosphate or melamine phosphate, do not have sufficient thermal stability for melt processing of PBT resins. Phosphorus-based systems are generally effective in imparting flame retardancy to amorphous thermoplastics such as PC/ABS blends and modified polyphenylene oxide. In PBT resins, these ingredients must be added at such high levels to obtain V-0 class that physical properties are negatively affected. Surface-treated red phosphorus is successfully used as an effective halogen-free flame retardant for FR PBT. Red phosphorus systems have very high active P components but may have a color limitation. Only a few successful developments have been carried out in this field. While halogen-free flame-retardant polyamide products have already been used in the market, corresponding PBT grades are still at the beginning stage. Table 7.7 shows a summary of properties of some flame-retardant, glass-fiber-reinforced PBT grades.

Processing of PBT

The melt of polybutylene terephthalate shows a low viscosity and very fast crystallization, hence allowing for easy processing. PBT resins can be processed by using conventional processes such as spinning, extrusion, injection molding, and gas-assisted injection molding. Injection molding is the processing method that is used most frequently for PBT compounds and its alloys. Processing is simple, with good flow properties leading to fast cycle times by using standard injection-molding machines [19]. Postmolding operations such as welding, fastening, and gluing are also easy, as are printing, painting, and laser marking.

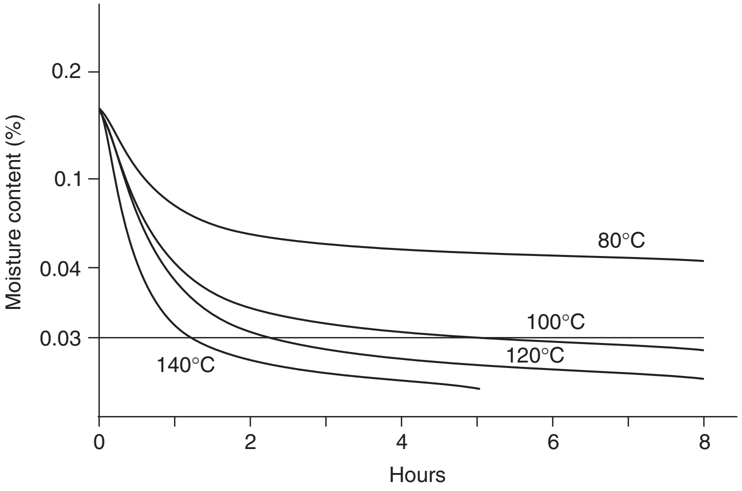

Figure 7.6 Effect of drying conditions on moisture content.

Moisture control and drying

Usually PBT absorbs only small amounts of water, but very small amounts of water can cause a drastic reduction in molecular weight due to hydrolytic degradation of the polymer chain at high-temperature conditions. PBT resins should be dried prior to processing to remove moisture that can reduce the part mechanical properties and result in surface imperfections. Moisture content below 0.03% prior to processing is recommended for PBT [20, 21]. In the case of injection molding, this drying is generally conducted in the form of solids drying prior to processing. Figure 7.6 shows typical drying curves of PBT resins at temperatures. Recommended drying conditions are 3 to 4 h at 120°C. The capacity of the dryer to be used should be determined on the basis of the resin's throughput rate in each case. It is very important to use only very dry resins in any step involving melt processing, such as injection molding and melt extrusion.

Injection molding

PBT resins are suitable for automated molding operations characterized by fast crystallization and cycles, and good release. Injection-molded parts are used for small electrical and automotive parts. The low viscosity of the PBT melt at the processing temperature allows easy filling of thin sections and complicated parts. The recommended injection-molding conditions for PBT are given in Table 7.8. It is recommended that injection-molding temperatures of PBT be from 240°C for unfilled to 270°C for reinforced grades. Melt temperatures higher than 280°C must be avoided, since some failures of physical properties may occur by thermal degradation of PBT.

TABLE 7.8 Recommended Injection-Molding Conditions for Various PBT and Blends

Division	Unit	Unreinforced	Reinforced	PBT/PC blend
Cylinder set				
Rear zone	°C	225–240	230–245	230–250
Middle zone	°C	230–245	235–250	240–260
Front zone	°C	235–250	240–260	250–270
Nozzle temperature	°C	235–255	240–260	250–270
Melt temperature	°C	235–255	240–260	250–270
Mold temperature	°C	40–80	50–100	40–80
Injection pressure				
First stage	MPa	40–70	60–110	50–80
Second stage	MPa	35–55	40–85	45–65
Backpressure	MPa	0–4	0–4	0–4
Screw speed	rpm	60–100	40–80	70–100
Drying conditions	°C, h	120, 4	120, 4	100, 4

SOURCE: Lupox PBT brochure and data sheets [20].

Flame-retardant grades are more sensitive to thermal degradation and should not be processed at temperatures over 260°C.

For economic reasons, fast cycle time and mold temperatures with the lowest possible values are preferred. If the mold temperature is too low, there will be a danger of an inadequate surface finish and part performance, which can be related to insufficient crystallization during the cooling time. Crystallinity should be controlled by the cooling rate and duration, which is in turn controlled by mold temperature. With reinforced PBT materials, a good surface finish can only be achieved with high mold temperature. If there is insufficient crystallization, part dimension is also affected by postshrinkage (see Fig. 7.7). Lower postcrystallization and postshrinkage can be obtained as the mold temperature is increased. For sufficient crystallinity of PBT, mold temperatures usually are set between 60 and 100°C.

The injection speed and pressure depend on the types of materials and the nature of the molding part. High injection speed is preferred to avoid premature freezing due to crystallization in the mold, particularly when parts are thin and complicated. High injection speeds and mold temperatures generally yield a better surface appearance, especially for reinforced PBT grades. In many cases, surface defects such as flow marks, jetting, streaks, and weld lines are mainly related to injection speed. Therefore, the optimum velocity profile of the molding process should be determined through optimization for specific parts. It is important to switch over to holding pressure stage at the right moment, to prevent overpacking in the molding part. Holding pressure serves to offset the volume shrinkage when the molded part cools in the mold cavity. In general, 40 to 80% of the maximum injection pressure is recommended as the proper level of

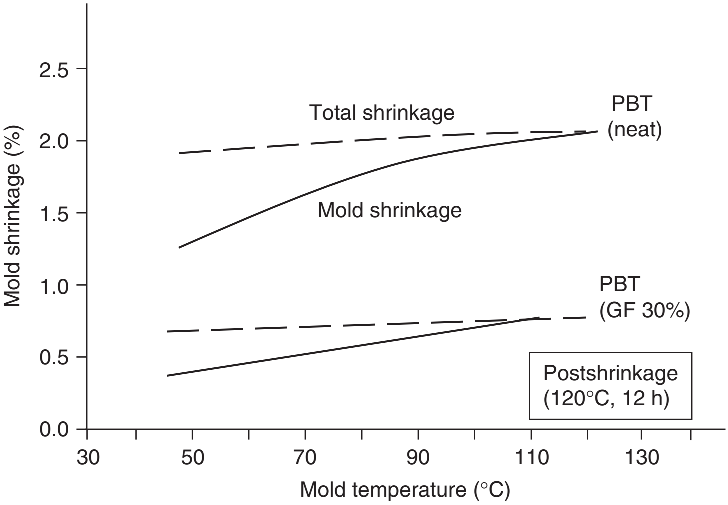

Figure 7.7 Mold shrinkage and postshrinkage for PBT.

holding pressure for molding. Holding pressure should be maintained until the gate has completely "frozen." In general, a lower screw speed is recommended to ensure melt uniformity and to prevent excessive shear heating. The screw speed should be adjusted in such a way that the screw retraction time is in the range of 70 to 80% of the available mold closed part cooling time. Backpressure will improve melt homogeneity and is particularly useful in obtaining good mixing efficiency when color concentrates are added. An excessive friction heating due to high screw speed and/or backpressure can lead to a thermal resin degradation or to a color change. Glass-reinforced PBT grades, high screw speeds, or high backpressure can also cause fiber breakage and reduce mechanical properties of molding parts. As there are many different grades for specific applications, one should refer to recommended processing conditions prescribed for the specific grades. If the injection cycle is interrupted for longer than a couple of normal cycle times, the cylinder should be purged with fresh resin. Failure to purge after such interruptions can result in defective parts due to thermal degradation of the resin. This is especially important in hot runner manifold molds. It is highly recommended to purge the molding machine when changing to a different resin family. In general, the best purging materials for PBT thermoplastics are extrusion-grade high-density polyethylene and polystyrene.

If the application permits the use of reground, less than 20% of regrind materials may be added to the virgin pellets after drying without a strong decrease in property. But the mechanical and thermal properties of molded parts may be inferior to those of fresh material, due to the thermal degradation or the breakage of reinforced fillers. It is important to keep the reground parts clean and to avoid contamination from other materials. Actual reground usage level should be determined for each specific application.

Extrusion

PBT can be extruded into a number of applications such a film, sheet, pipe, and tube. It can be achieved with commercial extruders whose screw has three distinct features, such as feed, transition, and metering zones, with length-to-diameter ratios (*L*/*D*) of at least 24:1. The feed zone at the rear end of the screw acts as a conveyor of resins from the hopper area through the heated barrel. The function of the transition zone is to compress the melt, and its length should be three to four turns between the feed and the metering section. The metering zone is located at the exit end of the screw and has a constant flight depth. Three zone screws should have a flight-depth ratio between 2:1 and 4:1, feed to metering section. The barrel and the screw should be provided with wear protection to prevent corrosion and abrasion. When glass-reinforced grades are to be processed, it is recommended to use special wear protection comprising a bimetallic barrel lined with a wear-resistant coating and a screw with hardened flights. In terms of the exact flight depths in the feed and metering sections, and the length of the transition section, the size and screw geometry should be selected to suit the part size and applications. For extrusion applications, due to the need of melt strength, a PBT with a high molecular weight is normally used. Depending on grades and application parts, the melt temperature of PBT should be between 230 and 260°C.

Injection-molding machinery and equipment

PBT resins can be processed in all standard screw injection-molding machines. Both toggle and hydraulic clamping machines fitted with either electrical or hydraulic drives can be used. In general, the classical three-zone screw injection-molding machines can be employed with adequate quality for the processing of PBT resins. A single-flighted, reduced flight depth, three-zone screw having a length-to-diameter ratio of 18 to 22 is recommended (Fig. 7.8). For the same screw diameter with reduced flight, screws ensure a shorter residence time of the melt in the cylinder and a more homogeneous temperature distribution in the melt. If demands on throughput and melt homogeneity are high, specific screw designs will afford significant advantages. Melt homogeneity and temperature uniformity may also be improved by using higher length-to-diameter screws and/or additional shear and mixing sections. The screw diameter is selected on the basis of the shot volume that is required to completely fill the mold

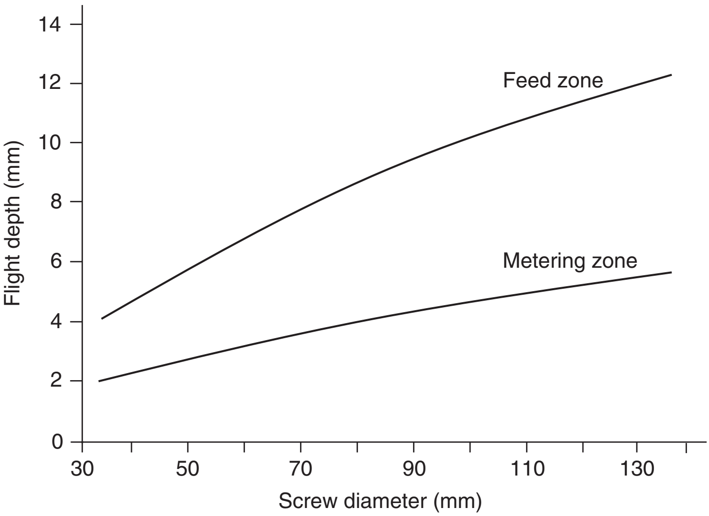

Figure 7.8 Screw diameters and screw flight depths of three-zone screws.

parts. A general guideline for molding machine selection is that every shot volume should be in the range of stroke between 1 and 3 screw diameters (30 to 80% of the machine capacity). For PBT blends where color control is critical, it is highly recommended that the shot volume be close to 60% of machine capacity in order to reduce residence times. Glass-reinforced PBT grades are abrasive and tend to wear the screw elements. Use of heat-treated alloy steel with a hard surface is highly recommended.

A nonreturn check ring is necessary during injection for PBT grades to ensure constant cavity pressure and shot uniformity. When used with reinforced grades, even when properly hardened, these check rings undergo rapid wear and should be periodically inspected and replaced after 3 to 4 months of operation. A sufficient clamping force is a further key factor when one is selecting molding equipment. The minimum clamping force required could be easily determined by multiplying the area of the molded part that is projected onto the plane of the clamping platen by the mean pressure in the mold cavity.

Applications

The most important applications of PBT are automotive and electrical, electronics and telecommunications, as well as precision engineering and general mechanical engineering. PBT, with its combined properties of resistance to heat and chemicals, as well as consistency of electrical property over a wide range of temperature, has numerous applications ranging from small parts such as connectors to large moldings used in automotive application. Electrical, automotive, and a variety of other consumer products benefit from the desirable property combination and moldability of thermoplastic PBT resins. Unmodified PBT is used in some applications, but the majority of PBT resins are modified by compounding with various contents of additives such as glass fibers, impact modifiers, flame retardants, and other polymers for various applications. Selection of the proper type and content of additive makes it possible to tailor the products to specific customer requirements. Table 7.9 illustrates the reasons for using PBT resins in various end applications. In many applications, PBT competes with other thermoplastics such as polyamide, polyacetal, and polycarbonate resins.

TABLE 7.9 Reasons for Use of PBT in Various Applications

Application	Material	Reasons for use
Door mirror stay	Glass-reinforced	Rigidity and hardness
Wire connector	Glass/nonreinforced	Impact resistance, dimensional stability
Ignition coil	Glass-reinforced, FR*	Electrical strength, high HDT
Distributor cap	Glass-reinforced, FR	Electrical property, rigidity
ABS/ECU housing	Glass reinforced, HR†	Dimensional stability, chemical resistance
Bumper fascia	PBT/PC alloy	Toughness, surface finish
Back beam	PBT/PC alloy, impact	Low-temperature impact
Door garnish	PBT/PC alloy	Surface finish, UV stability
Outdoor handle	PBT/PC alloy, glass-reinforced	Toughness, surface finish
Head lamp bezel	Mineral-reinforced	Surface finish, heat resistance
Electric connector	Glass/nonreinforced, FR	High HDT, stiffness, electrical property
Coil bobbin	Glass-reinforced, FR	Dielectric strength, high HDT, stiffness
Lamp socket	Glass-reinforced, FR	Heat resistance, UV stability
Switch	Glass-reinforced, FR	Stiffness, dimensional stability
Relay case	Glass-reinforced, FR	Heat resistance, stiffness, fluidity
FBT/focus pack	Glass-reinforced, FR, HR	Heat resistance, stiffness
Motor circuit breaker	Glass-reinforced, FR	Electrical property, dimensional stability
Cooling fan	Glass-reinforced, FR	Heat resistance, dimensional stability
Optical loose tube	Nonreinforced, extrusion	Toughness, dimensional stability
Pump case	Glass/nonreinforced	Chemical resistance, toughness
Hair dryer/steam iron	Glass-reinforced/ nonreinforced	Surface finish, temperature resistance
Cooker housing		Surface finish, chemical resistance
Oven handle	Glass/nonreinforced	Surface finish, chemical resistance

* FR: flame-resistant, UL-94 V-0.
† HR: hydrolysis-resistant.

Electrical and electronics

Electrical and electronics parts, which are becoming smaller and more complex and have increasing functionality, require high-performance molding materials. PBT is rigid, flame-resistant, and high-heat-resistant, and it has dimensional stability and outstanding long-term electrical performance. In some cases, PBT replaces thermosetting resins where good electrical properties are required together with better impact strength and easy processing in shorter cycle times with scrap reuse. Because of its high flow property, which enables PBT to fill thin sections readily, and its ease of processing, PBT is readily used in thin-wall connectors, bobbins, and ignition parts, all requiring electric endurance, flammability, and a good balance of strength and electric track resistance. Therefore it can also be used in switches, relays, terminal boards, TV focus blocks, TV transformers, DY, lamp sockets, and housings for electric parts. Parts molded in PBT thermoplastics are not sensitive to moisture and retain their electrical properties over a wide temperature range; their performance is maintained in almost all working conditions. Unfilled high-viscosity extrusion grades are also used in optical fiber protective tubes, monofilaments, and some sheath parts of cable wires.

Automotive

PBT resins are widely used for both exterior and under-the-hood parts of automobiles. Automotive electrical and electronic components especially are expanding at a high rate, which is driven by advanced technology related to convenience, improved fuel efficiency, and safety improvement. Automotive electrical components must function over a broad range of temperatures while withstanding impact, vibration, and corrosive chemical environments. In automotive electrical applications such as electrical control units, antilock braking systems, ignition systems, plug connectors, and air bag and engine control systems, PBT thermoplastics are widely used for their high stability. PBT is outstanding for its high heat resistance, good dimensional stability, low water absorption, and high resistance to many chemicals, such as fuels and lubricants. These properties have made PBT an indispensable material in many applications in automotive electronic engineering.

In other important automotive applications, increased requirements in terms of surface appearance, low-temperature toughness, flowability, and warpage properties have been met by PBT blends. Automotive exterior parts such as door handles, mirror housings, window delta molding, and sunroof frames must have an excellent surface finish, especially if they are unpainted. For large exterior body parts such as bumpers, elastomer-modified PBT/PC blends are used because of their surface appearance and high impact properties. Automotive applications of PBT include door mirror systems, brake unit components, housings and components for ECU blocks and ABS units, door lock components, distributor caps and rotors, ignition coils, sensor encapsulations, bumper back beam and fascia, window garnish, and headlamp structures.

General engineering and replacement of other materials

Its resistance to heat and chemicals, plus the wide range of coloring possibilities and good friction properties, enables PBT to be used in many industrial components and consumer applications. In industry, PBT resins are used for pump housings, impellers, functional parts of printers and copying machines, tool housings, casings, and replacements for metals in many types of load-bearing parts. PBT resins are noted for their excellent flow characteristics in thin-wall moldings, close mold tolerances, and high productivity with fast mold cycles.

The properties, processing characteristics, and competitive price of PBT engineering plastics lead to high performance, lower cost, and lower weight compared to die-cast metals and/or thermosetting resins. The main advantages of PBT resins compared to thermosetting resins are material reuse, design integrity, and productivities. Thermoplastic molding components require less material, because scrap such as sprues, runners, and failure parts can be reground and reused. With themoplastics, less processing time is needed due to faster cycle times and elimination of the secondary operation of thermosetting resins. The high rigidity with light weight, integrated design, and resistance to corrosion and chemicals make PBT an ideal replacement material for a wide range of industrial applications in place of die-cast metals. Among the many successful replacements of other materials are housings and covers, pump parts, motor parts, parts for electric drives, lamp parts, and automotive parts. Table 7.10 illustrates the reasons for using PBT, including replacement of other materials. The PBT thermoplastics have characteristics of processing ease and good economics.

Conclusions

PBT is a very versatile and cost-effective resin that can be combined with a wide range of additives to give a range of products for electrical, automotive, and other applications. Annual growth rate of 6 to 8% is predicted, and this is driven by many factors such as weight reduction, parts design consolidation, and metal replacement. Among the other polyesters, the benefit of PBT is an inherent fast-crystallizing kinetics, allowing for fast cycling and easy processing properties in injection molding. PBT is outstanding for

TABLE 7.10 Commercial Applications of PBT in Replacement of Other Materials

Application	Replacing material	Reasons
Metal replacement		
Vehicle door mirror stay	Glass-reinforced	Light weight, rigidity, cost saving
Pump housing	Glass-reinforced	Light weight, rigidity, productivity
Motor case	Glass-reinforced	Thermal resistance, stiffness
Autobody panel	PBT/PC alloy	Light weight, stiffness, toughness
Bumper back beam	PBT/PC alloy	Light weight, stiffness, toughness
Windshield wiper	Glass-reinforced	Light weight, rigidity, design freedom
Thermosetting replacement		
Sensor housing	Glass-reinforced, FR	Stiffness, high HDT, productivity
Lamp socket	Glass-reinforced, FR	Heat resistance, dimensional stability
Ignition coil housing	Glass-reinforced, FR	Heat resistance, electrical property
Circuit breaker	Glass-reinforced, FR	Rigid, heat resistance, dimensional stability
Food tray	PBT/PC alloy	Chemical resistance, heat stability
Other replacement		
Auto connector (nylon)	Glass/nonreinforced	Dimensional stability, heat resistance
FBT/focus pack (PPE)	Glass-reinforced, FR	Chemical resistance, heat resistance
Decoration film (PVC)	Extrusion	Heat resistance, surface finish

its high rigidity, dimensional stability, low water absorption, electrical properties, and chemical resistance. The ability to undergo modification for various applications, combined with a range of reinforcement and blend, has enabled PBT to be one of the most widely used engineering polymers.

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Chapter 8

Thermoplastic Polyetherimide (PEI)

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Introduction

Thermoplastic polyetherimides provide the strength, heat resistance, and flame retardancy of traditional polyimides with the ease of simple melt processing seen in standard injection-molding resins such as polycarbonate and ABS.

The key performance features of PEI resins include

- Excellent dimensional stability at high temperatures under load
- Smooth as-molded surfaces that are easily metallized or painted
- Transparency, optical properties, and excellent aesthetics
- Very high strength and modulus
- Good solvent resistance over a wide temperature range
- High continuous-use temperature
- Inherent ignition resistance without the use of phosphorous or halogen additives

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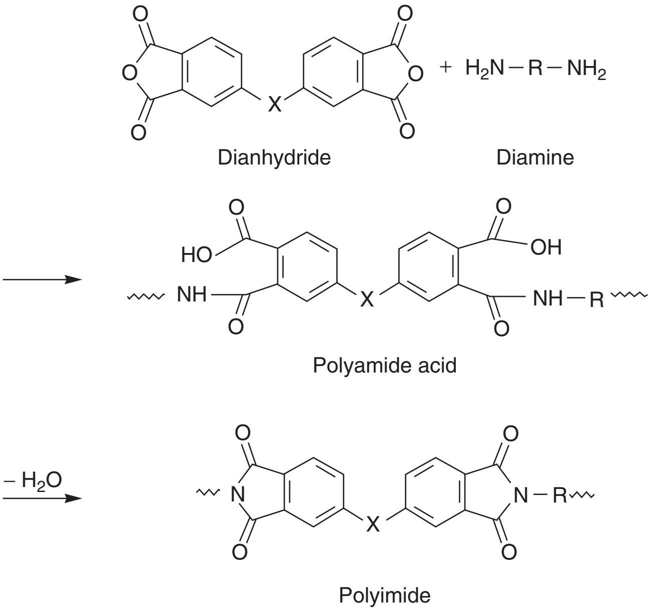
- High oxygen index and low smoke
- Medical- and food-contact compliance
- Sterilizable, and autoclave resistance
- Good electrical properties with low ion content
- Excellent machinability and secondary-finishing characteristics

Polymerization Chemistry

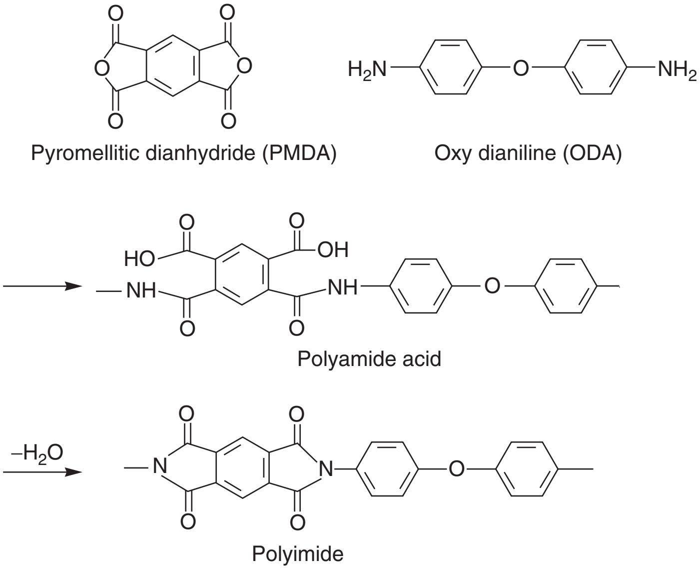
The chemistry of imidization has been reviewed elsewhere [1–5]. It is briefly outlined below in Eq. (8.1). The key elements are reaction of a diamine and a dianhydride to form an amide-acid polymer via ring opening of the anhydride by nucleophilic attack of the diamine. The polyamide acid is then formed into a polyimide by removal of water. These polymerizations are usually conducted in high-boiling polar solvents to dissolve the monomers and keep the polyamide acid in solution. Heating is frequently used to drive off water and form the polyimide. In some cases, other means of dehydration may be used.



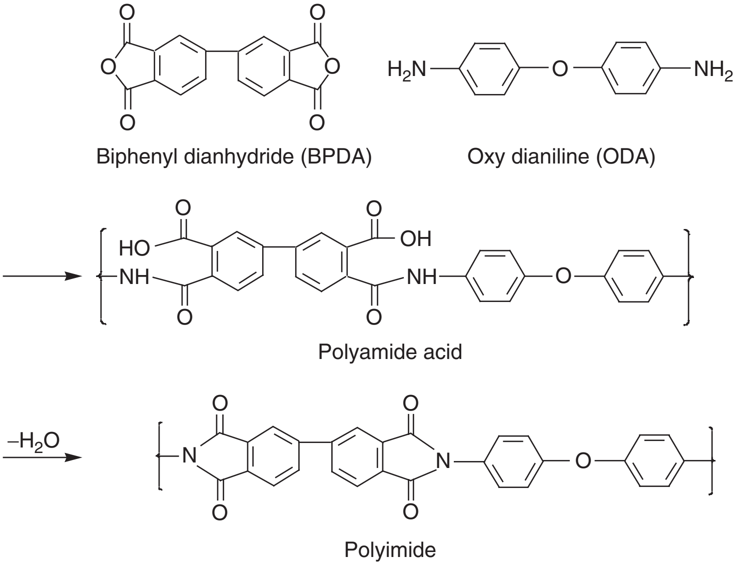
Equation 8.1 Imide polymerization scheme.

In most cases, the final polyimide is an intractable material that is very hard to shape and form. Traditional polyimides are usually made in solution as the amide-acid precursor to the polyimide. Often the polyamide-acid solution, or a solution that is only partially imidized, is used to make a film, laminate, or other shapes. The polyamide acid is then heated during (or after) the forming process to remove solvent and water to form the final polyimide. This complicates the forming process, which requires a chemical reaction, the elimination of water, in addition to removal of solvent. These additional requirements can be accommodated in simple operations, e.g., casting thin film, where a high surface area is present to aid in solvent and water removal. However, making more complex shapes is difficult.

The well-known polyimides based on *pyromellitic dianhydride* (PMDA) and *oxy dianiline* (ODA)—Eq. (8.2) (Kapton® from DuPont Co.) [6–8]—and the *biphenyl dianhydride* (BPDA) polymer with oxy dianiline—Eq. (8.3) (Upilex® from Ube Co.) [9]—are produced by using variations of the amide-acid process. The Kapton-type polyimides have thermal transitions between 360 and 410°C (680 and 770°F). The Upilex R grade has a glass transition temperature T_g of about 285°C (545°F). Upilex S resin is a crystalline polyimide made from BPDA and *para-phenylene diamine* (PPD). It has a very high modulus with a T_g of greater than 500°C (932°F). While these rigid polyimides have good properties, once imidized, they are not easily melted or re-formed. Simple stock shapes can be made by high-pressure sintering of polyimide powders. Polyimide parts can be machined from slabs and rod stock formed from the PMDA-ODA (Vespel® from DuPont) and BPDA-ODA (Upimol® from Ube, Inc.) polyimide powders. However, these methods are not attractive when large numbers of parts must be made.



Equation 8.2 PMDA-ODA polyimide.



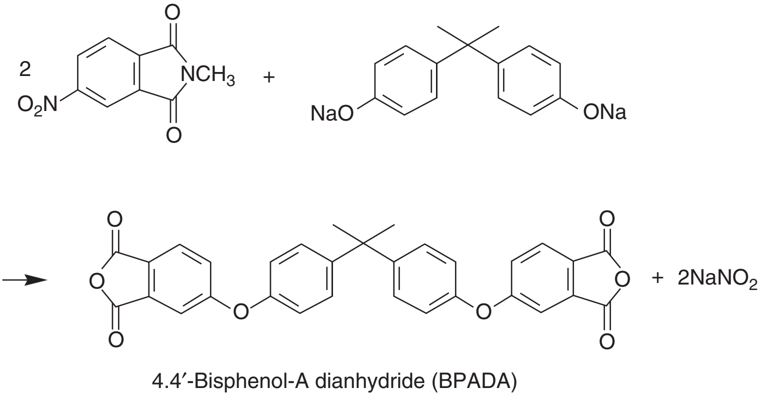
Equation 8.3 Biphenyl dianhydride ODA polyimide.

The solution-based polyamide-acid process limits the type and speed at which articles can be made from these polyimides. This limitation is true of many polyimides that have very rigid backbones. These polyimides, which have very little flexibility in the polymer chain and a high T_g, are very hard to melt process into complex shapes, especially on a commercial scale. Such intractable polymers are processed into articles in the more flexible polyamide-acid form, often with solvent present. The solvent needs to be removed and recovered to form the final polyimide article. This is true of polyimides based on PMDA and BPDA with ODA, as discussed previously. They have only one flexible link in the polymer chain—the ether group of the ODA—and can only be melt-formed in the amide-acid stage or by machining from a solid block of resin.

While such rigid polyimides have enjoyed tremendous commercial success based on good physical properties, the difficulties in processing them have limited their applications. It was, therefore, desirable to find a method to produce polymers that combined the excellent physical properties of traditional polyimides with the simple melt processability of other thermoplastics, such as polycarbonates, polyesters, or polyamides.

The key to developing a truly melt-processable polyimide was to build more flexible linkages into the polymer backbone. This had to be done in such a way that the polyimide still retained other desirable features (e.g., heat resistance, strength, high use temperature, and low flammability). Scientists at the General Electric Corporate Research and

Development Center achieved this in the late 1970s [10]. An important feature of this invention was the development of a process to make dianhydrides, specifically dianhydrides based on bisphenol-A. This was achieved by phase-transfer-catalyzed nucleophilic aromatic substitution, as shown in Eq. (8.4). A nitro group was displaced from a phthalimide by a bisphenol salt to yield a difunctional imide compound, which, in turn, was converted to the *bisphenol-A dianhydride* (BPADA). Sodium nitrite is made as a by-product.



Equation 8.4 BPADA synthesis.

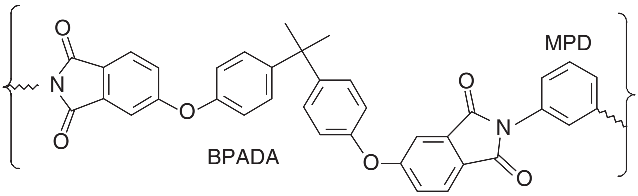
Polyetherimides made from this dianhydride have much greater melt processability than traditional polyimides, yet retain many of (but not all) their desirable features.

BPADA is reacted with a more or less equimolar amount of a diamine, for instance, *m-phenylene diamine* (MPD), to make the polyamide acid. Water is removed by heating to form the polyetherimide (PEI). In this case, after removal of water and solvent, the added flexibility of the polyimide allows the molten resin to be extruded into strands. Strands of the BPADA-MPD polyetherimide [Eq. (8.5)] are cooled and chopped into pellets, which can subsequently be remelted to form parts or film. PEI powder can be made by grinding pellets or through precipitation methods. Special processes have been developed to make small-particle (15-μm) PEI powders.

In general, melt-processable PEI resins have a *molecular weight* (MW) of 20,000 to 50,000, with lower-MW species yielding better flow and higher-MW species providing better impact in finished goods. Molecular weight is often controlled by addition of mono-functional anhydrides or amines, producing an imide end-capped resin. However, conducting polymerization with a slight excess of either monomer is a technique that can also be used to control molecular weight.

It is common practice to combine two polymers with the same overall chemical structure, but differing molecular weights, to control the melt viscosity of the resultant resin. This can be accomplished in several different ways, e.g., by blending pellets and melt-mixing in an extruder or molding machine.

By looking at the structure of the polyetherimide made from bisphenol-A dianhydride and *m*-phenylene diamine, as shown in Eq. (8.5), it can observed that the BPADA-MPD polymer has three flexible linkages: the two ether links and the isopropylidene group of the BPA. In addition, the MPD provides a kink in the polymer chain, disrupting long-range order and potential crystallinity, giving an amorphous, glassy polymer.



Equation 8.5 BPADA-MPD polyetherimide.

While these flexible links provide molecular mobility (melt flow), they also have sufficient bond strength to provide good thermal stability in the melt and in final use as formed parts. The methyl groups of the BPA isopropylidene linkage are reasonably stable, since only primary hydrogen-carbon bonds are present. In addition, the relatively high carbon-to-hydrogen ratio helps reduce flammability. Thus, a high-performance thermoplastic polyimide is produced that has the ease of melt processability. High heat capability is retained; the BPADA-MPD based PEI has a T_g of 217°C (423°F). This chemical structure is the key to allowing the resin to be melt-processable. Melt processability opens up many opportunities for complex design, parts consolidation, and rapid production rates to replace metal, ceramic, and other materials. Injection molding using the BPADA PEI allows complex parts to be made in a little as 20 s on a continuous basis.

As mentioned previously, the key to making BPADA was the development of nitro displacement chemistry, which forms ether linkages as shown in Eq. (8.4). This chemistry allows bisphenol salts, commonly used to make polycarbonates and epoxies, to become monomers for polyimide synthesis. The bis *N*-methyl imide intermediate is converted to the dianhydride that is used in imide polymerizations. Nitro displacement has been shown to work with many bisphenol salts to make a family of dianhydrides. The BPA dianhydride is commercially the most important.

The BPADA-MPD polymer is most conveniently processed as a fully polymerized polymer melt. All amide-acid groups have been closed to imide linkages, and no volatile species are liberated on heating (assuming the polymer has been adequately dried to remove a small amount of absorbed water).

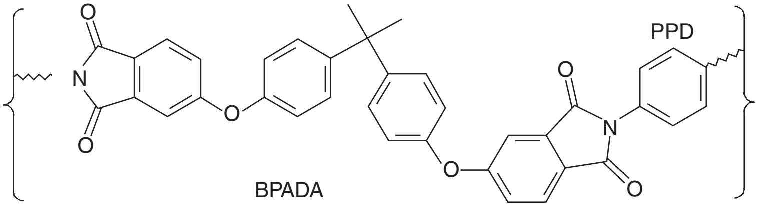
BPADA-MPD PEI is soluble in some polar aprotic solvents, such as *N*-methyl pyrrolidinone, dimethyl formamide, or dimethyl acetamide, as well as solvents such as chloroform, anisole, and dichlorobenzene [11]. If melt processing is not desired, thermoplastic PEI resin can also be cast into film, or solution-blended with other ingredients. Since the materials are fully polymerized, only the removal of solvent, rather than dehydration or chemical curing, is needed to form a molded component.

Polyetherimides are amorphous polymers with excellent dimensional stability. They are transparent with useful optical properties [12], but all thermoplastic polyetherimides are a yellow amber color (as are almost all polyimides). The *yellowness index* (YI) of a 3.2-mm (0.130-in) BPADA-MPD PEI injection-molded part is usually > 50.

PEI resins do not have outstanding impact strength, but they do have the practical toughness to be used in a variety of applications, including serving trays and freezer-to-oven cookware [13]. Additionally, PEI resins have good electrical insulating properties with stable dielectric constant and dissipation factor over a range of temperatures [14,15]. Furthermore, these materials have good inherent resistance to ignition and, in large fire situations, may give reduced heat release and low smoke in some formulations [16]. While PEI resins have good *flame-retardant* (FR) characteristics, testing of all articles using PEI resins in actual end-use conditions is strongly recommended to ensure FR performance and compliance with all codes and regulations.

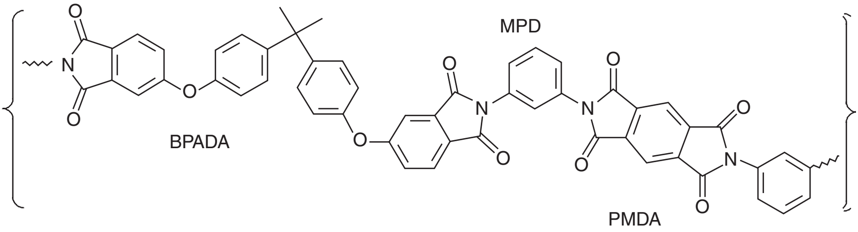
Other Thermoplastic Polyetherimides

BPADA has been polymerized with a wide variety of other diamines and other dianhydrides to produce a family of polymers and copolymers. Chief among these is the polymer of BPADA with *p-phenylene diamine* (PPD), as shown in Eq. (8.6). This PPD resin has a slightly higher T_g than the MPD resin and also has much better solvent resistance. Removal of the MPD-derived kink from the PEI chain makes the resin much less soluble, but symmetry is not so high as to allow for crystallization under most conditions. The presence of the three flexible links—two ether groups and an isopropylidene linkage—still allows for melt processability. The T_g is raised slightly to 227°C (441°F), and solvent resistance is much improved versus the BPADA-MPD polymer.



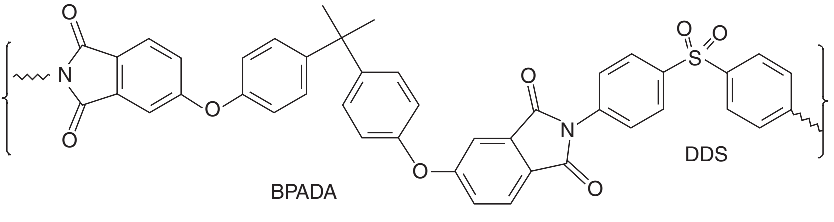
Equation 8.6 BPADA-PPD polyetherimide.

Copolymers of BPADA with PMDA and MPD have been made to yield a higher T_g. By incorporating a minor amount of PMDA, as used in Kapton® polyimide, the T_g is raised to 234°C (453°F) with a slight reduction in flow due to incorporation of the inflexible PMDA linkage in the polymer backbone [Eq. (8.7)]. Other properties are retained.



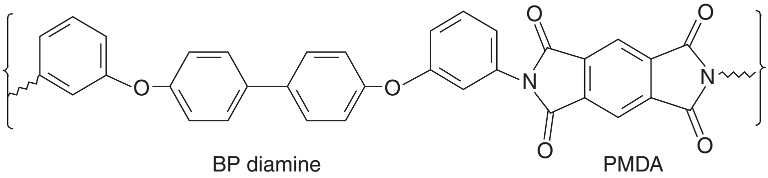
Equation 8.7 BPADA-PMDA-MPD copolyetherimide.

More recently, a higher-T_g resin [248°C (478°F)] was made by reaction of BPADA with *diamino diphenyl sulfone* (DDS) [17]. This high-T_g *polyetherimide sulfone* (PEIS) resin is still melt-processable; once again, the key lies in building flexible linkages into the polymer backbone. The BPADA-DDS polymer has four flexible links: the two ether linkages and the isopropylidene group from the BPADA, plus the sulfone link from the DDS [Eq. (8.8)]. This DDS-based resin is more polar than BPADA-MPD PEI (by virtue of the SO_2 group) and therefore absorbs a little more moisture than other BPADA-based polyimides. However, it still provides all the convenience of melt processing with higher heat capabilities. The BPADA-DDS polymer is miscible with BPADA-MPD PEI and shows similar solubility characteristics. Good mechanical and flame-retardant properties are retained.



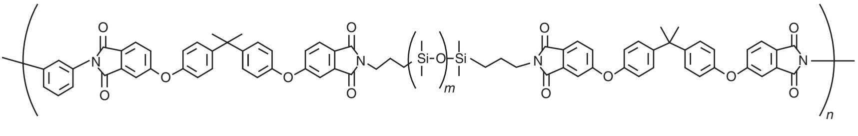
Equation 8.8 BPADA-DDS polyetherimide sulfone.

A crystalline polyetherimide derived from 3,3′-bis(4-aminophenoxy)-biphenyl diamine (BP diamine) and pyromellitic dianhydride is also commercially available [18]. The polymer structure is shown in Eq. (8.9). This resin has two flexible ether linkages as well as the rigid PMDA-derived units. Viscosity is high [3000 to 10,000 P at 400°C (752°F) and 100 s^{-1}], but the material may still be melt-processed. The T_g is ~250°C (482°F) and T_m is about 388°C (730°F). This PEI has sufficient symmetry—likely due to the biphenyl and PMDA linkages—that it will crystallize. The rate of crystallization is relatively slow, so parts formed of this material often require postmold annealing. Care must be taken to prevent distortion of the amorphous or semicrystalline parts during secondary heat exposure or in end use. Like many polyimides, these resins show high strength and ignition resistance. As molded, the parts may be transparent; crystallization results in opacity. The crystalline PEI resin has excellent solvent resistance. The BP diamine PMDA polymer has been melt-blended with BPADA-MPD polyetherimide to form miscible systems [19].



Equation 8.9 Biphenol diamine PMDA polyetherimide.

Another interesting commercial polyimide based on BPADA is an elastomer made by replacing a portion of the MPD with a diamino dimethyl siloxane [Eq. (8.10)]. This makes an elastomeric polyetherimide silicone block copolymer that has a lower softening point [T_g = 165°C (329°F)]. The silicone polyetherimides have lower modulus and greater impact resistance than the rigid BPADA-MPD polymer. This copolymer also has good flame retardancy and—with the appropriate choice of short silicone block length—can be made transparent [20–22].



Equation 8.10 Silicone polyetherimide copolymer.

A partial summary of commercial polyetherimide grade names and their suppliers is listed in Table 8.1. Table 8.2 shows properties of some of the commercial, fully amorphous, melt-processable thermoplastic polyimides listed in Table 8.1. They have high heat capability and excellent strength [23].

TABLE 8.1 Commercially Available PEI Resins and Their Trade Names

Chemical name	Reference equation in this chapter	Commercial trade name	Grade	Manufacturer
PMDA-ODA polyimide	(8.2)	Kapton®, Meldin®		DuPont Saint-Gobain
Biphenyl dianhydride ODA polyimide	(8.3)	Upilex®		Ube Industries
BPADA-MPD polyetherimide	(8.5)	Ultem®	1000 or 1010	GE Plastics
BPADA-PPD polyetherimide	(8.6)	Ultem®	5001 or 5011	GE Plastics
BPADA-PMDA-MPD copolyetherimide	(8.7)	Ultem®	6000	GE Plastics
BPADA-DDS polyetherimide sulfone	(8.8)	Ultem®	XH6050	GE Plastics
Biphenol diamine PMDA polyetherimide	(8.9)	Aurum®		Mitsui Toatsu Chemical Co.
Silicone polyetherimide copolymer	(8.10)	Siltem®	STM1500	GE Plastics

The BPADA-MPD-based PEI has surprisingly high strength for an unfilled resin; yield strength is similar to that of unannealed brass, and modulus is higher than that of other thermoplastics, such as polycarbonate. The thermoplastic PEI family provides inherently high strength, transparency, and ignition resistance, along with relatively good melt processability.

TABLE 8.2 Typical Properties of Various Thermoplastic Polyetherimides

	BPADA-MPD	BPADA-PPD	BPADA/PMDA-MPD	BPADA-DDS
CAS number	61128-46-9	71519-79-4	96557-46-9	77699-82-2
T_g ,°C (°F)	217 (423)	227 (441)	234 (453)	248 (478)
HDT at 1.9 MPa (264 psi), °C (°F)	200 (392)	207 (405)	211 (412)	237 (459)
HDT at 0.5 MPa (66 psi), °C (°F)	210 (410)	216 (421)	221 (430)	230 (446)
Tensile strength, MPa (kpsi)	110 (16)	103 (15)	117 (17)	97 (14)
Flexural modulus, MPa (kpsi)	3516 (510)	3103 (450)	3585 (520)	3103 (450)
Flexural strength, MPa (kpsi)	166 (24)	138 (20)	172 (25)	159 (23)
Rev. N Izod, J /m (ft·lb/in)	1335 (25)	961 (18)	2082 (39)	2082 (39)
Specific gravity	1.27	1.28	1.29	1.30
% Water absorption at 24 h	0.25	0.16	0.28	0.65

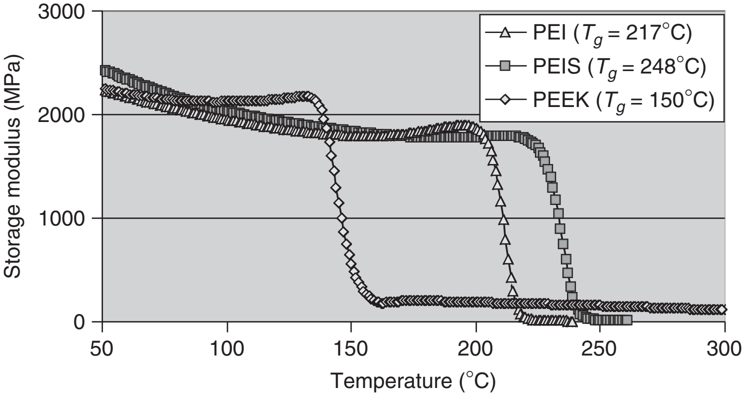


Figure 8.1 Dynamic mechanical analysis curve for PEI, PEIS, and PEEK: modulus versus temperature.

For an amorphous resin, polyetherimide provides good solvent resistance [11]. These materials are acid-resistant, but can be attacked by caustic, alkyl amines, and ammonia. The BPADA-PPD-based polyetherimide provides the best solvent resistance of the commercially available, fully amorphous thermoplastic PEI grades. It will not dissolve in chlorinated solvents.

PEI resins are useful for their advantageous combinations of performance features, such as dimensional stability plus high heat. Figure 8.1 shows the *dynamic mechanical analysis* (DMA) trace of BPADA-MPD PEI and the crystalline resin *polyetheretherketone* (PEEK). This test shows the loss modulus (stiffness) versus temperature. Crystalline PEEK has higher heat capability than PEI by virtue of its high-melting [340°C (644°F)] crystals. However, like most crystalline resins, PEEK actually contains about 60% amorphous regions. These amorphous regions have a T_g of only 150°C (302°F). Hence, once the T_g of PEEK is passed, the resin loses much of its stiffness. The high-melting crystals, dispersed in the molten glassy polymer, still contribute some rigidity to the PEEK sample, but much of the stiffness has been lost once 150°C (302°F) is passed, as can be seen in the DMA trace. On the other hand, the modulus of PEI and of the higher-T_g PEIS remains largely unchanged across the test temperature range. Having only a single T_g and, hence, a single phase change, PEI resins exhibit more uniform properties and better load-bearing capability as a function of temperature, as shown in Fig. 8.1. They also have excellent surface smoothness and high as-molded dimensional stability.

Amorphous resins like PEI and PEIS undergo less volume change transitioning from the amorphous molten state to the glassy solid state than do crystalline polymers. Therefore, PEI resins (being totally amorphous) exhibit less shrinkage than crystalline resins (which are a mixture of crystalline and amorphous regions). The amorphous resins also have better dimensional stability.

Crystalline resins like PEEK will not deform until they reach the melting point of their crystals. However, once they are above their T_g, they can only support a low load. PEI resins, however, will deform at lower temperature, since they have no high-melting crystals. Nevertheless, by virtue of the higher T_g, they can support a greater load and at higher temperature than the crystalline resin. In general, PEI resins are best used where crystalline resins are unable to meet application requirements due to issues of dimensional stability (such as warpage), flame retardance, or high-temperature end-use conditions.

End-use conditions will dictate which resin is best suited for which applications. Part testing at the conditions of the final application is always recommended when one is selecting a thermoplastic resin. There are many performance features to balance. No single material fills all needs, which is why so many polymers coexist in the marketplace.

Figure 8.2 shows the viscosity versus shear rate curves for a BPADA-MPD polymer at 355, 370, and 385°C (671, 698, and 725°F). Under similar conditions, more rigid polyimides, with only one flexible linkage, will show no flow. The comparatively easy processing of PEI resins allows melt extrusion of thin sheet and film [24], as well as numerous complex-shape parts. Melt processing also allows a number of polymer blends to be made by simple melt mixing.

Note that PEI resins should not be melt-processed by using nitride-treated steel since in some cases corrosion may ensue.

PEI resins are fairly polar and will absorb moisture. They are best dried prior to melt processing. Drying can be done at 150°C (302°F) for

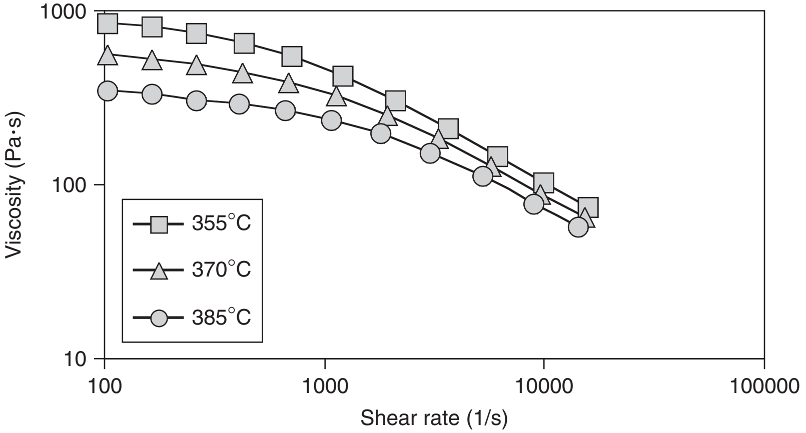


Figure 8.2 Viscosity versus shear rate for PEI based on BPADA-MPD intermediates at three temperatures.

at least 2 to 3 h, although longer drying times or higher temperatures [but at least 15°C (27°F) below the T_g] rarely cause problems.

When one is injection-molding PEI, care should be taken to keep temperatures high. This will yield parts with little molded-in stress and provide articles with better mechanical properties, especially in terms of impact. With transparent parts, polarized light can be used to determine the degree of stress [25]. Such techniques can be employed as nondestructive quality tests. Often, oil-heated molds are employed to prepare low-stress PEI parts. However, recent work has shown that, under some conditions, water-heated (cooled) molds can also be used to make stress-free parts [26].

While PEI resins are melt-processable, they still produce fairly stiff melts compared with other thermoplastics (largely due to their high T_g). They also generally exhibit good adhesion to metal. To open the melt-processing window for injection molding further, use of a mold release agent is recommended. Mold release grades of PEI—available in either transparent or opaque versions [27]—allow for fuller packing of the part, while still providing good release from the steel tool. In most instances, the milder processing achieved by using the mold release agent allows for production of parts with less molded-in stress and better practical impact strength. Surprisingly, in many cases the release agent does not have detrimental effects on subsequent bonding and metallization operations. Of course, in any application this assumption needs to be verified by part testing under actual assembly and end-use conditions.

Compounded Products

PEI resin can be compounded with a number of different ingredients to make a family of thermoplastic materials. One of the most useful of these additives is glass [28].

Combinations of the thermoplastic polyetherimides with 10 to 40 wt% fiberglass reinforcement are very effective for increasing strength and modulus, as shown in Table 8.3. Heat resistance is slightly increased too. The increase in stiffness is shown in Fig. 8.3, which compares modulus versus temperature for an unfilled BPADA-MPD-based PEI resin and blends with 10 and 30% short-chopped fiberglass.

Addition of glass improves both tensile and flexural strength, while also increasing impact strength. PEI's dimensional stability, which is very good in the unfilled (neat) state, is even better with added fiberglass. As shown in Fig. 8.4, a 40% fiberglass-filled PEI blend has a *coefficient of linear thermal expansion* (CLTE) in the flow direction that is lower than that of aluminum: 15 versus 23 μm/(m·°C). Unfilled PEI resins have a higher CLTE of about 50 to 60 μm/(m·°C).

TABLE 8.3 Comparative Properties for BPADA-MPD PEI Resin at Various Levels of Glass Reinforcement

Properties	10% Fiber-glass	20% Fiber-glass	30% Fiber-glass	40% Fiber-glass
HDT at 0.5 MPa (66 psi), °C (°F)	223 (434)	226 (438)	228 (442)	234 (454)
HDT at 1.9 MPa (264 psi), °C (°F)	207 (405)	209 (408)	212 (414)	208 (406)
T_g ,°C (°F)	217 (425)	217 (425)	217 (425)	217 (425)
Tensile stress *Y*, MPa (kpsi)	114 (16.6)	139 (20.1)	169 (24.5)	186 (27.0)
Tensile modulus, MPa (kpsi)	4482 (650)	6895 (1000)	8963 (1300)	11,721 (1700)
% Elongation	4.5	3.0	3.0	2.5
Flexural modulus, MPa (kpsi)	4482 (650)	6205 (900)	8963 (1300)	11,721 (1700)
Flexural stress, MPa (kpsi)	193 (28.0)	207 (30.0)	228 (33.0)	248 (36.0)
N. Izod, J/m (ft·lb/in)	59 (1.1)	91 (1.7)	107 (2.0)	107 (2.0)
% Ash	10	20	30	40
Specific gravity	1.34	1.42	1.51	1.61

Other forms of glass commonly used in PEI resin include chopped fiber, milled glass, glass beads, and glass flake. Glass fibers provide the best stiffness and strength (with longer fibers providing higher values but more orientation effects). Shorter-aspect-ratio glass fillers (e.g., milled glass and glass bead) produce parts with more isometric properties. Said another way, these lower-aspect-ratio fillers produce less anisotropy (less orientation of the filler) in the final molded part.

PEI resins can also be blended with numerous mineral fillers such as talc, clay, wollastonite, titanium dioxide, barite, and mica. In general,

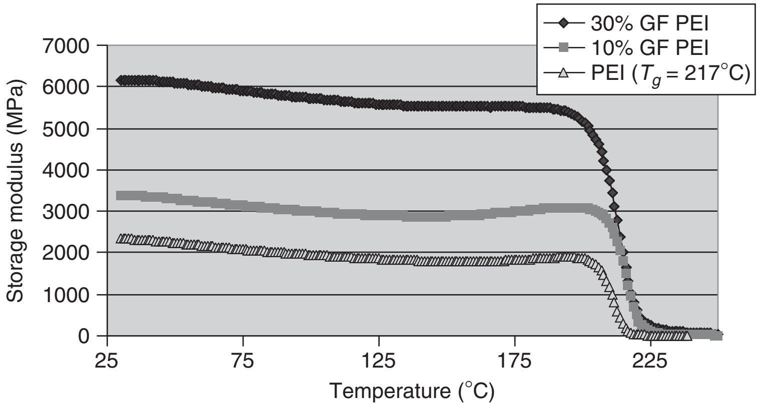


Figure 8.3 Storage modulus versus temperature for neat PEI resin and PEI at various levels of glass loading.

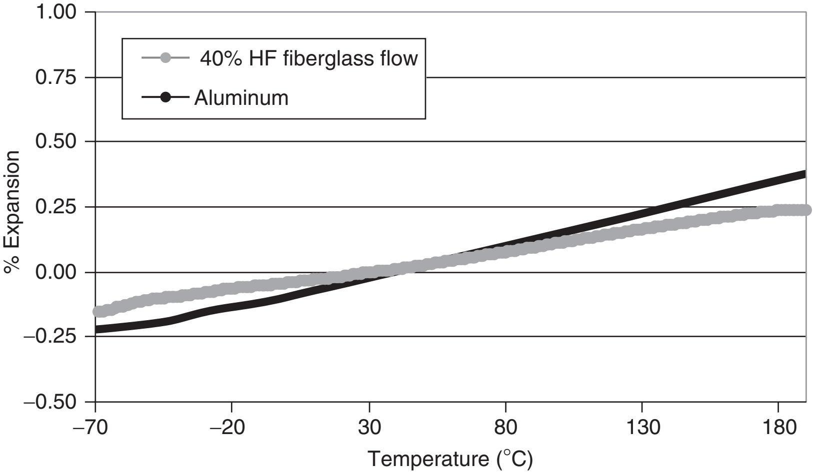


Figure 8.4 Thermal expansion: 40% glass-filled PEI versus aluminum.

mineral fillers increase strength, improve dimensional stability, and reduce shrink, but not to the same extent as fibrous fillers with higher aspect ratios. Use of coupling agents, specifically amino silanes, can improve dispersion of minerals (and glass), as well as bonding to the molded part. In many cases, these coupling agents also provide higher strength and impact. Mineral and glass fillers can be combined to tune specific properties; e.g., a mica- and glass-reinforced PEI is used in automotive engine throttle bodies due to its excellent dimensional stability, high strength, and resistance to hot fuels and engine heat. Combination of glass fibers with platelike fillers, such as mica or glass flake, can be very effective at controlling warp while providing high strength.

Melt flow is reduced by the addition of glass. Glass fibers reduce flow more than the same amount of milled glass or mineral filler. However, even with high levels of fiberglass, the PEI blends are still injection-moldable. Recent blend technology allows ~30% improvement in the melt flow of filled PEI compositions [29]. Fillers and fibers will, of course, also increase specific gravity and part weight, as well as improve impact, strength, and short- and long-term heat resistance.

Due to a close match in refractive index between PEI resins and borosilicate, "E" glass fiberglass-reinforced PEI blends are translucent.

Additionally, PEI can be blended with carbon fibers to give high-strength, higher-modulus blends with greater electrical conductivity. Depending on the loading of conductive filler and the part design, such blends have the ability to provide EMI / RFI shielding as well as static dissipation. PEI resin can also be blended with conductive carbon; carbon nanotubes; and metal fiber, flake, or spheres (or combinations thereof) to increase both thermal and electrical conductivity. Electrical properties will vary with filler loading as well as part design, gating, and melt processing. Normally, PEI resins are good electrical insulators. Often a resin-rich skin on a molded part can affect conductivity.

Polymer Blends

PEI resin may also be combined with other polymers. In general, to produce a useful blend, the free energy of mixing ΔG [Eq. (8.11)] must be favorable.

$$\Delta G = \Delta H - T(\Delta S)$$

Equation 8.11 Free energy of mixing.

Since the combinatorial entropy of mixing large-molecular-weight polymers always gives an unfavorable ΔS term, formation of compatible blends requires a favorable enthalpic interaction ΔH. The PEI resins have produced a surprising number of miscible (one-phase) and compatible blends. Compatible blends are phase-separated mixtures having sufficient attraction between phases to provide some level of molecular adhesion, resulting in stable morphology and giving rise to good mechanical properties.

PEI forms miscible blends with polyesters such as *polybutylene terephthalate* (PBT), *polyethylene terephthalate* (PET), and *polyethylene naphthanoate* (PEN) [30–32]. These blends have a single T_g between that of the PEI and that of polyester. In blends with slower crystallizing polyesters such as PET and PEN, crystallization is reduced and one-phase, transparent compositions can be molded. Such blends have reduced thermal performance versus the base PEI polymer, but improved melt flow, reduced yellowness, and slightly better solvent resistance.

Blends of BPADA-based polyimides are also miscible with polyaryl ether ketones such as PEEK [33, 34]. It appears that the isopropylidene moiety is important in developing miscibility in these systems [35]. In this case, the lower T_g (150°C) of PEEK acts to reduce the higher T_g of PEI. When injection-molded, many PEEK-PEI blends are transparent. Such miscible PEEK blends can be induced to crystallize with long molding cycles or secondary heat treatment, yielding opaque systems due to PEEK crystal formation. Care must be taken during such heat treatment (annealing) to ensure that the accompanying volume change—in going from amorphous to crystalline regions—does not distort the part. Films of PEEK-PEI blends have also been prepared.

Phase-separated PEI blends have been investigated. Combinations of PEI with *polycarbonate* (PC) or *polycarbonate ester* (PCE) copolymers have a fine, laminar two-phase morphology [36]. Combinations of PEI with polycarbonate or polyester carbonates yield a family of two-phase opaque systems that have reduced heat capability versus PEI, but show improved impact and better melt flow [37, 38].

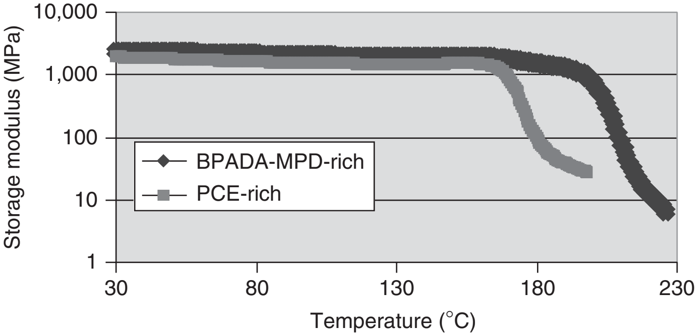


Figure 8.5 Dynamic mechanical analysis traces of PEI-PCE blends.

Figure 8.5 shows the DMA trace of two blends—one whose major phase is PCE (~85%) and the other having a major phase of BPADA-MPD PEI (~75%). Note that the PEI-dominant blend has slightly higher modulus and retains that stiffness to higher temperature, consistent with the PEI continuous phase. The blend with the PCE-rich phase shows lower stiffness and softens at the T_g [~175°C (347°F)] of PCE.

Figure 8.6 shows the tan delta values for the same blends. Tan delta is the derivative of the loss modulus, showing the rate of its change. The peaks indicate the T_g values for the two blends. Note here that the PEI-rich blend has a small shoulder at ~175°C (347°F), which represents the transition of the minor PCE phase. In the PCE-rich blends, due to the deformation of the sample, the higher-T_g PEI phase cannot be observed. The PCE-dominant sample shows better melt flow and improved impact versus the PEI-rich blend. Comparative physical and mechanical properties for these two blends are given in Table 8.4.

Combinations of PEI resins with polyamides (nylons) also produce phase-separated blends with fine particle morphology and good mechanical properties, likely arising from phase adhesion between the two resins

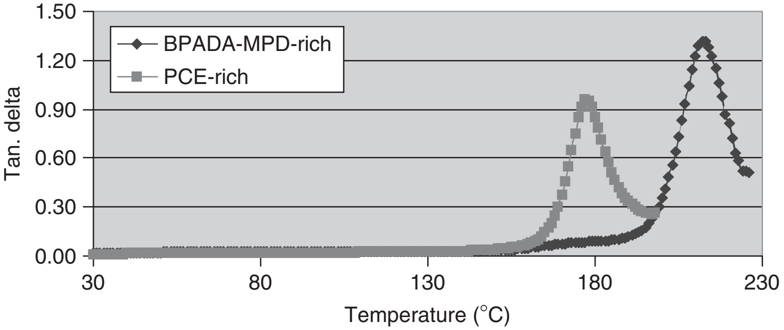


Figure 8.6 Tan delta curves for PEI-PCE blends.

TABLE 8.4 Comparative Properties for BPADA-MPD PEI:PCE Blends

Blend ratio	~ 85:15 PCE:PEI	~ 25:75 PCE:PEI
Melt flow rate, g/10 min, at 295°C (563°F)	6.0	2.8
Tg, °C (°F)	PCE = 174 (345) PEI = 215 (419)	PCE = 174 (345) PEI = 215 (419)
HDT, 1.9 MPa (264 psi), °C (°F)	157 (315)	191 (376)
HDT, 0.5 MPa (66 psi), °C (°F)	169 (336)	205 (401)
Tensile strength *Y*, MPa (kpsi)	69 (10)	97 (14)
Flexural modulus, MPa (kpsi)	2537 (368)	3172 (460)
Flexural strength, MPa (kpsi)	107 (15.5)	145 (21.0)
Unnotched Izod, J/m (ft·lb/in)	> 2083 (> 39)	2083 (39)
Notched Izod, J/m (ft·lb/in)	427 (8.0)	53 (1.0)
Specific gravity	1.21	1.26

on a microscale [39, 40]. When the polyamide is the continuous phase, the PEI acts as a melt-processable reinforcement, improving heat capability under load above nylon's T_g. The PEI also provides better dimensional stability due to its reduced shrink, as well as lower water absorption compared to the polyamide. As opposed to PEEK blends, the PEI-nylon blends usually show rapid crystallization as injection-molded. The crystalline polyamide phase provides high flow, higher ultimate heat resistance, and excellent solvent resistance. Presence of polyamide in the blend is usually detrimental to PEI's ignition resistance and thermal color stability. PEI can also be combined with amorphous polyamides.

PEI blends have also been further modified with silicone polyetherimide copolymer to improve impact strength, especially at lower temperatures. Use of a silicone polyetherimide as an impact modifier has the added benefit of retaining or even improving flame retardance, as it has a lower fuel value than traditional rubbery impact modifiers. The silicone-PEI copolymer also has the stability needed to survive high PEI processing temperatures without decomposition. These PEI-silicone copolymer blends are hazy or opaque, phase-separated systems.

Lubricants such as fluoropolymers [e.g., *polytetrafluoroethylene* (PTFE)], molybdenum disulfide, or graphite have also been blended with PEI polymers to achieve enhanced tribological properties, particularly improved lubricity, and reduced friction and wear.

With all blends, changes in the ratio of the constituent polymers will yield a range of resins. These blends can also be combined with fiber, fillers, colorants, and other additives to produce a full family of products for differing applications. Some blends may contain several different types of polymers.

Thermoplastic PEI resins are often colored with various pigments. Titanium dioxide (TiO_2) and carbon black are both widely used. Care must be taken to select colorants that can withstand the resin's high processing temperature [>350°C (662°F)] without shifting color or degrading the polymer. Due to the natural deep-yellow color of many PEI resins, relatively high levels of pigment (5 to 10 wt%) may be needed to achieve light colors. Sometimes this high pigment loading can affect other mechanical properties, such as impact. In *glass fiber* (GF) blends, the hardness of metal oxides, such as TiO_2, can cause fiber breakage, which results in lower strength and impact, although the modulus tends to be retained. Often there can be a 10 to 20% drop in strength and impact properties when one is comparing the same GF-PEI grade in white versus natural or black-colored versions. This effect of metal oxide colorants is generally true of all GF thermoplastics, not just polyetherimides. The property differences between natural and white colors in non-glass-reinforced grades will be less than in fiberglass-filled blends.

Note that due to their high melt-processing temperature, PEI resins are not compatible with many standard polymer additives. Often additives that work well in other, lower-temperature polymers will decompose or volatilize in the hot PEI melt. In general, like most amorphous polymers, PEI resins should be processed at least 150°C (270°F) above the polymer's T_g [340 to 400°C (664 to 752°F) for most polyetherimides]. Selection of appropriate additives to blend with PEI is best handled by the resin manufacturer or those with significant experience in the selection of suitable blending materials.

The presence of water can have several types of effects on PEI depending on the exact nature of exposure. For example, if undried resins are melt-processed, water (steam) will evolve and may cause degradation of the polymer chains. Loss of molecular weight, if excessive, may lead to a drop in mechanical properties. Additionally, molding of undried polymer usually results in surface defects such as splay or silver streaking. PEI should be dried prior to processing. At lower temperatures, below the softening point of the polymers, adsorbed water can lead to slight changes in mechanical properties (e.g., a slight loss of stiffness) as well as changes in the electrical properties of the molded parts [41–43].

In most cases, thermoplastic polyimides have very good retention of properties when in contact with water. However, in some extreme cases, the polymer chain could be cleaved by the action of water. Such hydrolysis would depend on many factors, including the nature of water contact (immersion, intermittent exposure, condensation, freshly renewed or stagnant water, salt content, etc.). Temperature will obviously be important as well as pH. Polyimides are more reactive at high pH than at lower pH. In some cases, short contact with caustic solutions (high pH) is used to etch polyimide surfaces to improve adhesion. Additionally, part design and molded-in stress will influence hydrolysis and retention of properties on exposure to hydrolytic conditions. Once again, due to the wide range of potential variables involved with hydrolysis, part testing at end-use conditions is the best method to evaluate a resin's fitness for use in a given part design and specific application.

PEI resins are made from high-purity intermediates and have very low ion content. With proper handling and isolation, total extractable inorganic ions are below 100 ppb. Sulfate and chloride ion content can be below 20 ppb. This high purity is useful for preparation of film and handling equipment to make semiconductor wafers and chips for microprocessors, as well as burn-in test sockets.

Uses of Polyetherimide Resins

There are two different types of performance needs that must be considered when one is discussing melt-processable polyetherimides. These two types of performance needs are those of the molders or extruders who fabricate the articles and those of the design engineers and the users of the articles made from the PEI resins.

The molders or extruders are most interested in the melt processing of the resin. Some of their concerns include

- Viscosity
- Molecular weight changes in the melt
- Part appearance
- Time needed to make the parts
- Yield of good parts
- Ability to recycle resins

The other families of users who need to be accommodated when one is developing a polymer (or blend) are the design engineers and end users, the people interested in the performance of the molded part or devices made from it. Their concerns can include the following.

- Is it stiff enough for the application?
- Will it hold up to temperature without deforming?
- How will it hold up to environmental factors such as water, light, heat, and solvent exposure?

The answers to these types of questions are often complex, being influenced by part design, molding, polymer type, and exact end-use conditions.

The concerns of both groups of users have to be accommodated in the molecular structure of the polyetherimides or their blends.

In the case of melt-processable BPADA-based polyetherimides, many of these concerns have been met with great success. However, some of the end-use features have been traded for the ease of processability. An example is that the flexible isopropylidene group introduces somewhat weaker carbon-hydrogen bonds, which can be attacked by oxygen [44–46]. A polyimide with no aliphatic hydrogens may not have this weakness, but may not be melt-processable. In the PEIS resin, the flexibilizing sulfone linkages in the polyetherimide sulfone resin may not be as photo-stable as other functional groups. So in areas of extreme performance, such as parts for external aerospace applications, the melt-processable, BPADA-based polyetherimides may not meet all application requirements. However, in applications requiring a large volume of parts, and where the time needed in making the part is an important factor, the melt-processable resins are very valuable.

Not all resins meet all application needs, which is why so many materials coexist in the polyimide marketplace, each filling a special set of consumer needs. Traditional, thermoset, and melt-processable polyimides each have their place.

Thermoplastic PEI resins provide a good balance of mechanical, physical, and rheological properties. Molded parts can handle short-term thermal excursions to about 240°C (464°F) and extended heat contact for as high as 170°C (338°F), while also providing high strength and stiffness, good dimensional stability, transparency, moderate solvent resistance, ignition resistance, and low smoke.

Photochemistry

PEI resins absorb ultraviolet (UV) as well as visible light. The UV-visible spectra of a typical BPADA-MPD polymer are shown in Fig. 8.7 at both 0.8- and 1.6-mm (0.032- and 0.063-in) thickness. Short exposure to light or UV radiation usually causes no significant changes in thermoplastic PEI.

Prolonged exposure to intense UV light causes a color change in PEI resins and may lead to degradation. However, as in many systems, the photochemistry is often dominated by the presence of pigments. In most cases, PEI resins exposed to high-intensity UV light show rapid color change and loss of gloss, which then levels out after short exposure times. Some glass-fiber-filled PEI resins have an Underwriters Laboratory (UL) listing of F1, which indicates good retention of mechanical and flame-retardant properties after exposure to moisture and light. Polyetherimides also have excellent resistance to ionizing radiation, such as gamma rays.

In applications where the thermoplastic PEI resins are exposed to light or radiation, molded parts should be tested as close as possible to actual end-use conditions to determine fitness for a specific application.

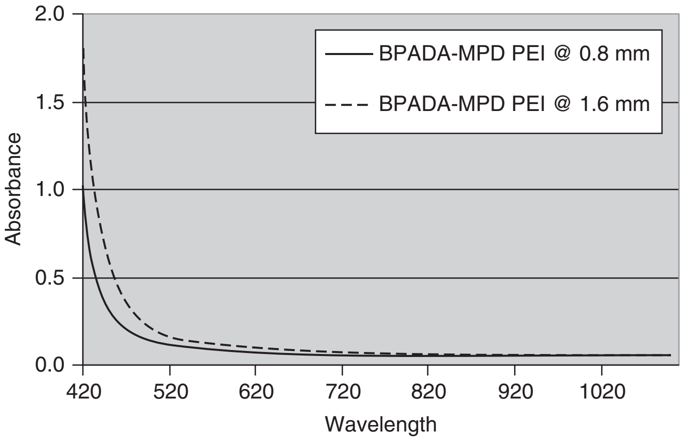


Figure 8.7 UV-visible spectra of a typical BPADA-MPD PEI at 0.8- and 1.6-mm (0.032- and 0.063-in) thickness.

Processing Options

Polyetherimides have been used as a metal, glass, ceramic, and thermoset replacement. Commercial grades have been used primarily in injection-molding applications where these fast-cycling resins have high efficiency for large production runs. In replacement of metals, PEI resins allow for design of complex shapes, often incorporating features that would otherwise require combinations of several metal parts into a single plastic part. This consolidation of parts often makes manufacturing simpler so that even if the cost of the resin is higher than the cost of the metal, the total cost of making and assembling the object is reduced. In addition, parts consolidation reduces the potential for errors during assembly and may simplify manufacturing supply concerns.

The pelletized form of the polymer supplied to converters is fully polymerized. No chemical-curing reaction is needed, and the polymer can be stored under ambient conditions almost indefinitely. There are no shelf-life issues as seen with some amide-acid polymers.

PEI resins have been extruded into film and sheet. Since they are thermoplastic, both sheet and film can be formed and drawn in secondary operations. PEI film can be used in many electrical applications, such as the manufacture of capacitors and flexible circuits. These films can also be laminated or coextruded to make various multilayer structures. PEI films are often laminated with metals, such as copper, which are then made into electric circuits.

PEI resins may also be extruded into rods and blocks, which can be subsequently machined into parts. This is useful where smaller production volumes do not justify the cost of cutting steel tooling in which to mold parts. Fine-denier fibers, which are useful in some flame-retardant applications, have also been drawn from various PEI resins [47, 48].

Because they are thermoplastic, PEI resins can be easily recycled via grinding up old parts and remelting them to form new shapes. This can be done with both post-industrial and post-consumer recycle. In some cases, such as automotive lighting, metallized reflectors may be reused to make parts without removing the thin metal layer [49]. As in all recycling operations, care must be taken to keep the recyclate free of contamination. In addition, since PEI resins can undergo degradation under abusive processing, parts containing recyclate must be tested to ensure they meet all end-use and regulatory requirements.

Thermoplastic PEI resins can be formed into either low-density or high-density (structural) foams [50, 51]. Structural-foam resins (10 to 30% density reduction) are useful in forming large parts with reduced weight, improved flow, and few sink marks. Both gas injection and chemical-blowing agents may be used. Low-density foams (>50% density reduction) are used as panels in transport applications where strength, ignition resistance, and sound damping are possible benefits. PEI resins may also be processed by using profile extrusion (single or multilayer), blow molding, or gas-assist molding.

As molded, PEI resins have very smooth, glossy surfaces. These surfaces may be directly metallized by vacuum sputtering or similar processes [52]. Parts can be metallized as molded with no base coating or secondary operation. They show good metal adhesion [53]. Metal-coated PEI resins are used in a variety of lighting applications as reflectors for high-temperature use such as projectors and automotive forward lighting. Their excellent dimensional stability makes them especially valuable where precise focus of the reflected light is important.

Applications

PEI resins have been used in a variety of applications such as electrical connectors, internal computer parts, printed-circuit boards, flexible circuits, optical fiber connectors, fire helmets, large appliances, aircraft interiors, trays, microwave cookware, reflectors, motor parts, gears, pumps, lubrication systems, wire coating, industrial applications, bearings, small appliances, films, and fibers. Polyetherimides are used in a wide range of applications. A few of the key markets for PEI resins and some of the benefits they bring to the application are summarized below.

- *Food service*: resistance to greases and oils, microwave- and dishwasher-safe, good practical impact, repeated food-contact compliant, and stain-resistant

- *Lighting reflectors*: heat resistant, excellent dimensional stability, smooth surface as molded, good metal adhesion without secondary operations, and light weight [52]
- *Medical*: autoclave and gamma radiation resistance to allow repeated sterilization, transparent, and break-resistant [54]
- *Fluid handling*: excellent dimensional stability, transparent, solvent- and hydrolysis-resistant, with high burst strength
- *Electrical*: high continuous-use temperature, nonhalogenated inherent ignition resistance, good dielectric properties, dimensionally stable, and very low levels of ionic species
- *Automotive underhood*: excellent dimensional stability, light weight, high strength and stiffness, resistance to hot solvents, complex part-design freedom, and parts consolidation
- *Wire coating*: high continuous-use temperature, flexibility (i.e., silicone PEI copolymer), ignition resistance, low smoke, and low smoke corrosivity

Summary

Thermoplastic PEI resins offer high performance with the benefits of melt processing. Chemical structures that provide two or more flexible linkages may result in polymers that are melt-processable. Proper choice of these flexible linkages can allow retention of both short-term and long-term heat resistance. Thermoplastic polyetherimides have high strength and dimensional stability as well as inherent ignition resistance, good electrical properties, transparency, and practical impact strength. PEI resins are easily metallized and recycled. They meet a variety of requirements for the molding and processing community as well as the demanding needs of many end-use applications. New members of this resin family are constantly under development.

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Chapter

9

Polyphenylene Ether (PPE) Blends and Alloys

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Introduction

In 1956, Allan S. Hay of the General Electric Company discovered a convenient catalytic oxidative route to poly(2,6-dimethylphenylene ether), or PPE. This amorphous polymer exhibited excellent hydrolytic stability, an extremely high glass transition temperature [T_g = 419°F (215°C)], outstanding electrical properties over a wide temperature range, low density relative to other engineering thermoplastics, and a high melt viscosity. The polymer was introduced commercially in 1964 under the PPO* trademark [1, 2].

It was soon realized that because of the high glass transition temperature, high melt viscosity, and the resulting elevated temperatures that were required for processing, it would be difficult to avoid oxidative degradation reactions during melt processing. The commercial solution to this problem was blends of PPE with *polystyrene* (PS).

PPE may never have achieved commercial success if PPE's novel compatibility with styrenic polymers had not been discovered at an early stage of development. This fortuitous and rather rare miscible, single-phase

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*Noryl, Noryl GTX, Noryl PPX, PPO, Noryl ETX, and Noryl EF are trademarks of the General Electric Company.

blend provided the basis for the family of PPE/PS alloys, which were commercialized in 1966 under the Noryl* trademark [3]. Modified PPE resins combined the best features of PPE resins and styrene polymers. The Noryl family of resins has become the world's most successful and best-known polymer blends or alloys.

Polymerization and Polymer Structure

The unique catalytic oxidative coupling polymerization to high-molecular-weight, linear aromatic ethers is typically carried out at room temperature by bubbling oxygen through a solution of 2,6-xylenol monomer in the presence of a copper-based catalyst [1, 2, 4].

An interesting feature of the oxidative coupling reaction is that it is a step-growth condensation polymerization. The rate of 2,6-xylenol oxidation is first-order in catalyst, first-order in oxygen pressure, and zero-order in 2,6-xylenol [5]. When the targeted molecular weight is reached, the polymerization is stopped by eliminating the oxygen.

The commercial synthesis of PPE is carried out at 77 to 122°F (25 to 50°C) [4, 6]. However, these polymerizations are exothermic and generally require cooling to attain high-molecular-weight products and selectivity. A typical catalyst is composed of a cuprous halide salt and one or more amines such as pyridine, dibutyl amine, or certain hindered diamines [5–8].

The accepted mechanism involves oxidation, radical coupling, dissociation, and enolization and is shown in Fig. 9.1 [9–11]. Initially 2,6-xylenol, **1**, is oxidized by the catalyst to generate aryloxy radicals [12]. Then two aryloxy radicals couple to form a quinone ether, **2**, which undergoes enolization to form dimer, **3**. The enolization gives a more stable phenol-terminated oligomer, which can be oxidized to generate a new aryloxy radical and continue the polymerization. In like manner dimers are converted to trimers and eventually oligomers to higher-molecular-weight oligomers until high-molecular-weight polymer, **6**, is obtained.

In addition, coupling can occur between various oligomers. For example, two dimer radicals, **4**, can couple to form a quinone ketal, **5**. The unstable quinone ketal then dissociates to trimer and 2,6-dimethylphenoxy radical. The coproduct of the dissociation, 2,6-dimethylphenoxy radical, can undergo further coupling reactions with other oligomers or another 2,6-dimethylphenoxy radical. By this mechanism oligomers would undergo oxidation, coupling, and dissociation to form higher-molecular-weight oligomers and eventually to polymer, **6**.

The principal repeat unit in high-molecular-weight polymer, **6**, is the 2,6-dimethyl-1,4-phenylene unit [13, 14]. In general, a 2,6-dimethylphenoxy tail end group and a 3,5-dimethyl-4-hydroxyphenyl head end group are present at opposite ends of the polymer chain [15].

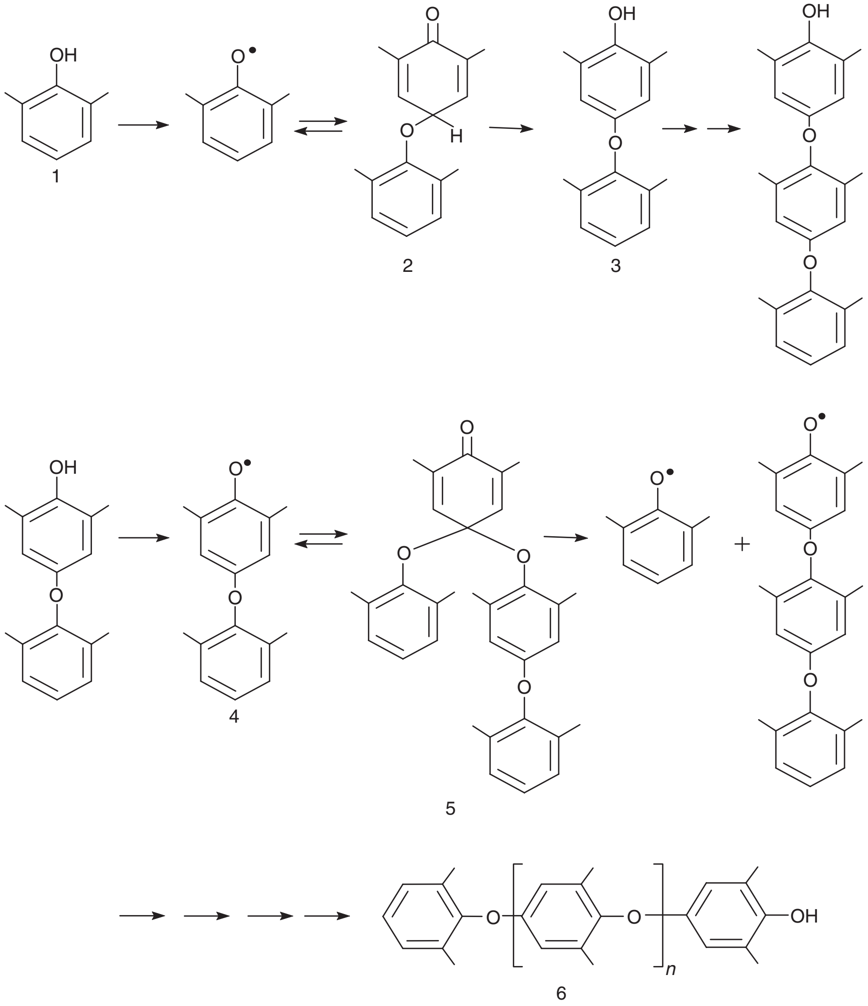

Figure 9.1 Polymerization mechanism and structure of PPE.

PPE/Polystyrene Blends—Modified PPE

The miscible blends of PPE and styrenic resins are often referred to as modified PPE resins. The styrenic resins can vary from crystal polystyrene to *high-impact polystyrene* (HIPS).

In theory, properties of miscible blends should be additive (linear behavior) based on the linear contribution from each polymer fraction [16]. Some properties such as glass transition temperatures and heat distortion temperatures exhibit near-linear behavior in PPE/PS blends, as shown in Fig. 9.2 [17, 18].

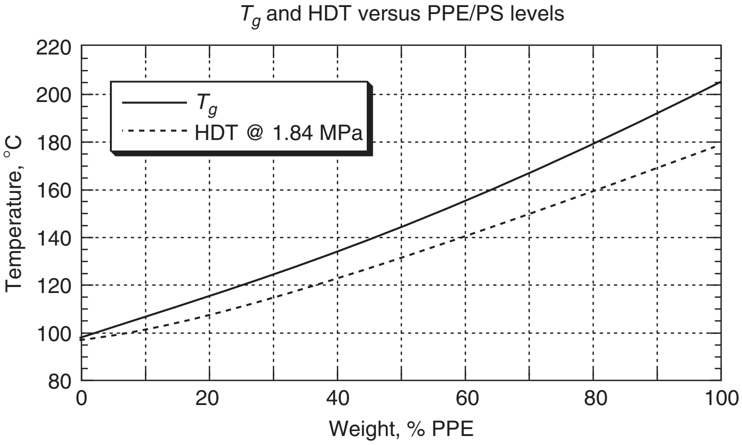

Figure 9.2 Effect of PPE on T_g and HDT.

However, other properties such as flexural modulus and strength, tensile strength, and notched Izod impact strength exhibit a synergistic behavior (positive nonlinear combination) wherein the properties are better than those predicted by linear behavior. The data appear in Fig. 9.3 [17, 18]. Such behavior suggests increased attractive energy between PPE and PS polymer chains.

Modified PPE resins tend to assume the best features of PPE and polystyrene [19, 20]. For example:

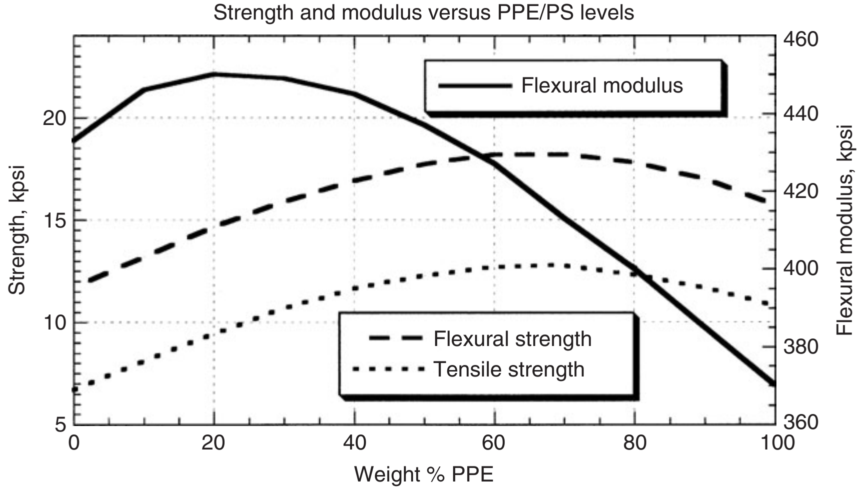

Figure 9.3 Effect of PPE on strength and modulus.

- PPE resins with very high *heat distortion temperatures* (HDTs) can readily raise the HDT of polystyrene polymers to over 212°F (100°C), which is a significant temperature because this allows the material to be used for many boiling water applications.
- Styrene polymers, with ease of processing and well-established impact modification, balance the refractory nature of PPE resins.
- PPE resins bring inherent flame retardance and facilitate making of nonhalogen flame-retardant blends.
- PPE resin and styrene polymers both have excellent water resistance and outstanding electrical properties.
- In addition PPE/PS blends exhibit lower specific gravity than many other engineering thermoplastics.

Modified PPE resins are relatively resistant to burning, and judicious compounding can increase their burn resistance by using nonbrominated, nonchlorinated flame retardants, making them ECO-label compliant.

Modified PPE resins are especially noted for their outstanding hydrolytic stability. They have no hydrolyzable bonds. Their low water absorption rates—both at room temperature and at elevated temperatures—allow the retention of properties and dimensional stability in the presence of water, high-humidity, and even steam environments. In addition, modified PPE resins are generally unaffected by a wide variety of aqueous solutions, detergents, acids, and bases.

Modified PPE resins will soften or dissolve in many halogenated and aromatic hydrocarbons. Laboratory data are available on the chemical resistance of plastics. However, such data should only be used as a screening tool. If a material is found to be incompatible in a short-term test, it will usually be found to be incompatible in a similar end-use environment. The converse, however, is not always true. Favorable results in a short-term test are no guarantee of actual performance in long-term, end-use conditions. The amount of molded-in stress found in any particular part will have a pronounced effect upon the relative chemical compatibility of a polymer. The acceptable chemical compatibility of a polymer in an application can be determined only by exposure or immersion of prototypes and suitably stressed samples in this type of environment under actual operating conditions [21].

The combination of various PPE/PS levels with other additives provides a family of resins covering a very wide range of physical and thermomechanical properties. General characteristics include high heat resistance, excellent electrical properties over a wide temperature and frequency range, low density, hydrolytic stability, chemical resistance to most acids, dimensional stability, low mold shrinkage, and very low creep behavior at elevated temperatures.

Modified PPE resins are available as unfilled and reinforced grades, as well as grades formulated with and without flame-retardant additives. Moreover, modified PPE can be opaque or transparent, rigid or flexible. In addition, modified PPE offers a broad range of processing options including injection molding, extrusion, blow molding, expanded foam, and structural foam molding. PPE is used in blends with polystyrene, alloys with polyamide and polypropylene, and thermoset resins. Clearly the PPE-based resins offer one of the most versatile product families.

The versatility of modified PPE resins has resulted in an extensive variety of applications which include automotive interior, exterior, and under-the-hood applications; computer and business equipment; electrical and electronic devices; health care; building and construction; telecommunications; appliances; water handling equipment; and microwavable food packaging. Noryl modified PPE resins have become the world's most successful and best-known polymer blends and alloys.

Representative grades are discussed in this chapter to show the scope and breadth of PPE-based grades available, and it is not intended to be an inclusive list.

Properties listed in this chapter are determined on standard test parts, using recommended molding conditions, and evaluated by using standard test methods. These data are intended for comparative purposes only and are not intended to give an indication of a material's ability to perform under various conditions. Indeed, plastic parts in end-use situations can encounter mechanical stress, impact, flexure, elevated temperatures, different environments, etc. Proper part design and correct molding conditions are equally important as resin grade selection for an application. It is of importance to minimize stresses in the part through both design and processing.

Abbreviations are used to describe some physical properties in this chapter:

RTI Relative thermal index (formerly named continuous-use temperature) is the maximum service temperature at which the critical properties of a material will remain within acceptable limits over a long time, as established by UL 746B. There can be up to three independent RTI ratings assigned to a material:

- *RTI Electrical* By measuring dielectric strength.
- *RTI with Impact* By measuring tensile impact strength.
- *RTI without Impact* By measuring tensile strength.

Vicat Vicat softening temperature (ASTM D 152) is the temperature at which a plastic starts to soften rapidly. There are two methods:

- *Vicat A* It has a load of 2.25 lb (10 N).
- *Vicat B* It has a load of 11.24 lb (50 N).

HDT Heat deflection temperature (ASTM D 648) is a relative measure of a material's ability to perform for a short time at elevated temperatures while supporting a load. There are typically two specified loads—64 psi (0.45 MPa) and 264 psi (1.82 MPa).

NI Notched Izod impact strength (ASTM D 256). NI can be measured at various temperatures.

UNI Unnotched Izod impact strength (ASTM D 481). UNI can be measured at various temperatures.

CTE Coefficient of thermal expansion is a measure of how much a material will lengthen when heated (or shorten during cooling) versus its original length with respect to the temperature range under which the material is tested as measured. CTE values typically take into account the direction in which the resin flowed during molding and are reported as follows:

- *CTE, flow* Measured in flow direction.
- *CTE, xflow* Measured in the crossflow direction.

Inst. Impact E @ Peak Instrumented impact energy at peak (ASTM D 3763) of a specimen is measured by dropping a load with a certain velocity onto a specimen plaque.

UL-94 V-0, UL-94 V-1, UL-94 V-2, UL-94 5V, UL-94 HB Flame class ratings following UL Bulletin 94. Typically the (minimum) sample thickness which is sufficient to pass the test is reported. Flammability ratings listed in this chapter are not intended to reflect hazards presented by these or other materials under actual fire conditions.

Typical Modified PPE Grades

Key properties are listed below for representative grades based on PPE/PS blends.

Standard grades. Unfilled, general-purpose, and automotive grades offer a broad choice of performance properties that have a range of heat resistance, mechanical properties, and flow characteristics. The combination of low specific gravity, hydrolytic stability, chemical resistance, and electrical properties helps make these resins an outstanding value in a wide range of applications. These versatile resins are used in demanding applications such as connectors, modules, mirror housings, and speakers and trim for the automotive market. Other common markets and applications include cellular phones and valve and pump components. In addition, NSF and FDA compliance grades are available. Representative properties of standard PPE/PS grades appear in Table 9.1. Standard grades and their key features include these:

PX0844: 235°F (113°C) HDT at 264 psi (1.82 MPa)

PX0888: 262°F (128°C) HDT at 264 psi (1.82 MPa)

TABLE 9.1 Properties of General-Purpose PPE/PS Grades

Property	PX0844	PX0888	PX1265	PX1391	STN15HF
Specific gravity	1.06	1.04	1.06	1.07	1.04
Water abs., 24 h at 73°F (23°C), %	0.10	0.10	0.10	0.10	0.2
Tensile strength at yield, psi (MPa)	7200 (50)	8500 (59)	9000 (62)	10,000 (69)	6700 (46)
Tensile elongation at break, %	42	30	35	25	70
Flexural modulus, psi (GPa)	325,000 (2.24)	342,000 (2.36)	335,000 (2.31)	355,000 (2.45)	290,000 (2.00)
Flexural strength, psi (MPa)	11,000 (76)	13,500 (93)	13,500 (93)	16,000 (110)	10,100 (70)
Hardness, Rockwell R	114	118	—	—	—
NI at 73°F (23°C), ft·lb/in (J/m)	4.4 (235)	3.7 (198)	4.6 (246)	4.2 (224)	8.5 (454)
NI at 0°F (–18°C), ft·lb/in (J/m)	—	—	—	—	4.7 (251)
NI at –40°C/F, ft·lb/in (J/m)	2.5 (134)	2.5 (134)	2.5 (134)	2.5 (134)	4.2 (224)
HDT at 66 psi (0.45 MPa), °F (°C)	250 (121)	265 (129)	285 (141)	321 (161)	245 (118)
HDT at 264 psi (1.82 MPa), °F (°C)	235 (113)	262 (128)	276 (136)	309 (154)	240 (116)
CTE, flow, 32 to 212°F, in/in-°F (m/m-°C)	4.1E-5 (7.4E-5)	4.1E-5 (7.4E-5)	4.0E-5 (7.2E-5)	3.8E-5 (7.0E-5)	6.5E-5 (11.7E-5)
RTI electrical, °C	—	—	50	—	—
RTI with impact, °C	—	—	50	—	—
RT. without impact, °C	—	—	50	—	—
UL-94 HB, in (mm)	—	—	0.062 (1.57)	—	—

PX1265: 276°F (136°C) HDT at 264 psi (1.82 MPa)

PX1391: 309°F (154°C) HDT at 264 psi (1.82 MPa); high heat resistance

STN15HF: 240°F (116°C) HDT at 264 psi (1.82 MPa); high impact

Glass-reinforced (general-purpose) grades. These offer a combination of high strength, stiffness, modulus, and dimensional stability. The heat performance and low specific gravity of modified PPE reinforced resins provide many value options versus other engineering thermoplastic resins and versus traditional materials such as brass, aluminum, and other metals. Applications for reinforced modified PPE resins include pump housings, impellers and components, structural parts such as motor mounts, frames and brackets, water filters, coils, and bobbins for automotive ignitions. Representative properties of glass-reinforced PPE/PS grades appear in Table 9.2. Glass-reinforced grades and key features include

Noryl GFN1: 10% glass-reinforced, 256°F (120°C) HDT at 264 psi (1.82 MPa); FDA compliant, NSF Standard 61 listed (restrictions apply)

Noryl GFN2: 20% glass-reinforced, 280°F (138°C) HDT at 264 psi (1.82 MPa); FDA compliant, NSF Standard 61 listed (restrictions apply)

Noryl GFN3: 30% glass-reinforced, 280°F (138°C) HDT at 264 psi (1.82 MPa); FDA compliant, NSF Standard 61 listed (restrictions apply)

TABLE 9.2 Properties of Glass-Reinforced PPE/PS Grades

Property	GFN1	GFN2	GFN3
Specific gravity	1.14	1.20	1.28
Water abs., 24 h at 73°F (23°C), %	0.06	0.06	0.06
Tensile strength at yield, psi (MPa)	10,800 (74)	13,000 (90)	15,000 (103)
Tensile elongation at break, %	—	5	5
Flexural modulus, psi (GPa)	520,000 (3.58)	767,000 (5.29)	1,040,000(7.17)
Flexural strength, psi (MPa)	15,600 (107)	21,000 (145)	23,500 (162)
Hardness, Rockwell L	104	106	108
NI at 23°C, ft·lb/in (J/m)	2.5 (134)	2.0 (107)	2.2 (117)
UNI at –40°C, ft·lb/in (J/m)	1.5 (80)	1.8 (96)	1.8 (96)
HDT at 66 psi (0.45 MPa), °F (°C)	—	293 (145)	317 (158)
HDT at 264 psi (1.82 MPa), °F (°C)	256 (120)	280 (138)	280 (138)
CTE, flow –40 to 200°F, in/in-°F (m/m-°C)	—	2.0E-5 (3.6E-5)	1.4E-5 (2.5E-5)
RTI electrical, °C	90	90	90
RTI with impact, °C	90	90	90
RTI without impact, °C	90	90	90
Dielectric constant, 60 Hz	—	2.86	2.93
Dielectric constant, 1 MHz	2.90	—	—
Dissipation factor, 60 Hz	—	0.0008	0.0009
Dissipation factor, 1 MHz	0.0014	—	—
UL-94 HB, in (mm)	0.058 (1.47)	0.058 (1.47)	0.058 (1.47)

Noryl IGN 320: 20% glass-reinforced, 318°F (159°C) HDT at 264 psi (1.82 MPa); designed for ignition coils

Noryl IGN 5531: 20% glass-reinforced, designed for pencil coils

Flame-retardant (unfilled) grades. These use a nonbrominated, nonchlorinated flame retardant, allowing for ECO-label compliance. They offer a range of thermal and mechanical properties and cost economy for applications including computers and business equipment, electrical, electronic, construction, telecommunications, and appliances. Representative properties of flame-retardant PPE/PS grades appear in Table 9.3. Flame-retardant grades and key features include

Noryl N190X: 190°F (79°C) HDT at 264 psi (1.82 MPa); UL-94 V-0/5VA ratings

Noryl N225X: 211°F (99°C) HDT at 264 psi (1.82 MPa); UL-94 V-0/5VA ratings

Noryl N300X: 293°F (145°C) HDT at 264 psi (1.82 MPa); UL-94 V-0 rating

Noryl SE100X: 199°F (93°C) HDT at 264 psi (1.82 MPa); UL-94 V-0/V-1 ratings

Noryl SE1X: 244°F (118°C) HDT at 264 psi (1.82 MPa); UL-94 V-0/V-1 ratings

Reinforced flame-retardant grades. These offer a broad range of fillers such as fiberglass, mineral, and other exclusive technologies, which provide increased levels of strength, stiffness modulus, dimensional stability, and electrical conductivity. In addition, these reinforced resin grades use a nonbrominated, nonchlorinated flame retardant, allowing for ECO-label compliance. These materials are generally useful to replace metal assemblies and consolidate parts. Applications include uses in computer chassis, pen bodies, paper path applications, electronic media carriers, lighting ballasts, timers, switches, and appliance parts. Representative properties of reinforced, flame-retardant PPE/PS grades appear in Table 9.4. FR reinforced grades and key features include.

Noryl SE1GNF1: 10% glass-reinforced; 269°F (132°C) HDT at 264 psi (1.82 MPa); UL-94 V-1 rating

Noryl SE1GNF2: 20% glass-reinforced; 270°F (132°C) HDT at 264 psi (1.82 MPa); UL-94 V-0/V-1/5VA ratings

Noryl SE1GNF3: 30% glass-reinforced; 275°F (135°C) HDT at 264 psi (1.82 MPa); UL-94 V-0/V-1 ratings

TABLE 9.3 Properties of Flame-Retardant PPE/PS Grades

Property	N190X	N225X	N300X	SE100X	SE1X
Specific gravity	1.12	1.11	1.12	1.10	1.06
Water abs., 24 h at 73°F (23°C), %	0.080	—	0.060	—	0.060
Tensile strength at yield, psi (MPa)	8000 (55)	8800 (61)	11,000 (76)	8400 (58)	9800 (68)
Tensile elongation at break, %	18	17	20	25	20
Flexural modulus, psi (GPa)	332,200 (2.29)	361,500 (2.49)	363,000 (2.50)	335,000 (2.31)	363,000 (2.50)
Flexural strength, psi (MPa)	13,250 (91)	14,400 (99)	16,000 (110)	12,000 (83)	14,800 (102)
Hardness, Rockwell R	120	—	119	—	—
Notched Izod at 23°C, ft·lb/in (J/m)	5.5 (294)	3.5 (187)	4.3 (230)	4.8 (256)	3.9 (208)
Notched Izod at –22°F, ft·lb/in (J/m)	1.2 (64)	1.8 (96)	—	—	2.0 (107)
Vicat softening temp., rate B, °F (°C)	235 (113)	229 (109)	—	—	—
HDT at 66 psi (0.45 MPa), °F (°C)	205 (96)	229 (109)	313 (156)	216 (102)	260 (127)
HDT at 264 psi (1.82 MPa), °F (°C)	190 (88)	211 (99)	293 (145)	199 (93)	244 (118)
RTI, electrical properties, °C	95	95	105	95	110
RTI, mechanical properties with impact, °C	80	80	105	80	105
RTI, mechanical properties without impact, °C	95	95	105	95	110
Dielectric constant, 60 Hz	2.74	2.69	2.68	2.66	2.52
Dielectric constant, 1 MHz	—	2.55	2.63	2.57	2.46
Dissipation factor, 60 Hz	0.0130	—	—	—	—
Dissipation factor, 1 MHz	—	0.0070	0.0090	0.0026	0.0021
Volume resistivity, Ω·cm	1.8E16	2.8E16	1.0E17	3.1E16	2.3E16
UL-94V-1 flame class rating, in (mm)	—	—	—	0.060 (1.52)	0.058 (1.47)
UL-94V-0 flame class rating, in (mm)	0.058 (1.47)	0.060 (1.52)	0.061 (1.55)	0.240 (3.10)	0.240 (3.10)
UL-94-5VA flame class rating, in (mm)	0.120 (3.0)	0.120 (3.0)	—	—	—

TABLE 9.4 Properties of Reinforced, Flame-Retardant Grades

Property	SE1GNF1	SE1GNF2	SE1GNF3	HS1000X	HS2000X
Specific gravity	1.16	1.23	1.31	1.23	1.24
Water abs., 24 h at 73°F (23°C), %	0.070	0.060	0.060	0.070	—
Tensile strength at yield, psi (MPa)	10,800 (74)	15,500 (107)	17,500 (121)	9500 (65)	11,000 (76)
Tensile elongation at break, %	5.0	5.0	5.0	30.0	20.0
Flexural modulus, psi (GPa)	580,000 (4.00)	830,000 (5.72)	1,130,000 (7.79)	420,000 (2.89)	515,000 (3.55)
Flexural strength, psi (MPa)	17,400 (120)	—	—	—	—
Hardness, Rockwell L	104	106	108	—	—
Hardness, Rockwell R	—	—	—	121	—
NI at 23°C, ft·lb/in (J/m)	1.8 (96)	2.0 (107)	2.2 (117)	2.5 (133)	2.4 (128)
NI at –40°C/F, ft·lb/in (J/m)	1.3 (69)	1.8 (96)	1.8 (96)	—	—
Vicat B, °F (°C)	298 (148)	—	—	258 (126)	292 (144)
HDT at 66 psi (0.45 MPa), °F (°C)	—	280 (138)	285 (141)	209 (99)	259 (126)
HDT at 264 psi (1.82 MPa), °F (°C)	269 (132)	270 (132)	275 (135)	200 (93)	240 (116)
RTI electrical, °C	110	110	110	100	100
RTI with impact, °C	105	105	105	85	85
RT. without impact, °C	110	110	110	100	100
Dielectric constant, 60 Hz	3.00	2.98	3.15	3.03	2.89
Dielectric constant, 1 MHz	3.00	—	—	2.83	2.70
Dissipation factor, 60 Hz	0.0017	0.0016	0.0020	0.0270	0.0170
Dissipation factor, 1 MHz	0.0016	—	—	0.0070	0.0044
Volume resistivity, Ω·cm	1.0E15	—	—	1.6E16	1.2E16
UL-94 V, in (mm)	0.058 (1.47)	0.058 (1.47)	0.058 (1.47)	—	—
UL-94 V-0, in (mm)	—	—	—	0.040 (1.02)	0.062 (1.57)
UL-94-5 VA, in (mm)	—	—	—	0.098 (2.49)	0.079 (2.00)

Noryl HS1000X: 13% mineral-filled; 200°F (93°C) HDT at 264 psi (1.82 MPa); UL-94 V-0/5VA ratings

Noryl HS2000X: 17% mineral-filled; 240°F (116°C) HDT at 264 psi (1.82 MPa); UL-94 V-0/5VA ratings

High-modulus reinforced flame-retardant grades. These offer a broad range of fillers, which provide increased levels of strength, stiffness modulus, dimensional stability, and electrical conductivity. These reinforced resin grades use a nonbrominated, nonchlorinated flame retardant, allowing for ECO-label compliance.

The Noryl HM resin grades have been developed to serve tight-tolerance, functional assemblies. These materials expand the fit of engineering thermoplastics into applications previously served exclusively by stamped steel and die-cast metal. Applications where high modulus is a primary consideration include printer bases, copier and desktop chassis, scanner and fax integrated bases, and notebook and connection box enclosures. Representative properties of high-modulus, reinforced, flame-retardant PPE/PS grades appear in Table 9.5. High-modulus grades and key features include

Noryl HM3020: 30% glass-reinforced/mineral-filled; 248°F (120°C) HDT at 264 psi (1.82 MPa); UL-94 V-1/5VA ratings

Noryl HM4025: 40% glass-reinforced/mineral-filled; 250°F (120°C) HDT at 264 psi (1.82 MPa); UL-94 V-0/5VA ratings

Noryl HMC3008A: 30% glass-, mineral-, carbon-fiber-reinforced; 248°F (120°C) HDT at 264 psi (1.82 MPa); UL-94 V-0 rating; static dissipative; for tight-tolerance molding

Noryl HMC202M: 25% carbon-fiber-reinforced; 348°F (176°C) HDT at 264 psi (1.82 MPa); UL-94 V-1 rating; static dissipative; for tight-tolerance molding

Automotive instrument panel grades. These are specifically formulated for the demanding requirements of instrument panel applications. These grade resins can maintain impact strength and toughness over a wide range of temperatures. They offer enhanced foam adhesion and consistent melt behavior. In addition, these resins can provide a low part weight due to modified PPE's inherent low specific gravity. Uses include instrument panel retainers, top covers, center stacks, structural components, and trim. Representative properties of instrument panel PPE/PS grades appear in Table 9.6. Noryl EM grades and key features include

Noryl EM6100: High impact strength; paintable; 240°F (116°C) HDT at 264 psi (1.82 MPa)

Noryl EM6101: High impact strength; improved flow; 250°F (121°C) HDT at 264 psi (1.82 MPa)

TABLE 9.5 Properties of High-Modulus, Reinforced Flame-Retardant PPE/PS Grades

Property	HM3020	HM4025	HMC3008A	HMC202M
Specific gravity	1.31	1.43	1.28	1.18
Water abs., 24 h at 73°F (23°C), %	0.060	0.060	0.060	—
Tensile strength at yield, psi (MPa)	15,000 (107)	18,450 (127)	14,500 (100)	15,000 (103)
Tensile elongation at break, %	—	5.0	4.0	3.8
Flexural modulus, psi (GPa)	1,100,000 (7.58)	1,400,000 (9.65)	1,430,000 (9.85)	1,200,000 (8.27)
Flexural strength, psi (MPa)	21,000 (1450)	23,000 (158)	18,500 (127)	21,300 (147)
Hardness, Rockwell M	88	90	—	—
Hardness, Rockwell R	—	—	120	—
NI at 23°C, ft·lb/in (J/m)	1.7 (91)	1.3 (69)	1.0 (53)	0.8 (43)
UNI at 23°C, ft·lb/in (J/m)	—	—	2.8 (150)	5.0 (267)
HDT at 264 psi (1.82 MPa),°F (°C)	248 (120)	255 (124)	250 (121)	348 (176)
CTE, flow –40° to 200°F, in/in-°F (m/m-°C)	1.3E-5 (2.3E-5)	1.2E-5 (2.2E-5)	—	—
CTE, xflow –40° to 200°F, in/in-°F (m/m-°C)	1.9E-5 (3.4E-5)	1.8E-5 (3.2E-5)	—	—
RTI electrical, °C	50	50	50	50
RTI with impact, °C	50	50	50	50
RTI without impact, °C	50	50	50	50
Volume resistivity, Ω·cm	1.0E16	1.0E16	—	—
UL-94 V-1, in (mm)	0.058 (1.47)	0.062 (1.57)	—	0.059 (1.50)
UL-94 V-0, in (mm)	—	0.126 (3.20)	0.98 (2.49)	—
UL-94-5 VA, in (mm)	0.101 (2.57)	0.100 (2.54)	—	—

TABLE 9.6 Properties of Instrument Panel PPE/PS Grades

Property	EM6101	EM7100	EM7301F	EM7304F	EM7430
Specific gravity	1.05	1.04	1.12	1.15	1.28
Water abs., 24 h at 73°F (23°C), %	0.20	0.10	—	—	—
Tensile strength at yield, psi (MPa)	7800 (54)	6000 (41)	10,000 (69)	11,300 (78)	15,700 (108)
Tensile elongation at break, %	50	48	5	2	1.5
Flexural modulus, psi (GPa)	335,000 (2.31)	320,000 (2.21)	529,000 (3.65)	660,000 (4.55)	1,210,000 (8.34)
Flexural strength, psi (MPa)	11,800 (81)	9000 (62)	14,000 (96)	15,800 (109)	23,500 (162)
NI at 73°F (23°C), ft·lb/in (J/m)	6.0 (320)	6.5 (347)	1.3 (69)	1.2 (64)	1.7 (91)
NI at –40°C/F, ft·lb/in (J/m)	3.0 (160)	3.0 (160)	—	—	—
Inst. impact E at peak, 73°F (23°C), ft·lb (J)	39 (53)	22.5 (30)	—	—	10.3 (14)
Inst. impact E at peak –22°F (–30°C), in·lb (J)	19 (26)	8.3 (11)	—	—	—
HDT at 66 psi (0.45 MPa), °F (°C)	255 (124)	215 (102)	—	—	265 (129)
HDT at 264 psi (1.82 MPa), °F (°C)	250 (121)	209 (98)	252 (122)	354 (123)	251 (122)
CTE, flow, 32 to 212°F, in/in-°F) (m/m-°C)	5.2E-5 (9.4E-5)	4.1E-5 (7.4E-5)	—	—	1.1E-5 (1.98E-5)

Noryl EM7100: Good impact strength; easy processing; 209°F (98°C) HDT at 264 psi (1.82 MPa)

Noryl EM7301F: 10% glass-reinforced; good polyurethane foam adhesion; 252°F (122°C) HDT at 264 psi (1.82 MPa)

Noryl EM7304F: 15% glass-reinforced; enhanced polyurethane foam adhesion; 254°F (123°C) HDT at 264 psi (1.82 MPa)

Noryl EM7430: 30% glass-reinforced; high modulus; excellent flow; 251°F (122°C) HDT at 264 psi (1.82 MPa)

Structural foam grades. These are specifically formulated as an efficient and economical way to gain high strength and rigidity required for structural parts. Thermoplastic structural foam is a form of injection molding. Structural foam parts have a foam core sandwiched between two dense skins. The foam core is achieved by introducing an inert gas which acts as a foaming agent for the molten resin. The gas is compressed in the barrel of the molding machine. When the molten resin/gas mixture is injected into the mold cavity as a short shot, the gas expands within the plasticized material, helps to carry the resin throughout the mold cavity, and fills the mold. Compressing the foam against the surfaces of the mold cavity creates the dense skin.

Structural foam is generally made in a low-pressure process where the cavity is not completely filled with the initial injection of the mixture. This low-pressure process features the ability to provide a large part molded with an internal cellular structure and a tough external skin while enjoying the economics of reduced clamp tonnage.

In general, wall thickness for structural foam applications ranges from about 0.150 to 0.500 in (3.81 to 12.7 mm) with an average thickness of 0.250 in (6.35 mm). Parts are referred to as having weight or density reduction. This describes how much the part weight has been reduced when compared to a solid injection-molded part. For example, a part having a 20% weight reduction is produced by filling the mold cavity 80% full. The other 20% of the mold cavity is filled by the expansion of the resin. Thick wall parts achieve higher weight reductions than thin walls.

Structural foam parts have the combination of performance properties and process features that deliver increased stiffness to weight ratio. Hence they are suitable for metal replacement in some applications.

Modified PPE structural foam grades can maintain the strength required for many structural parts. They are often used as an alternative to metal. The combination of performance properties and process features can deliver superior strength and rigidity per unit weight. Structural foam grades offer enhanced heat insulation, improved electrical and acoustical characteristics, excellent dimensional stability—including low creep and water absorption, less tendency to observe sink marks on the surface opposite ribs and bosses, and increased chemical resistance when compared to conventional injection molded parts. These grades are formulated with a non-brominated, non-chlorinated flame retardant.

Uses include electrical enclosures, medical equipment enclosures, copiers and large business machine housings and their structural bases, and lightweight structural interior components for transportation. Structural foam grades and key features include

Noryl FN150X: Thin-wall capability; 165°F (74°C) HDT at 264 psi (1.82 MPa); UL-94 V-0/5VA ratings

Noryl FN170X: 173°F (78°C) HDT at 264 psi (1.82 MPa); UL-94 V-1/5VA ratings

Noryl FN215X: 170°F (77°C) HDT at 264 psi (1.82 MPa); UL-94 V-1/V-0/5VA ratings

Noryl FM3020: 30% glass-reinforced/mineral filler; 230°F (110°C) HDT at 264 psi (1.82 MPa); UL-94 V-1/5VA ratings

Noryl FM4025: 40% glass-reinforced/mineral filler; 230°F (110°C) HDT at 264 psi (1.82 MPa); UL-94 V-1/V-0/5VA ratings

Table 9.7 contains representative properties of some PPE/PS structural foam grades. In general, properties on structural foam parts are measured on 0.25-in- (6.4-mm-) thick foamed parts. The weight reduction of the test parts of the various grades appears in this table. For flame ratings, the minimum density and the minimum thickness needed to achieve a flame rating are listed.

Expandable modified PPE grades. These are used to prepare low-density, foamed thermoplastic parts. Unlike with structural foam, the densities are significantly lower and are designed for applications requiring high energy absorption, temperature resistance, and light weight. Typically a volatile material is incorporated into modified PPE beads. When heated, the beads soften and expand. These preexpanded beads have a fine closed-cell structure. After a short maturation period the preexpanded beads become suitable for molding.

In the molding process, preexpanded beads are introduced into a closed mold and then heated, whereupon the beads soften, reexpand to fill the interstitial volume, and typically fuse together without the need for external pressure. Expanded foam modified PPE materials exhibit

- Fine and homogeneous closed-cell structures
- Low densities: 1.25 to 12.5 lb/ft^3 (0.02 to 0.2 g/cm^3)
- Outstanding thermal stability up to 248°F (120°C)

TABLE 9.7 Properties of Structural Foam PPE/PS Grades

Property	FN150X	FN170X	FN215X	FM3020	FM4025
Weight reduction	20	10	20	10	10
Specific gravity, solid	1.12	1.11	1.10	1.32	1.43
Specific gravity, foam-molded	0.90	1.00	0.88	1.19	1.29
Water abs., 24 h at 73°F (23°C), %	0.060	0.060	0.070	0.080	0.080
Tensile strength at yield, psi (MPa)	4100 (28)	4230 (29)	4200 (29)	10,500 (72)	12,000 (83)
Tensile elongation at break, %	14	13	—	—	—
Flexural modulus, psi (GPa)	253,000 (1.74)	309,000 (2.13)	276,000 (1.90)	950,000 (6.55)	1,150,000 (7.93)
Flexural strength, psi (MPa)	7600 (52)	9650 (66)	8900 (61)	15,200 (105)	17,600 (121)
Hardness, Rockwell M	—	—	—	83	85
Hardness, Rockwell R	121	—	—	—	—
NI at 73°F (23°C), ft·lb/in (J/m)	—	—	—	1.8 (96)	1.3 (69)
UNI at 73°F (23°C), ft·lb/in (J/m)	6.4 (342)	5.2 (278)	3.8 (203)	—	2.0 (107)
Inst. impact E at peak, 73°F (23°C), ft·lb (J)	—	42.5 (57)	8.1 (11)	—	—
Inst. impact E at peak, –22°F (–30°C), in·lb (J)	—	—	2.4 (3)	—	—
Vicat softening temp., rate B, °F (°C)	230 (110)	—	—	—	—
HDT at 66 psi (0.45 MPa), °F (°C)	193 (89)	193 (89)	192 (89)	245 (118)	245 (118)
HDT at 264 psi (1.82 MPa), °F (°C)	165 (74)	173 (78)	170 (77)	230 (110)	230 (110)
RTI, electrical properties, °C	50	85	85	50	50
RTI, mechanical properties with impact, °C	50	85	85	50	50
RTI, mechanical properties without impact, °C	50	85	85	50	50
Flame rating—minimum density, g/cc	0.90	1.00	0.85	1.12	1.26
UL-94 V-1 flame class rating, in (mm)	—	0.121 (3.04)	0.154 (3.9)	0.113 (2.87)	0.113 (2.87)
UL-94 V-0 flame class rating, in (mm)	0.156 (3.96)	—	0.240 (6.1)	—	0.195 (4.95)
UL-94 5 VA flame class rating, in (mm)	0.156 (3.96)	0.186 (4.7)	0.154 (3.9)	0.113 (2.87)	0.113 (2.87)

- Low thermal conductivity
- Excellent energy and shock absorption capability
- High strength-to-weight ratio
- Excellent dimensional stability
- Resistance to moisture
- CFC and HCFC free
- Recyclability

This versatility offers opportunities in automotive interior applications (door padding and panels, knee bolsters, head restraint systems, sun visors, instrument panels, rear parcel shelves), exterior applications (bumpers, body support), and cavity filling (car trunks, floor systems).

Noryl EF expandable beads, an interpolymer of PPE and expandable polystyrene EPS, are available in 100, 200, and 300 series. FR grades use a nonbrominated, nonchlorinated flame retardant. The grades are listed below along with an indication of their thermal stability, i.e., temperature at which there is no significant deformation after 1-h exposure (ISO 2796-1980). These grades and key features include

Noryl EF 150 and EF170: Medium heat resistance, 219°F (104°C)

Noryl EF 150FR and EF170FR: Flame retardant; medium heat resistance, 219°F (104°C)

Noryl EF 250 and EF270: Higher heat resistance, 230°F (110°C)

Noryl EF 350 and EF370: Highest heat resistance, 244°F (118°C)

Blow-molding grades. These take advantage of the excellent melt strength of modified PPE required for extrusion of the hollow parison of molten resin into various lengths without significant sagging during the process. In the blowing process, the molten parison is stretched outward to conform to the shape of the mold. Modified PPE provides opportunities for improved extrusion productivity. Blow-molding grades are formulated with and without a nonbrominated, nonchlorinated flame retardant. Applications include automotive exterior spoilers, office and hospital furniture, and business equipment enclosures. Representative properties of blow-molding PPE/PS grades appear in Table 9.8. Blow-molding resins and key features are

Noryl BN30: 180°F (82°C) HDT at 264 psi (1.82 MPa); UL-94 V-1/V-2/5VA ratings

Noryl BN31: 180°F (82°C) HDT at 264 psi (1.82 MPa); UL-94 V-0/5VA ratings

TABLE 9.8 Properties of PPE/PS Blow Molding-Grades

Property	BN30	BN31	BN5308	BN9003
Specific gravity	1.09	1.10	1.09	1.04
Tensile strength at yield, psi (MPa)	6200 (43)	7000 (48)	7300 (50)	7000 (48)
Tensile elongation at break, %	—	—	34	47
Flexural modulus, psi (GPa)	325,000 (2.24)	350,000 (2.41)	319,000 (2.20)	295,000 (2.03)
Flexural strength, psi (MPa)	8600 (59)	10,500 (72)	10,400 (72)	10,400 (72)
NI at 23°C, ft·lb/in (J/m)	5.0 (267)	5.0 (267)	7.5 (401)	8.2 (438)
NI at –40°F/°C, ft·lb/in (J/m)	—	2.0 (107)	—	5.0 (267)
Inst. impact E at peak, 73°F (23°C), ft·lb (J)	—	—	—	35.0 (47)
HDT at 66 psi (0.45 MPa), °F (°C)	—	—	—	255 (124)
HDT at 264 psi (1.82 MPa), °F (°C)	180 (82)	180 (82)	179 (82)	245 (118)
CTE, flow –40 to 200°F, in/in-°F (m/m-°C)	—	—	—	5.2E-5 (9.4E-5)
RTI electrical, °C	50	95	50	—
RTI with impact, °C	50	80	50	—
RTI without impact, °C	50	95	50	—
UL-94 V-0, in (mm)	—	0.058 (1.47)	—	—
UL-94 V-1, in (mm)	0.125 (3.20)	—	0.0583 (1.5)	—
UL-94 V-2, in (mm)	0.062 (1.57)	—	—	—
UL-94 5 VA, in (mm)	0.150 (4.45)	0.120 (3.05)	—	—

Noryl BN5308: 179°F (82°C) HDT at 264 psi (1.82 MPa); UL-94 V-1 rating

Noryl BN9003: 245°F (118°C) HDT at 264 psi (1.82 MPa); good ductility, low-temperature impact

Flame-retardant extrusion grades. These take advantage of the excellent melt strength of modified PPE and provide opportunities for improved extrusion productivity. Extrusion grades are formulated with a nonbrominated, nonchlorinated flame retardant. Extrusion grades find uses in PVC underground pipe replacement, office wire trim, fiber-optics raceways, bus trims, and roofing panels. Grades and key features are

Noryl EN185: Excellent impact strength; 210°F (99°C) HDT at 264 psi (1.82 MPa); UL-94 V-1/5VA ratings

Noryl EN212: 254°F (123°C) HDT at 264 psi (1.82 MPa); UL-94 V-1/5VA ratings

Noryl EN265: 254°F (123°C) HDT at 264 psi (1.82 MPa); UL-94 V-0/V-1 ratings

Noryl ENV105: Corrugated pipes; 176°F (80°C) HDT at 264 psi (1.82 MPa); UL-94 V-1 rating

Food packaging grades. These are a segment of extrusion grades formulated for the food packaging industry. Modified PPE offers impact and heat resistance, hydrolytic stability, dimensional stability, and high melt strength suitable for food packaging such as freezer-to-microwave packaging and takeout food containers. Key advantages of modified PPE packaging resins over other plastics include

- Microwavable: heat resistance >212°F (100°C)
- Available in opaque and transparent/translucent
- Colorable
- Freezer-safe—excellent impact strength at low temperatures
- Safe handling—practical stiffness over a wide temperature range
- Food contact compliant (FDA 21 CFR 177.2460)
- Hydrolytic stability
- No taste or odor transfer
- Design flexibility (e.g., hinge, multicompartment, deep draw, thinner gauge)
- Dimensional stability
- Suitable for mono-, multi-, and foam extrusion
- System cost reduction

Unlike polypropylene, PPE/PS resists breakage at freezer temperatures, and it maintains rigidity at much thinner gauge. In addition, practical stiffness at elevated temperature is better than PP or PET.

Further, modified PPE resins can be processed on most standard PS and PET extrusion and tooling equipment, enabling converters to extend their portfolio without a large capital investment.

These packaging grades can be used as an additive for polystyrene to improve material stiffness at elevated temperatures as well as increase impact at low temperatures.

Food packaging grades have the Noryl PKN designation and they include

Noryl PKN 4717: Transparent, foamable, 315°F (157°C) Vicat

Noryl PKN 4766: Transparent; 264°F (129°C) Vicat

Noryl PKN 4752: Transparent, 345°F (174°C) Vicat

Noryl PKN 4765: Opaque, 304°F (151°C) Vicat

Noryl PKN 4775: Opaque, 288°F (142°C) Vicat

Flexible flame-retardant grades. These are a new family of flexible modified-polyphenylene ether resins specifically developed for wire-coating applications. They are designed as an alternative to *polyvinyl chloride* (PVC), *flame-retarded polyethylene* (FR-PE), and *thermoplastic polyurethane* (TPU) in wire-coating applications for the direct-current (dc) cord and plug segments of the consumer electronics industry. Flexible PPE resins meet OEM requirements for bending strength, flexural strength, durability, hydrolytic stability, and insulating properties.

Flexible PPE grades are nonhalogenated, contain no heavy-metal pigments, offer broad thermal performance, and are lighter and more flexible than many competitive thermoplastics and offer lower systems costs. For example, PVC contains chlorine, which can break down into toxic and highly acidic gases when burned; flexible PPE exhibits a lower density than FR-PE and TPU—weight reductions of 20 to 30% are achievable; and the higher flow characteristics and faster extrusion rates suggest the potential for higher productivity.

The new grades Noryl WCD910 and Noryl WCP860 address several important needs of the electronics cord/plug segment, particularly the need for polymers of less environmental concern (ECO-label). Indeed, Europe and Asia are moving to the use of nonhalogenated materials and are also calling for a reduction or elimination of heavy-metal pigments, which also raise environmental concerns. Additionally, there is strong incentive to use polymers that can easily be recycled—both in the plant and at the end of component life—which favors thermoplastics over thermosetting polymers.

The new flexible PPE grades are candidates for a variety of consumer electronics applications. These include plug and cord applications for desktop and notebook computers, personal digital assistants, faxes, portable personal computers, printers, scanners, digital cameras, radio/cassette, portable CDs, microdisk, MP3, DVD players, video/TV games, sound system components, mobile phone accessories, and cordless phones.

PPE/Polyamide Alloys

Semicrystalline polyamide resins have a broad balance of engineering properties including excellent chemical resistance and toughness [22, 23]. However, the low T_g of polyamides results in dimensional changes at relatively low temperatures. The tendency of polyamides to absorb moisture results in limited dimensional stability and limits the performance window of unfilled polyamides. For example, upon exposure to moisture, polyamides will absorb high levels of moisture, which acts as a plasticizer for the polyamide and results in lower strength and rigidity. In addition, this increase in moisture is accompanied by an increase in the dimensions of molded parts.

The use of glass fiber and mineral fillers blended with the polyamide has been employed to address moisture uptake and growth. However, inorganic fillers increase the specific gravity and severely decrease the ductility of polyamides.

Alloying PPE with polyamide reduces the issues of polyamide moisture uptake and low dimensional stability. Blending PPE with polyamides gives an immiscible blend with two discrete phases. Compatibilization technology is used to improve the interfacial adhesion between the two phases, enhance properties, and give a stable morphology [24, 25]. A drawing of the morphology is depicted in Fig. 9.4.

Hence PPE/PA alloys have the polyamide as the continuous phase for good chemical resistance and processability. The discrete phase consists of finely dispersed particles of PPE. The PPE acts as an "organic filler" which lowers moisture uptake, increases properties at elevated

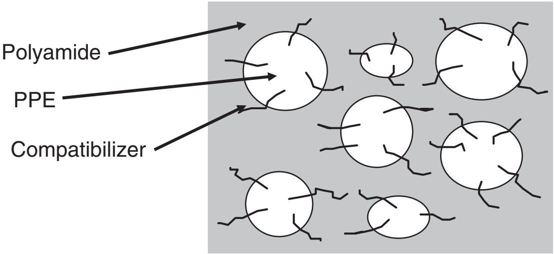

Figure 9.4 Model of morphology of compatibilized PPE/PA alloy.

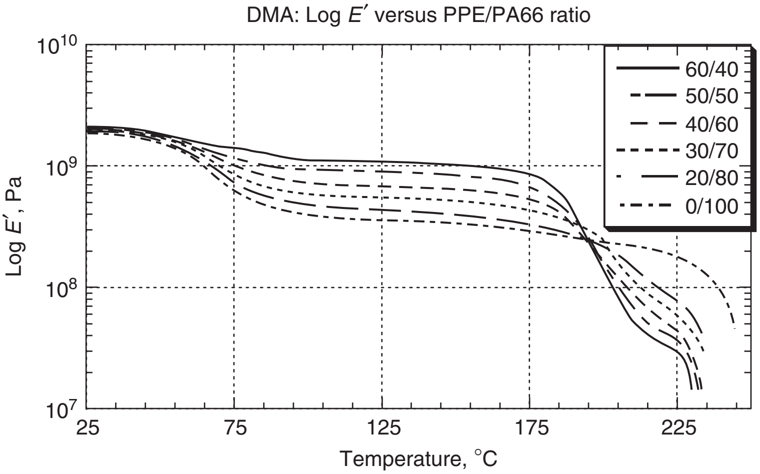

Figure 9.5 Effect of PPE on storage modulus of PPE/PA66 alloys.

temperatures, improves dimensional stability, and lowers the density. An example of the increased performance at elevated temperatures is shown by *dynamic mechanical analysis* (DMA) in Fig. 9.5. In a series of PA66/PPE alloys the storage modulus E' increases as the PPE level is increased. The effect of PPE lowering the moisture uptake is shown in Fig. 9.6. Generally, as the PPE content is increased, the moisture uptake is decreased.

In 1984 a unique family of PPE/PA alloys was commercialized under the Noryl GTX trademark [24, 26]. Initially, PPE/PA resins were

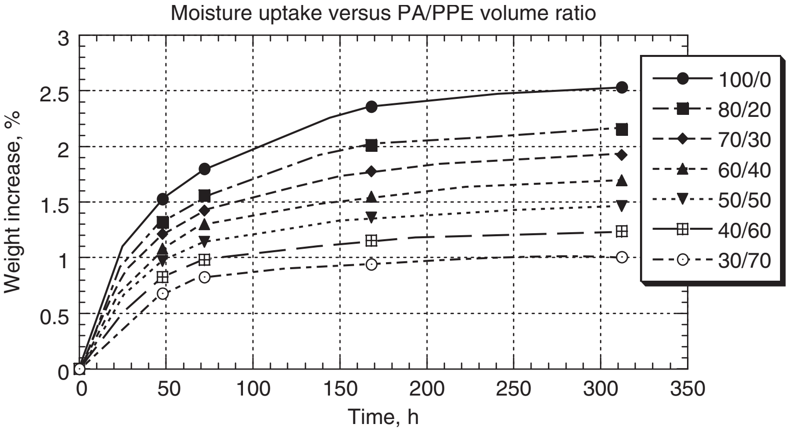

Figure 9.6 Effect of PPE on moisture uptake in PPE/PA alloys.

designed for use in exterior automotive parts, i.e., an injection-moldable thermoplastic with both the strength and rigidity needed for large panels and the high heat resistance for in-line or online painting. PPE/PA alloys offer a unique balance of properties, which is not available in a single resin. These include

- Good low-temperature impact
- High heat resistance
- Short-term thermal capability over 400°F (200°C)
- Online paint capability
- Lower moisture absorption and lower moisture growth over polyamide
- Higher properties at elevated temperatures
- Better dimensional stability over nylon
- Chemical resistance (automotive fluids)
- Lower density
- Surface appearance (Class A)

PPE/PA resins are available as unfilled and reinforced grades, a flame-retardant grade, and conductive grades. In addition, there are PPE/PA grades that can be processed by injection molding, extrusion, and blow molding. The performance advantages of long glass-fiber-reinforced PPE/PA66 materials have been studied [27].

PPA/PA resins exhibit broad environmental resistance to commonly used automotive fuels, greases, and oils. In addition, these resins are resistant to detergents, alcohols, aliphatic and aromatic hydrocarbons, and alkaline chemicals. Where an application requires exposure to, or immersion in, these or other harsh environments, the acceptable chemical compatibility of a plastic in an application can only be determined by exposure to or immersion of prototypes or suitably stressed samples in this type of environment under actual operating conditions [21].

The versatility of PPE/PA resins has resulted in an extensive variety of automotive and nonautomotive applications. These include automotive wheel covers, automotive exterior vertical body panels, automotive electrical connectors, fluid engineering, office furniture, and lighting.

PPE/Polyamide Grades

Unfilled PPE/PA grades. These offer enhanced dimensional stability, chemical resistance, and in most cases paintability. These grades are made with polyamide 66. Representative properties of PPE/PA66 grades appear in Table 9.9. Grades and key features include

TABLE 9.9 Properties of PPE/PA66 Grades

Property	GTX902	GTX910	GTX918W	GTX964W
Specific gravity	1.08	1.10	1.09	1.08
Water abs., 24 h at 73°F (23°C), %	0.4	0.5	0.5	0.6
Water abs., equilib. 73°F (23°C), %	1.0	1.0	1.3	1.2
Tensile strength at yield, psi (MPa)	8700 (60)	8600 (59)	9000 (62)	6500 (45)
Tensile elongation at break, %	52	60	53	56
Flexural modulus, psi (GPa)	325,000 (2.24)	326,000 (2.25)	343,000 (2.36)	266,000 (1.84)
Flexural strength, psi (MPa)	13,000 (90)	13,900 (96)	14,300 (99)	10,700 (74)
Hardness, Rockwell R	118	116	—	—
NI at 23°C, ft·lb/in (J/m)	5.1 (272)	4.5 (240)	3.8 (203)	9.9 (529)
NI at –22°F (–30°C), ft·lb/in (J/m)	2.2 (117)	2.5 (134)	1.0 (53)	1.5 (80)
NI at –40°F (–40°C), ft·lb/in (J/m)	1.0 (53)	—	—	—
UNI at 23°C, ft·lb/in (J/m)	60 (3204)	—	—	—
UNI at –40°F (–40°C), ft·lb/in (J/m)	60 (3204)	—	—	—
Vicat B, °F (°C)	451 (233)	450 (232)	473 (245)	347 (175)
HDT at 66 psi (0.45 MPa), °F (°C)	312 (156)	380 (193)	372 (189)	365 (185)
HDT at 264 psi (1.82 MPa), °F (°C)	262 (128)	290 (143)	300 (149)	—
CTE, flow 0 to 300°F, in/in-°F (m/m-°C)	5.0E-5 (9.05E-5)	5.0E-5 (9.0E-5)	4.4E-5 (8.0E-5)	5.0E-5 (9.0E-5)
RTI electrical, °C	50	50	120	—
RTI with impact, °C	50	50	110	—
RTI without impact, °C	50	50	125	—
UL-94 HB, in (mm)	0.058 (1.5)	0.058 (1.5)	0.058 (1.5)	—

Noryl GTX 902: 312°F (156°C) HDT at 66 psi (0.45 MPa); dimensionally stable; paintable; gives Class A surface appearance

Noryl GTX 910: 380°F (193°C) HDT at 66 psi (0.45 MPa); dimensionally stable grade useful in automotive online painted components; gives Class A surface appearance

Noryl GTX 918W: 372°F (189°C) HDT at 66 psi (0.45 MPa); high flow grade for under-the-hood and electrical applications requiring retention of properties under thermal load

Noryl GTX 964W: 365°F (185°C) HDT at 66 psi (0.45 MPa); high flow grade useful for body panels, large parts, and thin-wall applications

Glass-reinforced PPE/PA grades. These offer increased stiffness, chemical resistance, and dimensional stability. Compared with glass-reinforced polyamide 66 at equal glass levels, PPE/PA66 offers lower density and higher strength and modulus under humid conditions and at elevated temperatures. Comparative data appear in Table 9.10 [28].

Representative properties of glass-reinforced PPE/PA66 grades appear in Table 9.11. Grades and key features include

Noryl GTX 810: 10% glass-reinforced; 473°F (245°C) HDT at 66 psi (0.45 MPa); increased stiffness, high heat resistance, and high heat resistance; suitable for automotive electrical connectors and lighting applications

TABLE 9.10 Comparison of Glass-Reinforced PPE/PA66 and PA66

	10% GF		30% GF	
Property	PPE/PA66	PA66	PPE/PA66	PA66
Specific gravity	1.163	1.204	1.37	1.33
Dry as molded				
Flexural modulus, psi (GPa)	551,000 (3.8)	652,500 (4.5)	1,174,500 (8.1)	1,203,500 (8.3)
Flexural strength, psi (MPa)	21,170 (146)	21,895 (151)	36,395 (251)	39,875 (275)
Conditioned at 100% relative humidity				
Flexural modulus, psi (GPa)	377,000 (2.6)	333,500 (2.30)	841,000 (5.8)	594,500 (4.1)
Flexural strength, psi (MPa)	15,805 (109)	13,485 (93)	30,450 (210)	29,000 (200)
Properties at 302°F (150°C)				
Flexural modulus, psi (GPa)	232,000 (1.6)	130,500 (0.9)	623,500 (4.3)	464,000 (3.2)
Flexural strength, psi (MPa)	8700 (60)	7975 (55)	18,560 (128)	17,690 (122)

TABLE 9.11 Properties of Glass-Reinforced PPE/PA66 Grades

Property	GTX810	GTX8410	GTX820	GTX830
Specific gravity	1.16	1.17	1.24	1.33
Water abs., 24 h at 73°F (23°C), %	0.5	—	0.5	0.5
Water abs., equilib. 73°F (23°C), %	1.0	—	1.0	1.0
Tensile strength at yield, psi (MPa)	13,000 (90)	13,900 (96)	17,000 (117)	22,000 (152)
Tensile elongation at break, %	10	9	7	37
Flexural modulus, psi (GPa)	575,000 (3.96)	595,000 (4.10)	865,000 (5.96)	1,245,000 (8.58)
Flexural strength, psi (MPa)	22,500 (155)	21,000 (152)	28,200 (194)	36,000 (248)
Hardness, Rockwell R	119	—	119	120
NI at 23°C, ft·lb/in (J/m)	1.5 (80)	0.8 (43)	1.5 (80)	2.0 (107)
NI at –22°F (–30°C), ft·lb/in (J/m)	1.0 (53)	0.7 (37)	1.0 (53)	1.5 (80)
UNI at 23°C, ft·lb/in (J/m)	—	9.1 (486)	—	—
Vicat B, °F (°C)	465 (241)	460 (238)	480 (249)	480 (249)
HDT at 66 psi (0.45 MPa), °F (°C)	473 (245)	486 (252)	490 (254)	490 (254)
HDT at 264 psi (1.82 MPa), °F (°C)	410 (210)	410 (210)	450 (232)	465 (241)
CTE, flow 0 to 300°F, in/in-°F (m/m-°C)	2.8E-5 (5.04E-5)	4.0E-5 (7.4E-5)	2.2E-5 (4.0E-5)	1.7E-5 (3.1E-5)
RTI electrical, °C	120	—	120	120
RTI with impact, °C	60	—	60	90
RTI without impact, °C	125	—	125	125
UL-94 HB, in (mm)	0.058 (1.5)	—	0.058 (1.5)	0.058 (1.5)

Noryl GTX 8410: Higher flow, 10% glass-reinforced; 486°F (252°C) HDT at 66 psi (0.45 MPa); suitable for thin-wall automotive electrical applications

Noryl GTX 820: 20% glass-reinforced; 490°F (254°C) HDT at 66 psi (0.45 MPa); higher strength and stiffness; suitable for valve applications

Noryl GTX 830: 30% glass-reinforced; 490°F (254°C) HDT at 66 psi (0.45 MPa); high heat resistance; highest strength and stiffness grade; suitable for under-the-hood applications and pumps

Conductive PPE/PA grades. These uniquely combine high heat resistance for electrostatic-coat capability and conductivity to eliminate conductive primers and improve paint transfer capability. These grades are based upon GE's exclusive patented technology for dispersing conductive carbon black in PPE/PA alloys. This resin technology was originally developed to replace exterior automotive metal body panels requiring high ductility, and it has largely been driven by the industry's requirement to reduce weight in cars and for improved impact performance. In some cases, body panels and fenders made of this material have been shown to withstand an impact test without permanent deformation.

The potential for productivity improvements from conductive PPE/PA resins includes elimination of the paint primer, ability to coat plastic and metal parts on the same line, excellent color matches between metal and plastics, and overall system cost savings. These characteristics, coupled with its inherent light weight, improved efficiency of assembly, and high impact strength, can make PPE/PA resins exceptional alternatives to metal parts and other material substrates in a variety of applications, including automotive body components (tank flaps, spoilers, front grills, rear and front corner panels, license plate appliqué, pillar trim, mirror housings, and side trim and sill finishers), outdoor vehicles, lawn and garden equipment, appliances, office furniture, and lighting fixtures. These grades include

Noryl GTX 975: can be either painted or powder-coated in-line with metal parts in just one run, without the need for conductive primers. Furthermore, because of its extra high heat resistance [365°F (185°C) HDT at 66 psi (0.45 MPa)], it can replace lower heat-resistant resins which have to be painted off-line, thus contributing to greater efficiency in part assembly. In addition, the resin's increased stiffness and dimensional stability offer even greater design flexibility and integration potential in replacing metal, and hence even greater potential weight savings. The low thermal expansion enables better gap and flush management on the car body.

Noryl GTX 973, 976, and 979: These are new grades of conductive resins and are specially designed to withstand the higher heat of the powder coating process. They exhibit excellent performance levels in adhesion, high impact, chemical resistance, and 374, 347, and 352°F (190, 175, and 178°C) HDT at 66 psi (0.45 MPa), respectively.

Noryl GTX 4110: This is a 10% glass-reinforced, flame-retardant, conductive grade. It uses a nonbrominated, nonchlorinated, nonred phosphorous flame retardant, allowing for ECO-label compliance. It offers V-0 performance at 0.118 in (3.00 mm) and 5 VA at 0.098 in (2.5 mm). The HDT at 66 psi (0.45 MPa) is 455°F (235°C).

Extrusion and blow-molding grades. These are based on polyamide 6 and are designed for high melt strength to facilitate extrusion and blow molding. These grades and key features are

Noryl GTX 626: 355°F (179°C) HDT at 66 psi (0.45 MPa); extrusion and blow-molding applications

Noryl GTX 628: 363°F (184°C) HDT at 66 psi (0.45 MPa); blow-molding applications

PPE/Polypropylene Alloys

The newest PPE alloy combines PPE with *polypropylene* (PP). PPE and PP polymers are incompatible with each other. However, PPE/PP alloys are prepared using patent-pending compatibilization technology. PPE/PP alloys have excellent chemical resistance, low density, good dimensional stability, negligible moisture absorption, less creep than PP or ABS, cold-temperature impact, excellent processability, higher heat capability than PP, and a much wider stiffness/impact profile. Moreover, PPE/PP resins have better melt strength than PP and ABS, which facilitates extrusion and thermoforming operations. In addition, PPE/PP alloys are “regrind-friendly” with other polypropylene-based products.

In 2001, PPE/PP alloys were commercialized under the Noryl PPX designation. This new alloy creates a market niche between engineering thermoplastics and high-performance polyolefins. PPE/PP alloys offer product designers materials that fill the gap between the basic properties of high-end polyolefins and the stronger performance characteristics and attributes of engineering thermoplastics.

PPE/PP alloys offer a much wider stiffness/impact profile vis-à-vis PP-based *thermoplastic polyolefin* (TPO), which is maintained over a broader temperature range. Compared to glass-reinforced polypropylene, PPE/PP opens the performance envelope to include greater rigidity at elevated temperatures as well as better creep and scratch resistance.

Application areas for PPE/PP resins include performance packaging, automotive, transportation, lawn and garden tools, and fluid engineering. For example, in automotive bumper fascias PPE/PP offers low-temperature ductility after painting. Its higher modulus (30 to 50% greater than TPO) can allow for thinner walls and reduced material usage, and typically faster molding cycles. In addition, the high elongation, low specific gravity, and long-term heat resistance provide the opportunity to consolidate parts through multifunctional front-end design, which can result in significant weight and cost reductions.

In food service applications, PPE/PP resin can extend the life of retort trays and lower system costs because of its low-temperature toughness and high heat resistance, durability, cleanliness, and peel performance.

PPE/Polypropylene Grades

The Noryl PPX resin portfolio presently includes unfilled and filled grades. Representative properties of unfilled PPE/PP grades appear in Table 9.12. Key features of these grades include

Noryl PPX 7110: Designed for extrusion and blow molding

Noryl PPX 7112: Designed for extrusion and offers high impact and good paint adhesion

Noryl PPX 7115: Designed for extrusion and offers higher heat resistance and high impact and is NSF Standard 61 listed (restrictions apply)

Noryl PPX 7200: Designed for injection molding

Representative properties of reinforced PPE/PP grades appear in Table 9.13. Glass-reinforced grades and key features include

Noryl PPX 615: Designed with 15% glass-reinforced for injection molding

Noryl PPX 630: Designed with 30% glass-reinforced and is NSF Standard 61 listed (restrictions apply)

Noryl PPX 640: Designed with 40% glass-reinforced and is NSF Standard 61 listed (restrictions apply)

PPE in Thermoset Resins

PPE has been used in thermosets. In particular, PPE is used in the resin formulations to make GETEK* copper-clad laminates for high-end, high-performance printed wiring boards. GETEK laminates were developed by GE Electromaterials. Epoxy-PPE based laminates were commercialized in 1991 [28]. In 2002, PPE-cyanate ester based laminates were

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*GETEK is a trademark of Cookson Electronics.

TABLE 9.12 **Properties of PPE/PP Grades**

Property	PPX7110	PPX7112	PPX7115	PPX7200
Specific gravity	0.97	0.99	0.99	0.99
Tensile modulus, psi (GPa)	195,000 (1.37)	170,000 (1.20)	180,000 (1.27)	180,000 (1.27)
Tensile strength at yield, psi (MPa)	5200 (37)	4900 (35)	5200 (37)	4900 (34)
Tensile elongation at break, %	195	120	125	130
Flexural modulus, psi (GPa)	225,000 (1.58)	195,000 (1.37)	200,000 (1.41)	210,250 (1.45)
Flexural strength, psi (MPa)	7500 (53)	7200 (51)	7500 (53)	7100 (49)
Hardness, Rockwell R	—	70	60	—
NI at 23°C, ft·lb/in (J/m)	8.2 (443)	11.0 (587)	10.0 (534)	2.8 (150)
NI at –22°F (–30°C), ft·lb/in (J/m)	2.8 (149)	—	—	1.5 (80)
UNI at 23°C, ft·lb/in (J/m)	—	—	—	27.0 (1442)
Vicat B, °F (°C)	282 (139)	185 (85)	188 (87)	295 (146)
HDT at 66 psi (0.45 MPa), °F (°C)	236 (113)	235 (113)	235 (113)	230 (110)
HDT at 264 psi (1.82 MPa), °F (°C)	171 (77)	185 (85)	185 (85)	160 (71)
CTE, flow –40 to 100°F, in/in-°F (m/m-°C)	4.5E-5 (8.1E-5)	8.6E-5 (1.6E-4)	9.0E-5 (1.6E-4)	5.5E-5 (9.9E-5)
CTE, crossflow –40 to 100°F, in/in-°F (m/m-°C)	6.2E-5 (1.1E-4)	4.0E-5 (7.2E-5)	5.4E-5 (9.7E-5)	6.0E-5 (1.1E-4)
RTI electrical, °C	50	50	—	—
RTI with impact, °C	50	50	—	—
RTI without impact, °C	50	50	—	—
UL-94 HB, in (mm)	0.058 (1.5)	0.058 (1.5)	—	—

TABLE 9.13 Properties of Glass-Reinforced PPE/PP Grades

Property	PPX615	PPX630	PPX640
Specific gravity	1.08	1.19	1.30
Water abs., 24 h at 73°F (23°C), %	0.03	—	—
Tensile modulus, psi (MPa)	506,000 (3.56)	—	—
Tensile strength at yield, psi (MPa)	8600 (60)	11,500 (81)	13,900 (98)
Tensile elongation at break, %	5	8	6
Flexural modulus, psi (GPa)	444,000 (3.12)	806,000 (5.67)	1,206,000 (8.48)
Flexural strength, psi (MPa)	13,300 (94)	18,800 (132)	21,900 (154)
NI at 23°C, ft·lb/in (J/m)	2.0 (108)	3.1 (165)	2.0 (108)
NI at –22°F (–30°C), ft·lb/in (J/m)	1.2 (64)	1.9 (101)	1.8 (96)
UNI at –40°C, ft·lb/in (J/m)	10.9 (582)	15.5 (827)	10.8 (576)
Vicat B, °F (°C)	253 (123)	324 (162)	326 (163)
HDT at 66 psi (0.45 MPa), °F (°C)	302 (150)	311 (155)	318 (159)
HDT at 264 psi (1.82 MPa), °F (°C)	261 (127)	273 (134)	295 (146)
CTE, flow –40 to 100°F, in/in-°F (m/m-°C)	2.7E-5 (4.9E-5)	8.0E-6 (1.4E-5)	6.0E-6 (1.1E-5)
CTE, crossflow –40 to 100°F, in/in-°F (m/m-°C)	5.4E-5 (9.8E-5)	4.3E-5 (7.7E-5)	3.5E-5 (6.3E-5)
UL-94 HB, in (mm)	0.059 (1.5)	—	—

commercialized [29]. GETEK laminates offer superior thermal and electrical performance. In 2003, the Polyclad Laminates division of Cookson Electronics acquired the rights to GETEK copper-clad laminates.

In thermosets prepared via free-radical polymerization, the terminal OH end group of PPE needs to be capped because the aromatic hydroxyl will act to quench free radicals and inhibit the polymerization [30, 31]. Capping the OH with a reactive group facilitates incorporating the PPE into the thermoset matrix [32].

In 2003, GE Advanced Materials introduced Noryl ETX resins, which are designed to enhance the performance of thermoset resins.

Design

The successful use of engineering thermoplastics for end-use applications is dependent on important criteria such as

1. Selection of the proper resin grade that will give the desired performance
2. Proper design of the part and associated tooling
3. Use of the correct molding parameters

Selection of an appropriate resin is aided by property data. Depending on the application the data can be at ambient, low, and elevated temperatures.

Designing plastic parts involves very specific expertise. There are basic principles the designer follows for the best performance, e.g., minimum stress in the part (where the stress load is as low as possible) and uniform stress in the part (where the stress should be distributed uniformly). Consistent wall thicknesses facilitate achieving low and uniform stress. However, when the design requires varying thicknesses, then gradual transitions are essential.

Designs can get complicated with multicavity tools or multiple gates and hence weld lines or knit lines. Someone with plastic design experience is generally necessary for the correct design of plastic parts.

Proper molding conditions are another element for optimizing the performance of plastic parts. Improper molding can result in high molded-in stress and hence poor part performance.

Processing Modified PPE

Modified PPE grades cover a wide range of compositions. General guidelines on processing appear below. However, optimization of processing parameters is dependent on many things, such as the resin, tool design, and molding machine. The recommendations of the manufacturer for specific grades should always be considered in order to minimize molded-in stress and avoid resin degradation. Modified PPE resins, like other engineered thermoplastics, should not be left at elevated temperatures for prolonged periods without occasional purging.

Key molding parameters of modified PPE include the following:

Drying. Although modified PPE resin has the lowest moisture absorption of any engineering plastic and may be molded as received in many applications, it is a good practice, particularly where surface appearance is critical, to dry modified PPE resin before molding. Modified PPE resins should not be dried longer than 8 h. Excessive drying may result in loss of physical properties, color shift, loss of processability, or a combination of the three.

Melt temperature. Since modified PPE resins cover a wide range of compositions and melt viscosities, the manufacturers' recommended melt temperatures should be consulted. The majority of thermoplastic molding materials are sensitive to prolonged exposure to heat. Long residence times and excessive melt temperatures should be avoided to minimize material degradation. It is suggested that melt temperatures be measured using handheld pyrometers. These measures should be taken on the thermoplastic melts after the machine is on cycle.

Mold temperature. The usual range for processing unreinforced modified PPE grades is from 150 to 200°F (66 to 93°C). Operating molds in this temperature range can also be used to improve flow, knit-line strength, and surface finish.

Screw speed. Screw speeds (rpm) may be adjusted to permit screw rotation during the entire cooling cycle without delaying the overall cycle. Low screw speeds can help reduce glass fiber damage when molding reinforced grades. Suggested screw speed is dependent on screw diameter. Optimum linear velocity of screw outside diameter (OD) is about 8 in (202.4 mm) per second. Thus the rpm would be calculated from the screw diameter × π divided into the optimum linear velocity [8 in/s (202.4 mm/s) × 60 s/min].

Backpressure. A backpressure of 50 to 100 psi (0.3 to 0.7 MPa) is generally suggested to promote a homogeneous melt and helps maintain consistent shot size. Higher backpressures used to improve melt mixing can result in higher melt temperatures. When molding reinforced grades, low backpressure will help reduce glass fiber damage during plastication.

Shot size. The shot size should at least in part dictate the size of machine used. It is generally suggested that the optimum shot be 40 to

60% of the barrel capacity of the machine. However, shots that are 20 to 75% of machine capacity have been successfully molded when temperatures were precisely maintained and all processing conditions were very closely controlled.

When processing the resin at, or near, the upper limit of the recommended melt temperature range, the shot size should approach 70 to 80% of the machine's barrel capacity. If the cylinder temperature exceeds the upper limit of the suggested melt range, thermal degradation of the resin and loss of physical properties may result.

Ram speed. When one is selecting the injection speed, careful consideration must be given to adequate mold venting, resin melt temperature and injection pressure, along with the potential for jetting.

Injection pressure. The actual injection pressure will depend on variables such as melt temperature, mold temperature, part geometry, wall thickness, flow length, and other mold and equipment considerations. Generally, the lowest pressures that provide the desired properties, appearance, and molding cycle are preferred. Holding pressures from 60 to 80% of the injection pressure are usually adequate for normal requirements.

Cushion. The use of a small cushion, 1/8 in (3.18 mm), often reduces material residence time in the barrel and helps accommodate machine variations.

Cycle time. When one is adjusting cycle times, it is typically best to use a fast injection speed and a minimum holding time to achieve gate freeze-off and a short cooling time.

Purging. Polystyrene and reground cast acrylic are generally effective purging materials for all modified PPE resins. Purging is typically be done within the melt temperature range for that particular grade of resin. It is important to have proper ventilation during the purging procedures.

Regrind. If the application permits the use of regrind, reground sprues, runners, and nondegraded parts may be added to the fresh pellets up to a level of 25%. Typically grinder screen sizes are 5/16 to 3/8 in (7.9 to 9.5 mm). It is important to keep the ground parts clean and to avoid contamination from other materials. Regrind utilization may produce some effect on color. Actual regrind usage should be verified for each individual application.

Processing PPE/PA Resins

PPE/PA alloys generally have higher melt viscosities than polyamides and require higher processing temperatures. Processing PPE/PA resins using conditions for polyamides will result in increased molded-in stress. PPE/PA resins can be molded in most standard injection molding machines. Reciprocating screw machines are suggested.

PPE/PA resins, like other engineered thermoplastics, should not be left at elevated temperatures for prolonged periods without occasional purging.

Key molding parameters of PPE/PA resins include the following.

Drying. Like polyamides, PPE/PA alloys will absorb moisture but at much lower levels. However, moisture still plays an important role in material processing, part appearance, and part properties. Typically PPE/PA resins have 0.1% moisture content when manufactured and can increase to approximately 0.2% at the molder.

As a general guide, very good appearance in large parts can be obtained with a moisture content ranging from 0.02 to 0.07%. Occasional issues can occur at 0.08 to 0.10% moisture content. Splay and related appearance issues are common in large parts at 0.10% and greater moisture. Small parts or simple geometries typically exhibit little or no splay, even at moisture levels of 0.10 to 0.12%.

Reducing moisture content below 0.02 to 0.07% can result in stiffer flow. The residual moisture present in dried pellets will plasticize the molten polyamide during melt processing. Too low a moisture content can also lead to further polyamide polymerization during processing, and higher polyamide molecular weight could contribute to stiffer flow.

There is virtually no benefit in reducing moisture below 0.02%. Drying to below 0.02% generally does not improve appearance and could produce material with stiffer flow. This can cause inconsistent processing.

Modern desiccant, dehumidifying dryers offer excellent drying capabilities with many advanced features to assist the molder in obtaining a consistent drying process. However, measuring the moisture content will ensure the resin is in the 0.02 to 0.07% range. In addition the moisture content should be measured periodically to ensure that it has not drifted out of the 0.02 to 0.07% range.

Once moisture has equilibrated into the pellet, it typically hydrogen-bonds to the amide groups on the polyamide. Removing the hydrogen-bonded water molecule requires energy (time and temperature). High levels of moisture generally require long times in dryers. Hence efforts need to be made to keep the resin dry and minimize chances for moisture uptake.

Material handling procedures can affect the consistency of the starting moisture content of the resin. Although the special barrier liners used in PPE/PA resin bags and boxes greatly reduce the diffusion of water vapor into the resin, they do not eliminate it. Working from box to box or bag to bag will lead to a greater probability of varying initial moisture content than working from a bulk truck or a railcar where the materials are generally blended through bulk handling systems.

When one is working with boxes or bags, some general guidelines include these:

- Routinely monitor the starting moisture content of the resin or container several times during a shift. This will help to minimize variability and point out situations that have resulted in higher than normal moisture contents.
- Use the resin in the order it is received. Aged inventory is more susceptible to picking up moisture.
- Reseal the package after use to retard exposure to moisture in the environment.
- The number of partial containers in use at any one time in the molding operation should be minimized.
- Keep track of the time from when a box is opened to when it is emptied—especially in humid weather, during start-up, shutdown, downtime, end of the workweek, etc.

General comments on melt temperature, mold temperature, etc., are similar to those listed earlier for modified PPE

Shot size. It is suggested that the total shot size (all cavities plus runners and sprues) be 30 to 50% of the machine capacity. Very small shots in a large barrel machine may create unnecessarily long resin residence times that may lead to resin degradation. If it is necessary to mold at the high end of the temperature range, reduced residence time (6 min or less) is usually required to reduce the possibility of material heat degradation. Generally the shot size should be between 40 to 50% of the machine capacity for higher-temperature molding situations. Shot sizes in excess of 50% barrel capacity can lead to difficulties resulting in inconsistent, nonhomogeneous plastic melt.

Nozzle requirements. Short, open-bore nozzles with a minimum orifice of 3/16 in (4.76 mm) in diameter are generally useful for molding unfilled PPE/PA resins. For glass-reinforced grades of PPE/PA an orifice of 5/16 in (7.81 mm) is suggested. Land lengths should generally be no longer than 3/16 in (4.76 mm). The nozzle bore should be 0.5 in (12.7 mm) minimum. The nozzle opening should typically be kept 1/3 in (0.8 mm) smaller than the orifice dimension on the sprue bushing. Accurate heat control and full heater band coverage are important for maintaining part appearance.

Specialty nozzles such as static mixers, shutoff nozzles, and screen pack filters are not typically suggested, as they generally have sharp corners and areas of high pressure drop that can cause a variety of molding problems.

Regrind. In addition to the regrind comments for modified PPE, increased drying time is recommended since the sprues, runners, and nondegraded parts before and after grinding will have absorbed moisture.

Summary

Clearly the PPE-based resins offer one of the most versatile product families. Products based on blends with polystyrene are available as unfilled and reinforced grades and nonbrominated and nonchlorinated flame-retardant (ECO-label compliant) grades. Moreover, modified PPE can be opaque or transparent, rigid or flexible. In addition, modified PPE offers a broad range of processing options including injection molding, extrusion, blow molding, expanded foam, and structural foam molding.

In addition, PPE alloys with polyamides and polypropylene are available in unfilled and reinforced grades. These grades exhibit enhanced performance over polyamides and polypropylene. Moreover, the PPE/polyamide grades include conductive grades for use in electrostatic online painting and a nonbrominated, nonchlorinated, nonred phosphorous flame-retardant grade.

Finally, PPE is used in thermoset resins to enhance their performance.

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Chapter 10

Thermoplastic Polyimide (TPI)

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Introduction

In the case of polyimides, aromatic polyimides polymerized from aromatic monomers which were insoluble and infusible had always been present. Of all the polyimides, nonthermoplastic polyimides polymerized from *pyromellitic dianhydride* (PMDA) and bis(4-aminophenyl)ether (ODA) have a long history of roughly 40 years since commercialization under DuPont. The polyimide cannot be melted or injection-molded and therefore has some limitations for complicated design and productivity. In the late 1980s, Mitsui Chemicals, Inc. [1] began investigating and developing a thermoplastic polyimide to meet industry needs. As a result of these efforts, a super engineering plastic called Aurum® was launched. This material is synthesized from pyromellitic dianhydride and 4′-bis (3-aminophenoxy)biphenyl and has a high heat resistance with glass transition temperature $T_g = 482°\text{F}$ (250°C). Aurum® is an injection-moldable semicrystalline polyimide, but it has a very slow crystallization rate. The part obtained through injection molding is amorphous, not crystalline, although Aurum® is a semicrystalline polymer. The postcuring after injection molding enabled crystallization, but control of the tight dimension was not sufficient. In the early 2000s, another new thermoplastic polyimide entered the market, called SuperAurum,™ an in-mold crystallizable polyimide, which has an excellent HDT of 752°F (400°C) with carbon fiber filler. It is in a crystalline state during injection molding, because of the enhancement of the crystallization rate. SuperAurum™ has better chemical and mechanical properties. The polymer was completed through an optimum monomer selection.

Polymers—Chemistry of Thermoplastic Polyimide[1]

Typical polymerization of polyimide

Polycondensation is a typical method for polyimide syntheses, which need aromatic tetracarboxylic acids and aromatic diamines as monomers. Figure 10.1 shows that the polymerization process goes through two reactions: The ring-opening polyaddition of aromatic diamines to aromatic tetracarboxylic dianhydrides in solution at room temperature gives soluble precursor polyamic acids, followed by solid-state thermal cyclodehydration to polyimides.

Chemical structure and thermoplasticity

The melt processability depends upon a combination of monomers. Very critical points for the designs of polyimides, according to Mitsui Chemicals, Inc., include (Fig. 10.2 and Table 10.1)

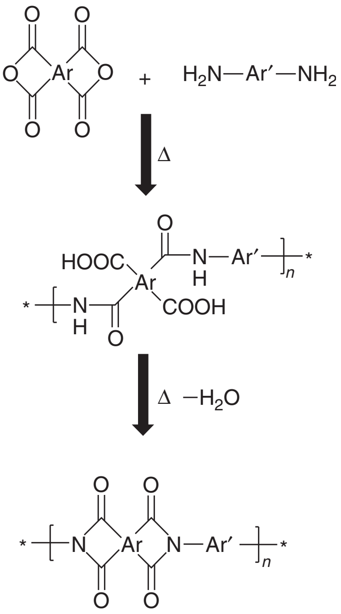
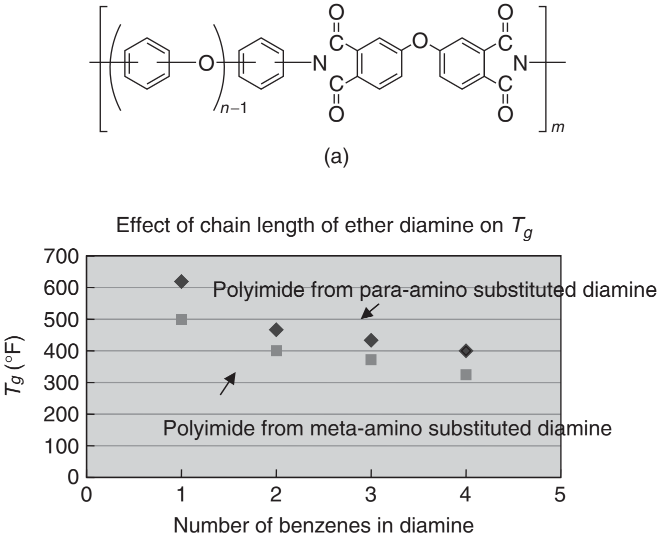


Figure 10.1 Typical polymerization of polyimide.



(a)

(b)

Figure10.2 Effect of chain length of ether diamine on T_g.

TABLE 10.1 Melt-Flow Start Temperatures of Polyimides and Their Structures

Diamine			Melt-flow start temperature, °F		
			Dianhydride		
Amino-substituted position	Number of benzene rings	Structure	PMDA	BPDA	ODPA
Para	1	1a	NF	NF	NF
	2	2a	NF	NF	680
		3a	NF	NF	806
	3	3b	NF	NF	653
	4	4a–p	NF	—	635
		4b–p	NF	806	—
Meta	1	1b	NF	NF	NF
	2	2c	NF	590	536
	3	3c	—	734	608
		3d	599	545	428
	4	4a–m	500	518	473
		4b–m	725	572	518
		4c–m	626	572	527
		4d–m	509	491	455
		4e–m	536	527	482
		4f–m	653	—	—
		4g–m	716	477	491

- The effect of the amino-substituted position of the etherdiamine
- Number of benzene rings in ether diamine (Table 10.2)
- Amino substituted position in ether diamine
- Optimum molecular weight

These factors affect the thermoplasticity of polyimides. Then it was concluded that

1. Thermoplasticity can be controlled through the selection of ether diamine with a specific chain length.
2. Polyimide from meta amino substituted diamine has less heat resistance than polyimide from the para form. The polymer of the meta form, however, has much better plasticity than that of the para form, in light of T_g and T_m.

Aurum® has a chemical structure consisting of repeating units of pyromellitic dianhydride and 4,4′-bis(3-aminophenoxy)biphenyl, with T_g = 482°F (250°C) and T_m = 734°F (390°C).

Products and Design

Applications Using Mitsui Chemicals Aurum® TPI

There are five major categories for the applications:

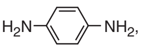
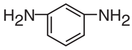
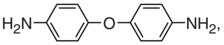
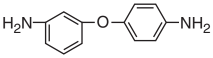
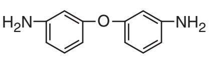
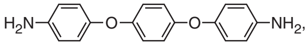
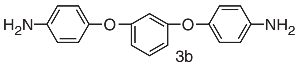
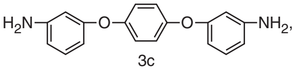
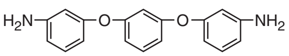
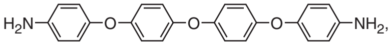
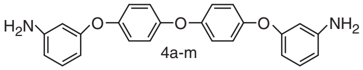
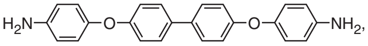
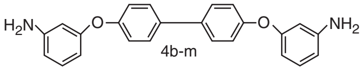
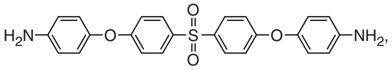
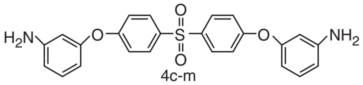
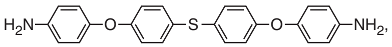
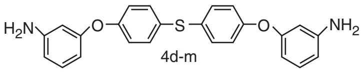
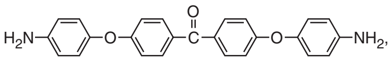
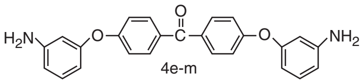
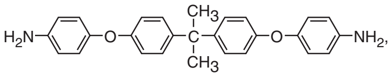
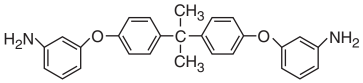
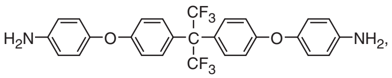
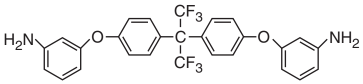
1. Electronics, electrical, and semiconductor
2. Automotive
3. Industrial (including business machinery)
4. Wire, cable, film, and fiber
5. Aircraft and aerospace

The heat resistance has helped applications in various parts that need high-temperature resistance, up to 455°F (235°C).

Moreover, the dimensional stability based on high heat resistance has increased applications requiring tight tolerances of the parts. The superior wear and friction properties of polyimide have fascinated many engineers who had to design parts used under harsh conditions. This is so because many kinds of parts made with Aurum® have been commercialized.

Electronics, electrical, and semiconductor. The excellent dielectric properties and resistance to heat and abrasion that characterize Aurum®

TABLE 10.2 Diamines Defined by Number of Benzene Rings

Number of benzene rings	Diamine
	Diamines having one benzene ring
1	 1a  1b
	Diamines having two benzene rings
2	 2a  2b  2c
	Diamines having three benzene rings
3	 3a  3b  3c  3d
	Diamines having four benzene rings
4	 4a-p  4a-m  4b-p  4b-m  4c-p  4c-m  4d-p  4d-m  4e-p  4e-m  4f-p  4f-m  4g-p  4g-m

Dianhydride
Pyromellitic dianhydride (PMDA)
3,3′,4,4′-Biphenyl tetracarboxylic dianhydride (BPDA)
3,3′,4,4′-Diphenylether tetracarboxylic dianhydride (ODPA)

have led to an increasing number of electronics and electrical applications. The polyimide is produced by Mitsui Chemicals, and cleanliness is controlled during the polymerization without catalysts. The parts that require cleanliness, such as parts inside of HDD and other drive devices, have been feasible for polyimide. In addition, Aurum® is increasingly specified in silicon wafer and microprocessor handling, fabrication, and testing operations for its unique combination of attributes:

1. High purity and low trace metal content
2. Low thermal outgassing at elevated temperatures
3. Dimensional stability at elevated temperatures
4. Surface resistivity control

All-Aurum® and Aurum®–metal hybrid hard disk carriers provide exceptional dimensional stability at elevated temperatures (see Fig. 10.3). Aurum® injection-molded *liquid crystal display* (LCD) glass carriers can withstand LCD processing temperatures.

Ultrahigh-temperature (UHT) trays, called Olive, have been commercialized by 3M. The material enabled its use in certain reflow applications, meeting JEDEC standards for flatness after multiple exposures to 446°F (230°C).

Automotive. The rise in popularity of injection-molded polyimide and seals within the automotive industry has been driven by the demand for longer-life, extremely heat-resistant and ultrahigh-PV materials that offer cost reduction opportunities over metallics and conventional polyimides. In vehicle locations including the transmission, engine, and

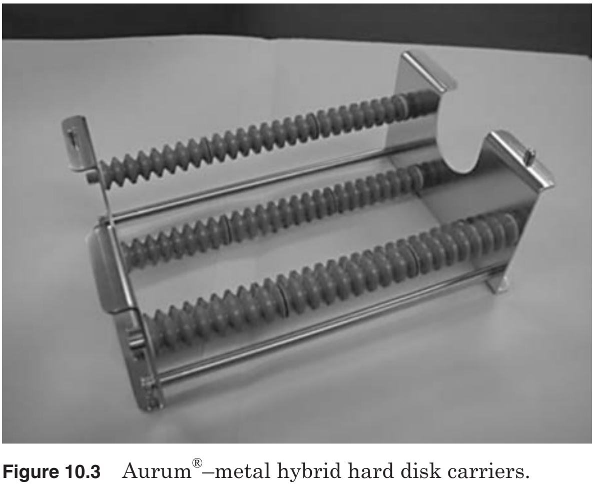


Figure 10.3 Aurum®–metal hybrid hard disk carriers.

electric motors, injection-molded Aurum® components replaced metals in extreme heat and high-PV applications for longer component life, reduced weight, and higher performance levels.

In automotive and off-highway vehicle applications, Aurum® is increasingly specified by designers for its

1. Excellent tribological performance, high strength, and impact resistance at temperatures to 455°F (235°C)
2. Outstanding creep resistance
3. Low coefficient of friction
4. High PV capability
5. Resistance to chemicals and automotive fluids
6. Sealing (leakage control) capability
7. Low coefficient of thermal expansion
8. Injection moldability for complicated part design

The outstanding properties mentioned above have enabled Aurum® to be used in many varieties of automotive parts. The following are some examples of the applications.

Automotive transmission and torque converter parts. Aurum® thrust washers can replace metal washers and needle thrust bearings with greater packaging space and cost reduction. The transmission Aurum® JCL3030 thrust washer for Ford F series superduty pickup trucks is in the torque converter where previously only thermosets and metals had been utilized (Fig. 10.4). The reduced thickness has made possible critical packaging space for more

Figure 10.4 Aurum® thrust washers.

Figure 10.5 Aurum® seal rings.

robust piston and higher-durability applications. In addition, torque converter Aurum® thrust washers for the Allison transmission 9000 series replaced expensive metal washers for engineered cost reduction [2].

Moreover, seal ring parts in automotive transmissions have been widely used in Aurum® automotive applications (Fig. 10.5). Aurum® with thermoplastic properties has made possible the three-dimensional gap design required for oil leakage control. Also, a tight thermal coefficient enabled the gap adjustment demanded for each design. JCF3030 is a representative grade for seal applications.

Automotive turbocharger system parts. Aurum® has been selected by NSK, one of the world's largest manufacturers, for production of turbocharger bearing retainers. Aurum® bearing retainers performed well in under-the-hood conditions of low pressure, maximum velocity of 120,000 rpm, temperature from 392 to 572°F (200 to 300°C), and steel mating material with oil lubrication [2].

Other applications are a fluid dam and a valve system washer in a new generation of viscous fan drives for the on-highway truck and agricultural vehicle markets by Borg Warner Automotive Turbo Systems. JCL3030 was selected for the superior combination of thermal resistance, dimensional stability at elevated temperatures under load, wear resistance, and close tolerance by injection-molding capability [2].

Industrial (including business machinery). Designers of industrial machinery specify Aurum® components for a unique combination of high strength at high temperatures, chemical resistance, and wear resistance. In applications ranging from bushings for hot-melt glue guns to seals for reciprocating compressors, the close tolerance moldability of Aurum® is another critical feature. Aurum® gears can be insert-molded around a metal hub and have a safe working stress of 4500 psi at 392°F (200°C). In addition, Aurum® pump components are widely used. Gears, bearings, seals, and housings take advantage of the exceptional chemical resistance of Aurum® at elevated temperatures.

Business machinery is another industrial application. Aurum has the ability to operate efficiently at elevated temperatures in dry and intermittent-lubrication environments, which has led to an extensive list of business machinery applications. In high-speed digital copiers and printers, Aurum® thermal insulators, paper stripper fingers, end caps (called gudgeon), gears, and drive couplings operate at temperatures to 480°F (249°C). Specially formulated, low-wear Aurum® compounds are available that function exceptionally well against counter surfaces including steel, aluminum, and rubber.

Wire, cable, film, and fiber. Aurum® can be extruded into wire, cable, film, and fiber (Fig. 10.6). The extruded wire and cable are for electrical insulation with outstanding thermal, mechanical, chemical, and electrical properties. Aurum® film is available in 1- to 22-mil-thick rolls from Westlake Plastics. The applications include wire, cable, and optic fiber insulation; industrial belts; heat and radiation panels; and other electric and thermal insulation devices. Aurum® monofilament and multifilament can be woven and braided into a variety of high-performance industrial and aircraft products including paper-making belts and jet-engine insulation.

Aircraft and aerospace. Aurum® components are increasingly specified in the aerospace industry as metal and ceramic replacements where

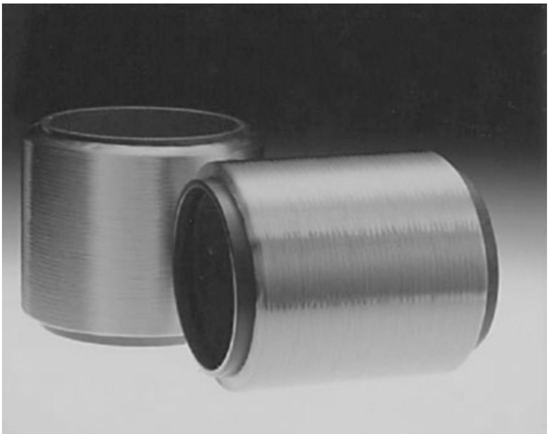


Figure 10.6 Aurum® fiber.

thermal resistance, resistance to aircraft fluids, creep and fatigue resistance, and low wear are required.

Aurum® JCN3030 has been chosen by Ishikawajima-Harima Heavy Industries Co., Ltd. (IHI), a major jet engine manufacturer, for the outer platform of the V-2500 jet engine. The outer platform supports the outer vane, which rectifies the airstream coming from the engine. The outer platform has to be corrosion-resistant and have high impact strength since jet engines often inhale birds while cruising and ingest sand or gravel during takeoff and landing. The conventional material, a forged aluminum alloy, was replaced by Aurum® since it reduced jet engine mass and led to fuel efficiency improvement [2].

Properties

General-purpose and application-specific properties

High-temperature capability (short-term). The short-term heat resistance of resins depends upon the glass transition temperature T_g. The T_g of Aurum®, 482°F (250°C), exceeds the T_g of conventional engineering plastics. Therefore, Aurum® can be applied to many kinds of heavy-duty or precision machine parts demanding excellent mechanical properties at high temperatures and under high loads. Fig.10.7 shows the change of tensile strength of Aurum® up to high temperature.

High-temperature capability (long-term). One of the features of Aurum® is excellent long-term heat capability at elevated temperatures. Long-term heat resistance is usually represented by the retention of properties after the specimens are exposed to high temperatures. Table 10.3 shows the

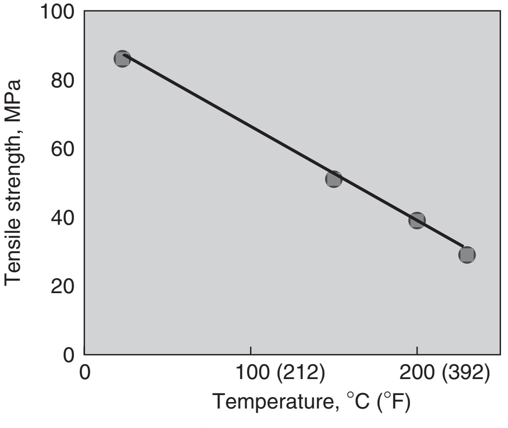


Figure.10.7 Aurum® PL450C (no filler), tensile strength versus temperature.

TABLE 10.3 Retention of Tensile Strength after Exposure at High Temperatures

	100 h	500 h	1000 h	2000 h
Retention of tensile strength	90%	85%	90%	100%

The value before the testing is 100%.

change of tensile strength of Aurum® after it is exposed to 392°F (200°C).

Wear and friction properties. Aurum® grades, where Mitsui's unique compounded materials are based on the proper selection of matrix, fillers, and additives, have excellent wear and friction properties. Aurum® has both outstanding wear resistance and low friction even at 302°F (150°C) in dry conditions. The PV limit, which can show the maximum capability of high load and high speed, is the highest of all thermoplastics in dry environments (100 kpsifpm) (Table 10.4).

Moreover, its tribological properties are exceptional under oil conditions since the coefficient of friction is surprisingly low and stable in oil. This is why Aurum® can withstand high-duty loads.

Chemical resistance. Aurum® is widely regarded as a material with outstanding chemical resistance, and it has a remarkable resistivity against oil, even at elevated temperatures. The properties and appearance of Aurum® do not change even under harsh conditions such as 392°F (200°C). Therefore, the stable properties are guaranteed under ordinary usage conditions, such as below 302°F (150°C).

However, there are some limitations on usage against alkali, concentrated sulfuric acid, concentrated nitric acid, dichloromethane, and chloroform since Aurum® is a polyimide and is amorphous after injection molding.

Other. There are other interesting properties of the polyimide that most people are unaware of:

- *Metal impurity and outgassing*. Aurum® is polymerized without catalysts and has no residual solvent after being polymerized. Therefore, it has outstanding cleanliness and can be used for semiconductor equipment parts requiring tighter specifications of cleanliness.

TABLE 10.4 Aurum® High-PV Capability in Applications

Grades	Applications	Typical operating PV	Recommended PV range
JCL3030	Thrust washers	810 kpsifpm	480–1400 kpsifpm
JCF3030	Seal rings	1100 kpsiftpm	480–1400 kpsifpm

TABLE 10.5 Retention of Tensile Strength(%) after Exposure to Radiation

	Radiation power, Mrad			
	0	1000	3000	10000
Beta beam	100	100	100	110
Gamma beam	100	100	100	100

- *Plasma properties*. Aurum® has outstanding plasma properties that enable applications for etching equipment parts for semiconductors.
- *Radiation resistance*. Aurum® has an exceptional radiation resistance since it behaves as a cross-linked plastic despite being a thermoplastic polymer. See Table 10.5.

Aurum® grades

Neat (nonfiller)

Powder: PD400, PD450, PD500
Pellets: PL400C, PL450C, PL500C
PD400 and PL400C—high-flow type
PD450 and PL450C—medium-flow type
PD500 and PL500C—low-flow type

Both powder and pellet grades are available as natural materials (nonfiller). Powder grades can be used for coating, blending components to plastics, and compounding materials. The unfilled pellet grades (PL400C, PL450C, and PL500C) offer a unique balance of mechanical and thermal properties in demanding automotive, business machinery, industrial equipment, electronics, electrical, and semiconductor applications (Table 10.6). The grades exhibit outstanding resistance to radiation, a low coefficient of thermal expansion, ultrahigh purity, low outgassing in a vacuum, excellent electrical properties, and flame resistance. Aurum® PL450C can be conventionally extruded to produce high-performance wire and cable insulation and thin-wall tubing and fiber. (See Fig. 10.8.)

Carbon fiber filled—JCN3030. The JCN3030 is a carbon fiber 30% filled grade, which offers high strength and modulus even at elevated temperatures and outstanding durability, such as creep resistance. It can replace metals, ceramics, and other plastics. High performance of JCN3030 includes structural parts for industrial, automotive, and aircraft applications. An outer platform on the V-2500 commercial jet engine is one example of Aurum® JCN3030 use.

TABLE 10.6 Standard Aurum® Grades

Properties	Unit	PL450C	JCN3030	JGN3030
Filler		Natural	Carbon fiber	Glass fiber
Specific gravity	—	1.33	1.43	1.56
Mold shrinkage (MD/TD)	%	0.74/0.85	0.00/0.66	0.16/0.78
Tensile strength	Mpa	92	228	165
Elongation	%	90	2	3
Flexural modulus	GPa	2.9	19.0	9.5
Izod impact	J/m	88	108	118
HDT	°F (°C)	460 (238)	478 (248)	473 (245)
CTE MD/TD	(E-5)/F	3.1/3.1	0.3/2.6	0.9/2.9
Flame retardance UL-94 (0.4 mm)	—	V-0	V-0	V-0

MD = Machine direction
TD = Transverse direction
HDT = Heat deflection temperature
CTE = Coefficient of thermal expansion

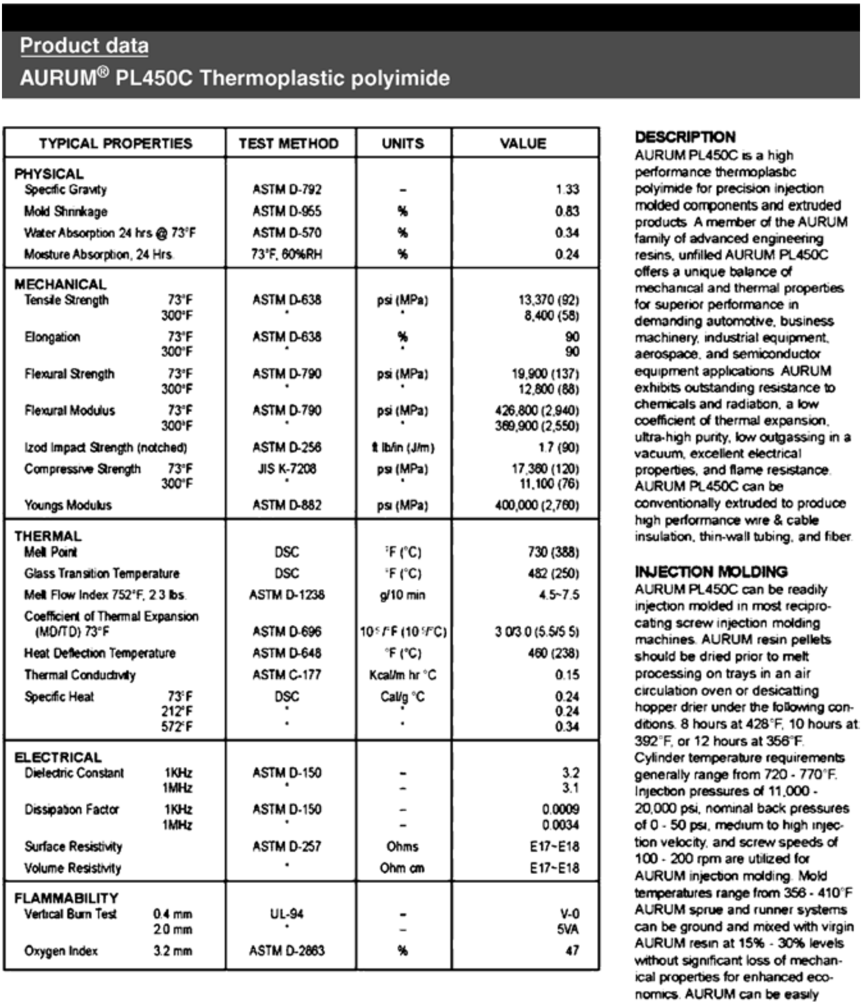
Glass-fiber-filled—JGN3030. JGN3030 consisting of 30% glass fiber has outstanding thermal and electrical properties as well as mechanical properties. It is used for high-temperature burn in sockets needed for tight tolerance, test sockets, insulator bushings and picker fingers and gudgeons in copiers and printers, pistons for compressors, LCD treatment supporters, and radiation parts.

Wear and friction grades—JCL3030, JCF3030, JNF3020. The JCL3030, JCF3030, and JNF3020 are standard Aurum® wear and friction grades, which offer outstanding wear resistance to mating metals for many kinds of bearing applications. See Table 10.7.

JCL3030 with 30% carbon fiber and a small amount of lubricant filler has a unique balance of mechanical, tribological, and thermal properties. It can be used in oil or dry conditions against hard metal, such as steel and cast iron. Since it has a high amount of carbon fiber, it can withstand high loads. This is why Aurum® is used in copier thermal insulator bushings, high-load thrust washers in automotive and off-vehicle transmissions, vane wear strips, valve seats, gears, pads, and chains in industrial applications.

Aurum® JCF3030 components are excellent replacements for metal and other plastics. A combination of 15% carbon fiber and 15% PTFE enables tight leakage properties in automotive transmission seal ring applications. The grade offers outstanding tribological properties at high speed in oil environments.

JNF3020 is the softest material of all Aurum® grades, which consists of 20% PTFE. It is feasible for wear and friction properties against soft metals such as aluminum, copper, and brass.



Product data

AURUM® PL450C Thermoplastic polyimide

TYPICAL PROPERTIES	TEST METHOD	UNITS	VALUE
PHYSICAL			
Specific Gravity	ASTM D-792	-	1.33
Mold Shrinkage	ASTM D-955	%	0.83
Water Absorption 24 hrs @ 73°F	ASTM D-570	%	0.34
Moisture Absorption, 24 Hrs.	73°F, 60%RH	%	0.24
MECHANICAL			
Tensile Strength 73°F	ASTM D-638	psi (MPa)	13,370 (92)
300°F	•	•	8,400 (58)
Elongation 73°F	ASTM D-638	%	90
300°F	•	•	90
Flexural Strength 73°F	ASTM D-790	psi (MPa)	19,900 (137)
300°F	•	•	12,800 (88)
Flexural Modulus 73°F	ASTM D-790	psi (MPa)	426,800 (2,940)
300°F	•	•	369,900 (2,550)
Izod Impact Strength (notched)	ASTM D-256	ft lb/in (J/m)	1.7 (90)
Compressive Strength 73°F	JIS K-7208	psi (MPa)	17,360 (120)
300°F	•	•	11,100 (76)
Youngs Modulus	ASTM D-882	psi (MPa)	400,000 (2,760)
THERMAL			
Melt Point	DSC	°F (°C)	730 (388)
Glass Transition Temperature	DSC	°F (°C)	482 (250)
Melt Flow Index 752°F, 2.3 lbs.	ASTM D-1238	g/10 min	4.5~7.5
Coefficient of Thermal Expansion (MD/TD) 73°F	ASTM D-696	10^{-5}/°F (10^{-5}/°C)	3.0/3.0 (5.5/5.5)
Heat Deflection Temperature	ASTM D-648	°F (°C)	460 (238)
Thermal Conductivity	ASTM C-177	Kcal/m hr °C	0.15
Specific Heat 73°F	DSC	Cal/g °C	0.24
212°F	•	•	0.24
572°F	•	•	0.34
ELECTRICAL			
Dielectric Constant 1KHz	ASTM D-150	-	3.2
1MHz	•	-	3.1
Dissipation Factor 1KHz	ASTM D-150	-	0.0009
1MHz	•	-	0.0034
Surface Resistivity	ASTM D-257	Ohms	E17~E18
Volume Resistivity	•	Ohm cm	E17~E18
FLAMMABILITY			
Vertical Burn Test 0.4 mm	UL-94	-	V-0
2.0 mm	•	-	5VA
Oxygen Index 3.2 mm	ASTM D-2863	%	47

DESCRIPTION

AURUM PL450C is a high performance thermoplastic polyimide for precision injection molded components and extruded products. A member of the AURUM family of advanced engineering resins, unfilled AURUM PL450C offers a unique balance of mechanical and thermal properties for superior performance in demanding automotive, business machinery, industrial equipment, aerospace, and semiconductor equipment applications. AURUM exhibits outstanding resistance to chemicals and radiation, a low coefficient of thermal expansion, ultra-high purity, low outgassing in a vacuum, excellent electrical properties, and flame resistance. AURUM PL450C can be conventionally extruded to produce high performance wire & cable insulation, thin-wall tubing, and fiber.

INJECTION MOLDING

AURUM PL450C can be readily injection molded in most reciprocating screw injection molding machines. AURUM resin pellets should be dried prior to melt processing on trays in an air circulation oven or desicatting hopper drier under the following conditions. 8 hours at 428°F, 10 hours at 392°F, or 12 hours at 356°F. Cylinder temperature requirements generally range from 720 - 770°F. Injection pressures of 11,000 - 20,000 psi, nominal back pressures of 0 - 50 psi, medium to high injection velocity, and screw speeds of 100 - 200 rpm are utilized for AURUM injection molding. Mold temperatures range from 356 - 410°F. AURUM sprue and runner systems can be ground and mixed with virgin AURUM resin at 15% - 30% levels without significant loss of mechanical properties for enhanced economics. AURUM can be easily

Mitsui Chemicals Inc., Technical Data Sheet N. 961002

Figure 10.8 Product data sheet for Aurum® PL450C.

Electrically static dissipated (ESD) grade—PL8001. The PL8001 is a carbon nanotube filled material, which shows even fewer particles generated from parts during the cleaning process than carbon fiber reinforced or carbon black filled material, resulting in outstanding properties when cleanliness is required in the environment. Also, the fact that the grade has less outgassing and lower impurities makes it very feasible for semiconductor and electronics and electrical applications requiring cleanliness. The exceptional dispersion of nanofiller in resin by the proprietary

TABLE 10.7 Aurum® Wear and Friction Grades

Properties	Unit	JCL3030	JCF3030	JNF3020
Filler		Carbon fiber lubricant	Carbon fiber PTFE	PTFE
Features		High PV	High speed	
Mating metal		Steel, cast iron	Steel, cast iron	Aluminum
Environment		Oil and dry	Oil	Dry
Specific gravity	—	1.42	1.44	1.44
Tensile strength	MPa	230	170	72
Flexural modulus	GPa	17.1	10.8	2.4
Izod impact	J/m	110	110	137

technology has led to its reasonable cost, although the raw material is expensive.

Processing

Flowability

Aurum® is a thermoplastic, and there are three basic grades of neat resin, depending on the melt viscosity (Table 10.8).

Since Aurum® is a heat-resistant resin, it is necessary to set the processing temperatures high enough. The polyimide has similar spiral flow length to PES with processing temperatures about 72°F (40°C) higher than that of PES. Although flow length changes with mold temperature, the degree of such change is relatively small compared with the influence of processing temperature or pressure. A 54°F (30°C) change in mold temperature corresponds to approximately a 9°F (5°C) change in processing temperature.

Predrying conditions before molding

Drying conditions. Required drying time is dependent on the thickness of resin layer. Normally 10 h or more at 356°F (180°C) is recommended.

Dryer. A shelf-type dryer with hot air circulation with a temperature control range of 392°F (200°C) or more is recommended.

TABLE 10.8 Aurum® Melt Viscosity and Molecular Weight

Grade	Melt viscosity, P, at 752°F (400°C)	Melt flow, g/10 min, at 752°F (400°C)	Molecular weight, LALLS*
PL400C	3,000–4,000	12–28	25,000
PL450C	6,000	4.5–9.0	28,000
PL500C	10,000	2.5–4.5	30,000

* LALLS: low-angle light scattering.

At least 356°F (180°C) is required for predrying in order to keep less than 100 ppm, which is needed to obtain appropriate molded parts. An exposure to air even after drying can result in moisture absorption that affects molded parts. Before molding, resin should be removed from conditions of moisture.

Hopper dryer. It is necessary to seal the top of the hopper to avoid contamination and humidity. A hot air circulation type of dryer with dehumidifier is recommended for high drying efficiency and lower running cost.

Molding condition

See Table 10.9.

Molding temperature. Resin melt temperature is required to be 752 to 788°F (400 to 420°C). Filler grades such as JCL3030 should be set at 788°F (420°C) while neat resin can be molded at 752 to 770°F (400 to 410°C).

Mold temperature. A temperature of 356°F (180°C) or preferably 392°F (200°C) is recommended.

Injection machine. Part volume should be more than 20% of the maximum injection capacity of the injection machine.

Purging

PEI (Ultem) should be used as the purging material before and after molding.

SuperAurum™

In the early 2000s, another new thermoplastic polyimide entered the market, called SuperAurum,™ an in-mold crystallizable polyimide, which has an excellent HDT of 752°F (400°C) with carbon fiber filler. The enhancing crystallization speed enables a crystalline state even during

TABLE 10.9 Typical Molding Conditions

	Cylinder temperature, °F		
Grade	Hopper side	Center, nozzle	Mold temperature, °F
Natural	752	752	338–356
GF, CF filled	752	788	374–410

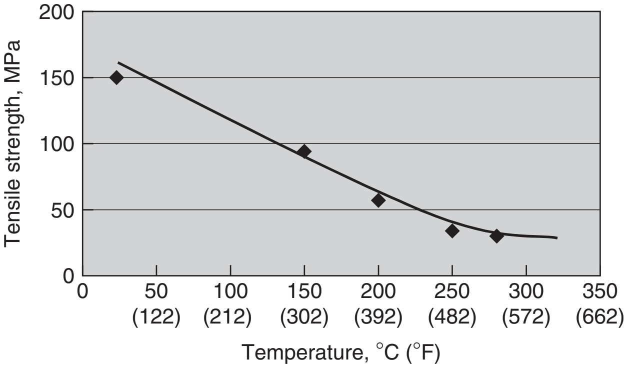


Figure 10.9 SuperAurum™ XPL, tensile strength versus temperature.

injection molding. SuperAurum™ has better chemical and mechanical properties as well.

High-temperature properties

Figure 10.9 shows the features of SuperAurum™. Aurum® is an amorphous polymer after injection molding. Therefore, the designs for more dimensionally precise parts require Aurum®, along with superior wear and friction up to 455°F (235°C). SuperAurum,™ however, is in a different category since it is crystallized during injection molding. It has outstanding mechanical, wear and friction, and chemical properties up to elevated temperatures beyond 455°F (235°C). It is much easier to understand the differences between other engineering superplastics and SuperAurum™ by examining the modulus versus temperature curve. Aurum® can keep a high modulus at up to 235°C, but the modulus decreases beyond 235°C since the T_g is 250°C and it is amorphous. Since SuperAurum™ has T_g of 374°F (190°C) but is a crystalline polymer, it can maintain high rigidity even at wide-ranging temperatures of 482 to 626°F (250 to 330°C).

SuperAurum™ grades

The following SuperAurum™ grades are commercially available. See Table 10.10 for a list of properties.

1. Natural grade: powder, XPD; pellets, XPL
2. Carbon fiber reinforced: XCN3030
3. Glass fiber reinforced: XGN3030
4. Wear and friction grade: XCL3030

TABLE 10.10 Properties of SuperAurum™ Grades

Properties	Unit	XPL	XCN3030	XGN3030
Filler		Natural	Carbon fiber	Glass fiber
Specific gravity	—	1.39	1.47	1.59
HDT, 1.82 MPa	°F (°C)	436 (224)	752 (400)	740 (393)
HDT, 0.45 MPa	°F (°C)	732 (389)	752 (400)	752 (400)
Tensile strength	MPa	147	194	189
Elongation	%	3	1	2
Flexural modulus	GPa	8.3	26.6	14.4
Izod impact	J/m	49	45	76

Applications of SuperAurum™

Since SuperAurum™ has a high HDT of 752°F (400°C), it can replace other polyimides, ceramics, and metals. XCL3030 is a representative grade as a wear and friction material, offering

1. Limit PV exceeding that of Aurum® and the capability of 1.3 times as great as Aurum® grade JCL3030
2. Much higher temperature resistance up to 572°F (300°C) as a bearing material

Therefore, it can be used for applications where PEEK and Aurum® cannot be used. Application examples include

1. LCD and semiconductor handling parts
2. Carriers such as wafer carriers, HDD carriers, and LCD carriers
3. Industrial machinery, electrical insulators for high-pressure usage
4. Oil exploration parts
5. Aircraft and aerospace
6. Chip seals and piston rings

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1. S. Tamai, A.Yamaguchi, and M.Ohta, *Polymer*, **37**(16):3683, 1996.
2. Aurum® website: www.aurumtpi.com.

Chapter 11

Liquid Crystal Polymer (LCP)

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Introduction

Polyester-based *liquid crystal polymer* (LCP) is one of the most attractive materials in the field of engineering thermoplastics because of its superior heat resistance, stiffness, accuracy of dimensions, moldability, and excellent balance of these properties. LCP is recently expanding its applications, in particular, those for the precision electronic parts appropriate for *surface mount technology* (SMT). The historical perspective of LCP is outlined below.

In 1972, Cottis and coworkers at Carborundum patented wholly aromatic polyesters based on *p-hydroxybenzoic acid* (HBA), 4,4′-*dihydroxybiphenyl* (DHB), and *terephthalic acid* (TPA), one of which was later commercialized as EKKCEL® I-2000 [1]. In 1974, Kuhfuss and coworkers at Eastman Kodak reported a new polyester based on HBA and *poly(ethylene terephthalate)* (PET), which was later marketed under the code of X-7G. X-7G is the first thermotropic liquid crystalline polymer to be fabricated by injection molding or melt spinning [2]. However, then Eastman Kodak withdrew its plan of marketing of X-7G and changed the target with a wholly aromatic polyester commercialized as TITAN® (THERMX®) in 1996. As described later, it was acquired by DuPont in 2003.

Sumitomo Chemical bought the EKKCEL® business from Carborundum and began to supply the product in the Japanese market under the trademark of EKONOL® in 1979. Sumitomo Chemical has manufactured EKONOL® (SUMIKASUPER LCP®), using a kneader-type polycondensation reactor [3]. The technology of Carborundum was also sold to Dartco, and the LCP was commercialized as XYDAR® in 1984. XYDAR® was also marketed in Japan by Nippon Petrochemical in 1986, but Dartco sold the XYDAR® business to Amoco in 1989 [4, 5]. Then Solvay acquired XYDAR® from Amoco in 2001. In 1985, Celanese commercialized VECTRA®, whose composition is HBA/6-hydroxy-2-naphtoic acid (HNA)[6, 7]. Hoechst acquired Celanese in 1987, and then the LCP business was transferred to the independent company Ticona. VECTRA® is also being marketed in Japan by Polyplastics. Unitika developed RODRUN® based on HBA/PET under the license from Eastman Kodak in 1986. At the same time, Mitsubishi Kasei commercialized NOVACCURATE® based on HBA/PET, which was produced by a unique polymerization technique. Since LCPs have various excellent characteristics not realized by the conventional engineering plastics, other chemical companies such as BASF (ULTRAX®), Bayer (POLYSTAL®), ICI (VICTREX® SRP), Idemitsu Petrochemical (IDEMITSU LCP®), Granmont (GRANLAR®), Rhone-Poulenc (RHODESTER®), Kawasaki Steel (K-LCP®), Tosoh Susteel, and Mitsubishi Gas Chemical had been engaged in the development of LCPs from 1986 to 1990 [8]. Thus, many chemical companies were seeking new business opportunities in the LCP market, but at that moment, the worldwide market for LCPs still remained small. Accordingly, most of above-mentioned companies had withdrawn from the LCP business. In the 1990s, Toray (SIVERAS®) and DuPont (ZENITE®) started commercial production of LCP. DuPont announced that it acquired Eastman's TITAN® (THERMX®) and strengthened its ZENITE® LCP lineup in 2003 [9]. Suppliers of LCP at present are shown in Table 11.1.

TABLE 11.1 Suppliers of LCP

Supplier	Trade name
Solvay (Amoco) (United States)	XYDAR®
Nippon Petrochem. (Japan) (importers)	XYDAR®
DuPont (United States)	ZENITE®
Ticona (United States)	VECTRA®
Sumitomo Chem. (Japan)	SUMIKASUPER LCP®
Polyplastics (Japan)	VECTRA®
Toray (Japan)	SIVERAS®
Ueno Fine Chem. (Japan)	UENO LCP®
Unitika (Japan)	RODRUN®
Mitsubishi Chem. (Japan)	NOVACCURATE®

TABLE 11.2 Classification of LCP

Type	DTUL (°C, 1.82 MPa)	Supplier/trade name
I	> 270	Solvay (Amoco)/XYDAR®, Sumitomo/SUMIKASUPER LCP®, DuPont/ZENITE®, Eastman/TITAN® (THERMX®)
II	240–270	Solvay (Amoco)/XYDAR®, Sumitomo/SUMIKASUPER LCP®, DuPont/ZENITE, Ticona (Hoechst) / VECTRA®, Toray/ SIVERAS®, Mitsubishi/NOVACCURATE®, Ueno/UENO LCP®
III	< 240	Unitika/RODRUN®, Mitsubishi/NOVACCURATE®

DTUL as high as 240°C is acceptable for surface mount technology.

LCPs are classified into three types by the *deflection temperature under load* (DTUL) of the molded articles (Table 11.2).

Recently, the greatest application of LCP was revealed to be that for molded electronic parts appropriate for SMT, which demands as high heat resistance as that of type II LCP. From the trend of the demand for LCPs, the research and development of type II LCP with improved moldability (flowability) have been actively pursued by many companies by suppressing the heat resistance of type I LCP. On the other hand, type III LCP has a structure derived from HBA/PET, and it has been insufficient for SMT applications due to its low DTUL, although it has the advantage of low-cost starting materials. A chronological table of the development of the three types of LCP is shown in Table 11.3.

Polymers

Chemistry of liquid crystal polymerization: Molecular architecture

Polyesters based on HBA or *hydroquinone* (HQ)/TPA do not exhibit a liquid crystalline state due to their high melting temperature. To lower the melting temperature of the polymers based on HBA, three approaches have been employed [10]:

1. Incorporation of unsubstituted rigid, rodlike segments such as 4,4′-biphenylene and 2,6-disubstituted naphthalene ring into the main chain
2. Incorporation of flexible aliphatic units such as 1,2-dioxyethylene into the main chain
3. Incorporation of rigid kinks such as 1,3-phenylene ring into the main chain

On the other hand, to lower the melting temperature of polymers based on HQ/TPA, two approaches had been employed [11]:

TABLE 11.3 Milestones of Three Types of LCP

	Thermotropic LCP		
	I	II	III
1960			
1970	1972 EKKCEL® (Carborundum) 1979 EKONOL® (SUMIIKASUPER LCP®) (Sumitomo Chem.)		1974 X-7G (Eastman)
1980	1984 XYDAR® [Solvay (Dartco)] 1985 EKONOL FIBER® (EKF) (Sumitomo Chem.) 1987 HAG, HBG® (ToSoh Susteel) 1988 GRANLAR® (Granmont)	1984 VECTRA® [Ticona(Hoechst)] 1986 ULTRAX® (BASF) 1987 VICTREX SRP® (ICI) 1988 RHODESTER® (Rhone-Poulenc) HX® (DuPont) UENO-LCP® (Ueno Fine Chem.) VECTRAN® (Fiber)(Kuraray) 1989 K-LCP® (Kawasaki Steel)	1985 RODRUN® (Unitika) EPE(NOVACCURATE®) [Mitsubishi Kasei (Mitsubishi Chem.)] 1986 POLYSTAR® (Bayer) 1987 IDEMITSU-LCP® (Idemitsu Petrochem.)
1990	1994 ZENITE® (DuPont) 1996 TITAN® (THERMX®) (Eastman)	1990 MGC-LCP® (Mitsubishi Gas Chem.) 1994 SIVERAS® (Toray) ZENITE® (DuPont)	
2000	2003 TITAN® (DuPont acquired from Eastman)		

4. Use of asymmetrically substituted hydroquinones such as phenylhydroquinone
5. Use of comonomers containing nonlinear structures such as 4,4′-diphenyl ether

Commercialized LCPs at present are based on HBA, and approaches 1 to 3 are employed.

Synthesis

LCPs can be manufactured by applying the conventional polycondensation process for polyesters. Although Grammont's process was based on the solution method using acid chloride developed by Owens-Coming [12, 13], processes of other producers are based on the following melt polymerization process [14–17].

1. Acidolysis-type polycondensation reaction using acetyl derivatives of aromatic hydroxyl compounds (such as HBA, HNA, and DHB) and

aromatic dicarboxylic acids [such as TPA, *isophthalic acid* (IPA), and 2,6-*dicarboxynaphthalene* (NDA)].

2. Acidolysis-type polycondensation reaction using aromatic hydroxyl compounds (such as HBA, HNA, and DHB), aromatic dicarboxylic acids (TPA and/or IPA), and acetic anhydride.
3. Acidolysis-type polycondensation reaction using acetyl derivative of HBA and PET or PET oligomers.

XYDAR® and SUMIKASUPER LCP® (type I) must be ground and advanced to high molecular weight by solid-state polymerization because of their high melting temperatures. Toray started the research on its own ultimate LCP, which has both the type II comparable heat resistance and the type III competitive cost, not starting from the type I LCP, but from the type III LCP by improving its heat resistance. In addition, we had paid great attention to the flowability appropriate for precision molding. Finally, we set up our goal as an LCP with DTUL above 250°C, improved flowability, and superior cost performance, as shown in Fig. 11.1 [9].

These polycondensation reactions proceed without any catalyst, but in some cases, it is preferable to add a metallic compound as catalyst. Sumitomo Chemical announced a new manufacturing process of LCP using a basic organic catalyst in 2002. The company also mentioned that the new catalyst increased the rate of reaction between monomers while restraining undesired side reactions. Although another melt polycondensation process involving removal of phenol, starting from phenyl ester of

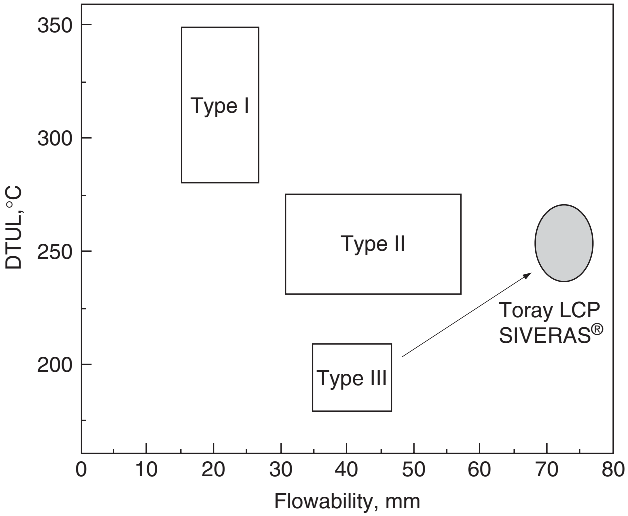
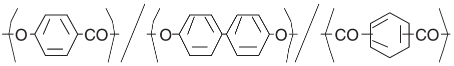
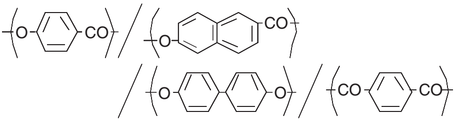
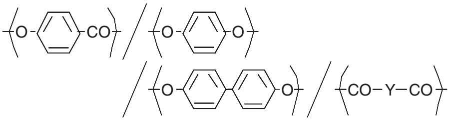
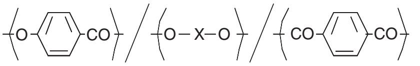


Figure 11.1 Target of Toray LCP SIVERAS®.

TABLE 11.4 Composition of Principal LCPs

		GF-reinforced	
Supplier/trademark	Composition	Grade	DTUL, °C
Sumitomo Chem., Solvay/ SUMIKASUPER LCP®, XYDAR®		E5008 E4008 E6008 E7008	335 313 279 242
		RC210 FC110 G430 G330 G540	349 345 314 260 240
Ticona, Polyplastics/ VECTRA®		S135 T130 E130i C130 A130	340 300 275 240 230
DuPont/ZENITE®		7130 6130	295 265
Toray/SIVERAS®		L304G35 L204G35	275 250

aromatic carboxy compound such as TPA and IPA and aromatic dihydroxy compound, is well known, this process is not believed to be feasible in commercial production.

The compositions of principal LCPs are shown in Table 11.4.

Properties

Characteristics of LCP [18]

As can be seen from Fig. 11.2, many fibrils are observed in the cross section of tensile fractured as-spun fiber LCP. These fibrils are acting as if they are reinforcements, and therefore LCP is often referred to as *self-reinforced polymer*. However, this anisotropy is a big practical problem when LCPs are used in injection-molded parts because LCPs produce oriented moldings with anisotropic mechanical and thermal properties. Properties along the flow direction tend to be superior to those across the flow direction. Fillers represented as glass fiber are often added to LCPs to reduce the anisotropy because the addition of any filler disrupts the alignment of the LCP molecules. This is just the reverse of what is experienced with

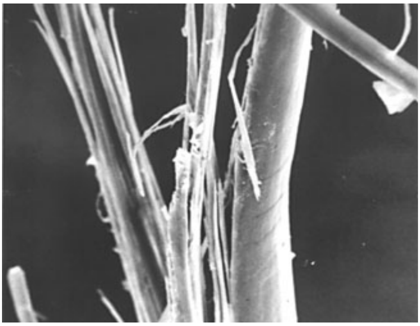


Figure 11.2 Typical SEM image of tensile fractured as-spun fiber of LCP.

conventional thermoplastics. Filled LCPs are, therefore, recommended for injection molding (Fig. 11.3).

Filled LCPs offer the following advantages in properties compared to the conventional engineering plastics:

1. Excellent processability that leads to short cycle time because of the low heat of fusion and the high flowability even in thin sections due to low melt viscosity under high shear
2. Little or no flash due to the low injection pressure and the shear sensitivity of viscosity
3. High modulus due to the high oriented skin structure

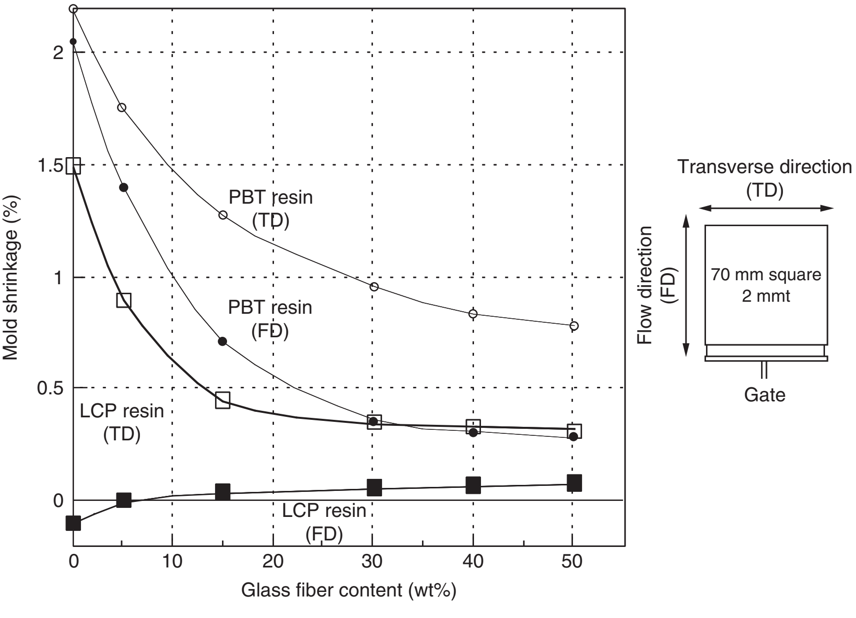


Figure 11.3 Mold shrinkage versus glass fiber content.

4. High DTUL
5. High dimensional stability [low *coefficient of thermal expansion* (CTE)]
6. Low permeability (low oxygen and water vapor permeability)
7. Flame retardancy
8. Damping properties due to the skin-core structure
9. Chemical resistance

These superior properties of LCP compared with other engineering plastics are shown in Fig.11.4.

Typical grades of GF filled LCPs by various manufacturers are shown in Table 11.5.

SIVERAS® GF filled regular grade

SIVERAS® has an excellent heat resistance that is appropriate for SMT applications. Here we present several important properties superior to the typical GF filled LCP materials for SMT applications:

1. *Moldability (flowability).* SIVERAS® shows the highest flowability among all the commercial LCPs, which is reflecting its excellent homogeneity.
2. *Flash properties.* In general, LCP materials generate low flash during injection molding compared with other engineering thermoplastics.

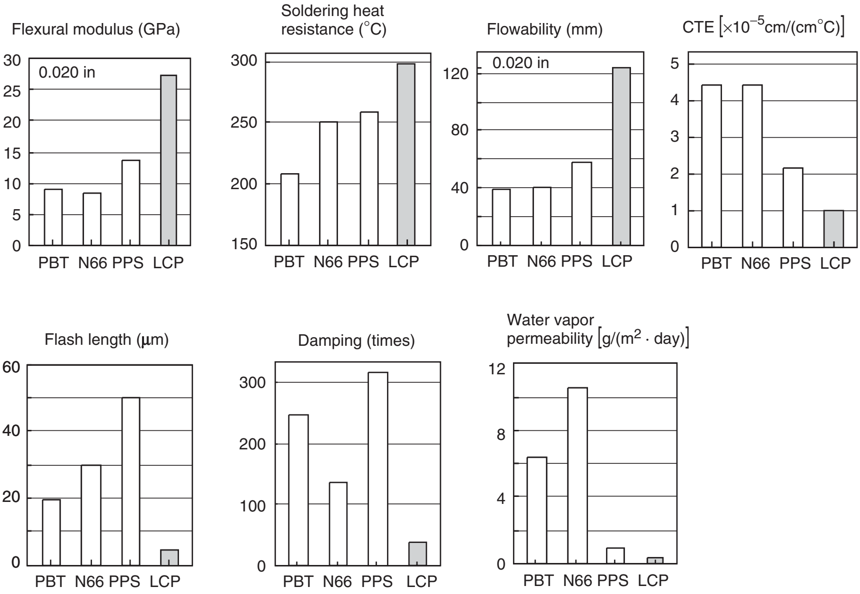
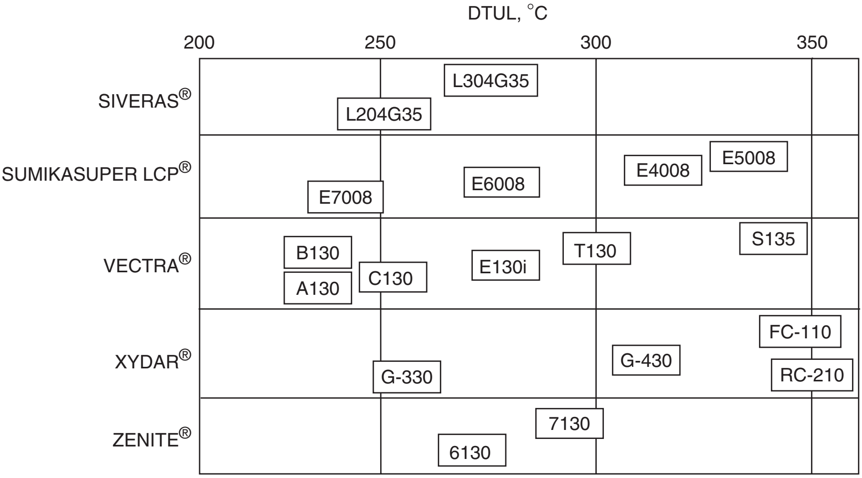


Figure 11.4 Typical properties of LCP compared with other engineering plastics.

TABLE 11.5 Typical Grades of GF Filled LCPs



SIVERAS® can realize a much lower level of flash than other type II LCPs on the market because of its low injection pressure due to its excellent flowability.

3. *Mechanical properties.* SIVERAS® has the highest level of mechanical properties among all the commercial LCPs; in particular, it has the highest weld strength, which is the most desired property of LCP materials.

SIVERAS® low-warpage grade

Although the anisotropic character of LCP can be suppressed by a higher load of GF, the flowability that is the strong point of LCP is sacrificed by the high load of GF as much as 50%. To avoid the loss of flowability, LCP compositions contain shorter GF, or the combination of GF and other inorganic fillers is developed and commercialized. SIVERAS® low-warpage grade L204M50 exhibits very small difference of mold shrinkage between flow direction and the transverse direction, and it can actualize the injection-molded articles with a very low level of warpage. In addition to the low warpage, a higher level of flowability is desired in LCP because small and complicated electronic parts should be molded with low injection pressure to avoid deformation. The characteristics of SIVERAS® low-warpage grades are shown in Table 11.6.

SIVERAS® specialty filler grades

Recently, the application of LCP is expanding not only in the field of electric and electronics but also in the field of automobile and industrial

TABLE 11.6 Characteristics of SIVERAS® Low-Warpage Grades

		L204G35	L204M50	L204M35
	Unit	Standard	Low warpage	
Specific gravity		1.68	1.84	1.69
Tensile strength	MPa	145	130	125
Elongation	%	3.0	2.6	3.0
Flexural strength	MPa	190	170	175
Flexural modulus	GPa	14.0	16.5	13.7
Izod impact strength	J/m	70	60	75
DTUL (18.2 MPa)	°C	250	250	245
Flammability	UL-94	V-0	V-0	V-0
Mold shrinkage (MD)	%	0.06	0.20	0.18
Mold shrinkage (TD)	%	0.50	0.29	0.32
Flowability (0.5 mmt)	mm	74	65	90

machinery. To fit the desires of the new fields, many new special grades of LCP are being developed that contain various highly functional fillers. Both fibrous and granular functional fillers can be used. Examples of typical fibrous fillers are carbon fibers, rockwool fibers, potassium titanate whiskers or metal fibers, as well as the granular fillers, talc, mica, kaolin, silica, clay, glass beads, glass micro balloons, and carbon black. SIVERAS® has several specialty grades such as high-stiffness grade, antiabrastion grade, and antistatic grade other than the regular GF or filler grades shown in Fig. 11.5.

SIVERAS® new grade with highest weld strength

Toray recently succeeded in developing a new series of LCP with vastly improved weld strength and toughness, which have been problems of LCP that needed to be solved for a long time [19]. The new lineup of LCP was developed by using our own polymer nanotechnology consisting of precise molecular design, nanoscale control of molecular mobility and molecular

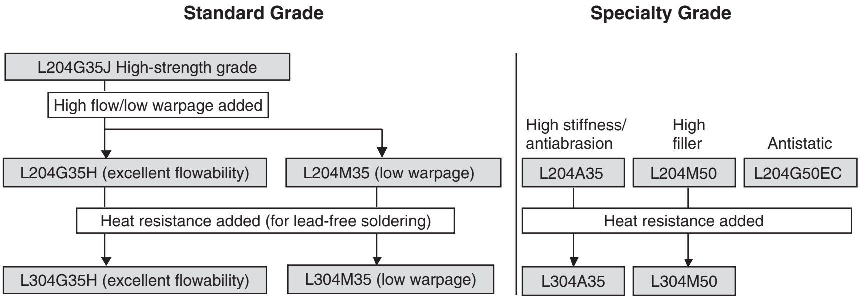


Figure 11.5 Variation of SIVERAS® grades.

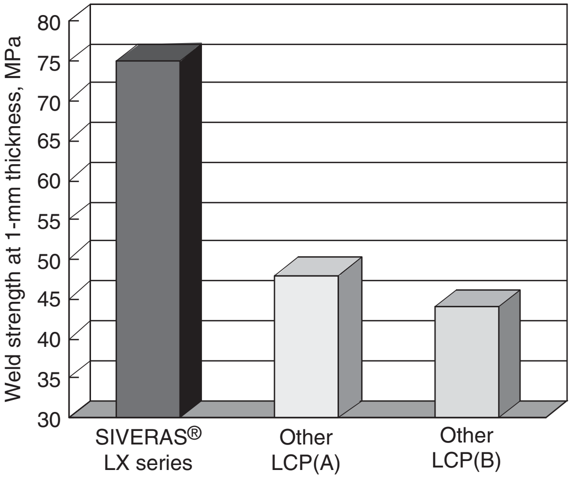


Figure 11.6 Weld strength of LCPs.

arrangement, and so on. The new lineup of LCP was developed by our polymer nanotechnology consisting of the analysis of thermal motion of the molecules and the control technology of liquid crystal structures. The new LCP realized the following outstanding features:

1. The highest weld strength among all LCPs (Fig. 11.6)
2. High dimensional stability due to low coefficient of thermal expansion
3. Retention of strength under high-temperature use
4. Low outgas in melt processing
5. Thermal resistance fit for lead-free soldering

The new LCP is expected to be used especially in expanding applications such as electronic parts for automobiles. More specifically, the weld strength of the new LCP is 50% and above higher than those of ordinary LCPs, and the amount of outgas on injection molding is less than one-third of those of ordinary LCPs. The flowability is one of the strong points of LCP. The new LCP has flowability the same as that of regular SIVERAS®, which is about 30% higher than that of the ordinary LCPs. In other words, the new LCP with excellent properties overcomes the weakness of the ordinary LCPs as well as improves the strong points of LCPs.

Polymer alloys

Extensive studies of polymer alloys are being continued by industry, government, and academic institutes in close cooperation with the aim of improvement of moldability, mechanical properties, heat resistance, dimensional stability, and gas barrier properties. The melt blending of an incompatible isotropic polymer and a thermotropic LCP produces a composite in which fibrous LCP domains play a role of reinforcement in the isotropic matrix polymer, because the molten LCP at the processing temperature comes out as elongated reinforcing fibers with cooling. Thus, the insitu formation of the reinforcing species during the fabrication process leads to the term *insitu composite*. SIVERAS® LC is a blend of polycarbonate and Toray LCP SIVERAS® by using micro composite technologies. In addition to the good properties of polycarbonate such as dimensional stability and electrical properties, SIVERAS® LC attains better flow even in thin parts and improves the dependence of impact strength on thickness.

Features of SIVERAS® LC

1. Excellent flowability for molding of thinner parts (Fig. 11.7)
2. Excellent vibration resistance
3. Higher impact strength in reduced thickness
4. High heat resistance
5. Excellent dimensional stability

Injection molding. Type II LCP can be molded with general-purpose injection-molding machines. The points of injection molding of LCP are shown below [18, 20, 21].

1. *Preliminary drying*. Although the water absorption of LCP is very little, preliminary drying is required before injection molding to prevent hydrolysis.
2. *Injection molding machine*. Because the principal application of LCP is fine and precisely molded parts, the electromotive injection-molding

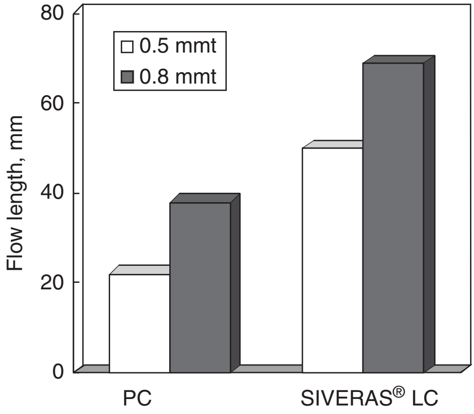


Figure 11.7 Flowability of SIVERAS® LC blend.

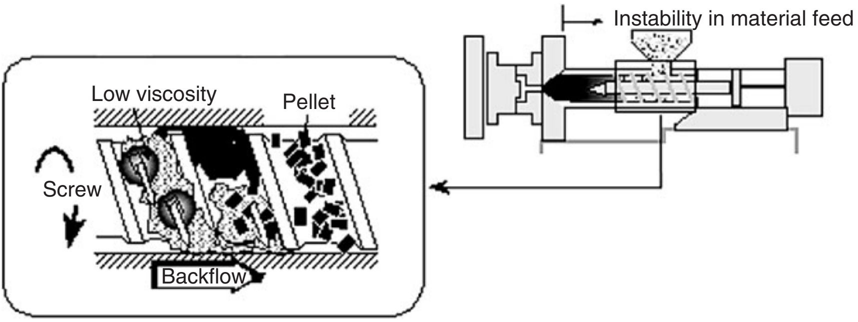


Figure 11.8 The backflow phenomenon in injection molding of a liquid crystal polymer.

machine, which can precisely control the molding conditions, is preferred. Normal components such as cylinder, heater, and screw can be applied without any problems. However, as shown in Fig. 11.8, since the melt viscosity of LCP decreases rapidly in the melt process, backflow of low viscous polymer or slipping of pellets is sometimes observed. Therefore, it is preferred to use the injection-molding machine, which can precisely control the temperature of the metering zone and the revolution of the screw.

A general open nozzle type of injection unit can be used for injection molding of LCP. However, a shutoff nozzle is very effective in preventing dripping down of polymer.

3. *Molding condition.* LCP can be molded by lower injection pressure compared to other thermoplastics. As shown in Table 11.7, it is possible to mold such a fine-pitch multipin connector as 0.8 mm or less, which has the partition of 0.1-mm thickness according to low-pressure high-speed

TABLE 11.7 Typical Processing Conditions for Molding LCP of SMT-Type Connectors

	LCP SIVERAS® L204G35	GF reinforced PPS
Cylinder temperature, °C		
Rear	280	300
Center	315	330
Front	320	340
Nozzle	310	330
Mold temperature, °C	120	140
Injection speed, mm/s	70	200
Injection pressure, MPa	90	230
		Short, large flash

Injection machine: 30-ton electric injection machine.
Mold: 100-pin 0.8-mm pitch board to board SMT connectors (pin-gate, two pieces).

conditions, at one-point gate. It is possible for LCP to flow and fill up the mold by shearing below its melting point. However, blisters on the surface of the product may occur by involvement of air or by the remaining distortion of the product caused by jetting in the mold in that case.

4. *Mold design*. Since the mold shrinkage of LCP is very small, it is easy to ask for a product size. However, it is necessary to pay great attention to gate position in designing the mold for LCP, because the weld strength of LCP is very low, the anisotropy is strong, and the stiffness may vary depending on the thickness of molding due to polymer orientation.

Consumption. In 2004, global consumption of LCP was considered to be 19,800 tons/yr. In the market of LCP, electrical and electronic parts, and office automation (OA), AV parts consume about 87 % and 10 % of the total demand, respectively (Figure 11.9).

Application

Injection molding. The primary targets for the LCP market are electric and electronic. And both electric and electronic parts actually account for more than 85% of the total demand. Recently, demand for super-miniaturizing design and SMT is increasing. In addition to excellent heat resistance, outstanding flowability has also been demanded for polymeric materials these days, and LCP is the only material exhibiting these two characteristics at the same time. The second-largest market for LCPs is office equipment and precise machines, because LCPs exhibit reduced mold shrinkage and excellent dimensional stability due to their low thermal expansion and high modulus.

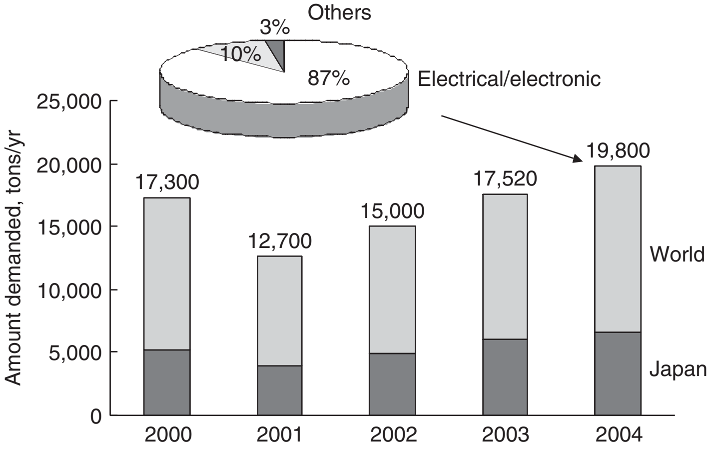


Figure 11.9 Annual worldwide demand of LCP.

Concerning the demand for LCP according to applications, connectors including sockets make up more than one-half of the whole demand for LCP, and more than 85% of the whole demand for LCP is considered to be for electrical and electronic parts. As other important applications, slide bases of optical pickup for CD and DVD, parts of hard disk drives, and parts of copiers and facsimiles are examples. Although LCP has enlarged its demand especially in the market of electronic parts appropriate for SMT, recently new prospective applications such as for the automobile have begun to germinate. Here we show the important applications of LCP according to these categories:

1. Electrical and electronic parts, various types of connectors (board-to-board connectors, flexible printed circuit connectors, card connectors, flash memory connectors, optical connectors), various types of sockets (PGA sockets, ZIF sockets, SIMM sockets, RIMM sockets, SO-DIMM sockets), relay casings, switches, quartz oscillators, piezoelectric elements, capacitors, sensors, coil bobbins, optical sensors, and encapsulant
2. Office equipment, audiovisual devices, various parts for still cameras and camcorders, mechanical parts for FDD and HDD, optical pickup parts for CD and DVD (lens holders, slide bases), parts for mobile phones, chassis of copiers and facsimiles, mechanical parts for laser printers, and speaker cones
3. Other parts for microwave ovens, lighting parts, dental trays, IC transport trays, and parts for various pumps

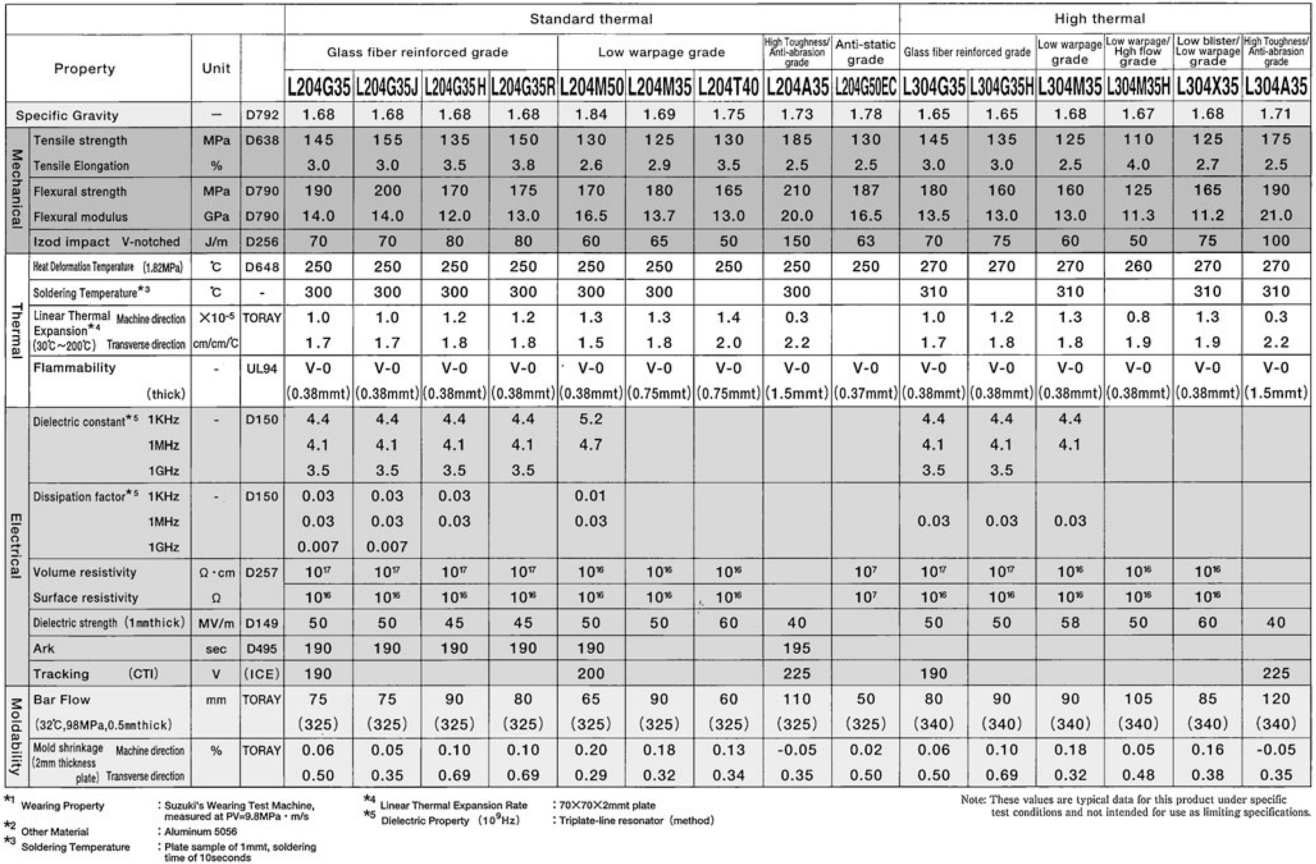
Toray's LCP SIVERAS® is widely used in OA equipment and IT devices due to its above-mentioned excellent properties. In particular, its flowability during injection molding is far superior to that of other LCPs, and it is suitable for precise molding with low-pressure and fine-pitch molding. In consequence, SIVERAS® achieved high market share as a material for connectors attached to flexible printed circuits used in mobile phones and digital cameras. On the other hand, SIVERAS® is used in SO-DIMM sockets, which need good flowability and low warpage. As the specialty grades, L204G50EC is used as coil encapsulant of HDD actuators due to its antistatic character, and L304A35 is used as an optical pickup of portable MD players due to its high flowability, antiabrasion property, and excellent dimensional stability.

Appendix

A1. Typical Properties of SIVERAS® (Fig. A.1)

A2. Properties of SIVERAS® Compared with Other Materials (Fig. A.2)

A3. Comparison of Toray SIVERAS® and PPS Resin TORELINA® (Fig. A.3)



	Property		Unit		Standard thermal									High thermal					
					Glass fiber reinforced grade				Low warpage grade			High Toughness/ Anti-abrasion grade	Anti-static grade	Glass fiber reinforced grade		Low warpage grade	Low warpage/ Hgh flow grade	Low blister/ Low warpage grade	High Toughness/ Anti-abrasion grade
					L204G35	L204G35J	L204G35H	L204G35R	L204M50	L204M35	L204T40	L204A35	L204G50EC	L304G35	L304G35H	L304M35	L304M35H	L304X35	L304A35
	Specific Gravity		—	D792	1.68	1.68	1.68	1.68	1.84	1.69	1.75	1.73	1.78	1.65	1.65	1.68	1.67	1.68	1.71
Mechanical	Tensile strength		MPa	D638	145	155	135	150	130	125	130	185	130	145	135	125	110	125	175
	Tensile Elongation		%		3.0	3.0	3.5	3.8	2.6	2.9	3.5	2.5	2.5	3.0	3.0	2.5	4.0	2.7	2.5
	Flexural strength		MPa	D790	190	200	170	175	170	180	165	210	187	180	160	160	125	165	190
	Flexural modulus		GPa	D790	14.0	14.0	12.0	13.0	16.5	13.7	13.0	20.0	16.5	13.5	13.0	13.0	11.3	11.2	21.0
	Izod impact	V-notched	J/m	D256	70	70	80	80	60	65	50	150	63	70	75	60	50	75	100
Thermal	Heat Deformation Temperature	(1.82MPa)	℃	D648	250	250	250	250	250	250	250	250	250	270	270	270	260	270	270
	Soldering Temperature*3		℃	-	300	300	300	300	300	300		300		310		310		310	310
	Linear Thermal Expansion*4 (30℃～200℃)	Machine direction	×10^{-5} cm/cm/℃	TORAY	1.0	1.0	1.2	1.2	1.3	1.3	1.4	0.3		1.0	1.2	1.3	0.8	1.3	0.3
		Transverse direction			1.7	1.7	1.8	1.8	1.5	1.8	2.0	2.2		1.7	1.8	1.8	1.9	1.9	2.2
	Flammability		-	UL94	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0
		(thick)			(0.38mmt)	(0.38mmt)	(0.38mmt)	(0.38mmt)	(0.38mmt)	(0.75mmt)	(0.75mmt)	(1.5mmt)	(0.37mmt)	(0.38mmt)	(0.38mmt)	(0.38mmt)	(0.38mmt)	(0.38mmt)	(1.5mmt)
Electrical	Dielectric constant*5	1KHz	-	D150	4.4	4.4	4.4	4.4	5.2					4.4	4.4	4.4			
		1MHz			4.1	4.1	4.1	4.1	4.7					4.1	4.1	4.1			
		1GHz			3.5	3.5	3.5	3.5						3.5	3.5				
	Dissipation factor*5	1KHz	-	D150	0.03	0.03	0.03		0.01										
		1MHz			0.03	0.03	0.03		0.03					0.03	0.03	0.03			
		1GHz			0.007	0.007													
	Volume resistivity		Ω・cm	D257	10^{17}	10^{17}	10^{17}	10^{17}	10^{16}	10^{16}	10^{16}		10^{7}	10^{17}	10^{17}	10^{16}	10^{16}	10^{16}	
	Surface resistivity		Ω		10^{16}	10^{16}	10^{16}	10^{16}	10^{16}	10^{16}	10^{16}		10^{7}	10^{16}	10^{16}	10^{16}	10^{16}	10^{16}	
	Dielectric strength	(1mmthick)	MV/m	D149	50	50	45	45	50	50	60	40		50	50	58	50	60	40
	Ark		sec	D495	190	190	190	190	190			195							
	Tracking	(CTI)	V	(ICE)	190				200			225		190					225
Moldability	Bar Flow (32℃,98MPa,0.5mmthick)		mm	TORAY	75	75	90	80	65	90	60	110	50	80	90	90	105	85	120
					(325)	(325)	(325)	(325)	(325)	(325)	(325)	(325)	(325)	(340)	(340)	(340)	(340)	(340)	(340)
	Mold shrinkage (2mm thickness plate)	Machine direction	%	TORAY	0.06	0.05	0.10	0.10	0.20	0.18	0.13	-0.05	0.02	0.06	0.10	0.18	0.05	0.16	-0.05
		Transverse direction			0.50	0.35	0.69	0.69	0.29	0.32	0.34	0.35	0.50	0.50	0.69	0.32	0.48	0.38	0.35

*1 Wearing Property : Suzuki's Wearing Test Machine, measured at PV=9.8MPa・m/s
*2 Other Material : Aluminum 5056
*3 Soldering Temperature : Plate sample of 1mmt, soldering time of 10seconds
*4 Linear Thermal Expansion Rate : 70×70×2mmt plate
*5 Dielectric Property（10^9Hz） : Triplate-line resonator（method）

Note: These values are typical data for this product under specific test conditions and not intended for use as limiting specifications.

Figure A.1 Typical properties of SIVERAS®.

	Unit	Test method (ASTM)	SIVERAS (LCP)	TORELINA	TORELINA	AMILAN (N6)	AMILAN (N66)	TORAYCON (PBT)	TORAYCON (PBT)	Modified resin PPO	PET	Metal (Al DC)
			L304G35H	A504 X90	A310M X04	CM1011 G30	CM3001 G30	1101 G30	Standard of competitor	Standard of competitor	Standard of competitor	
			GF 35%	GF 40%	GF/filler65%	GF 30%	GF 30%	GF 30%	GF 30%	GF 30%	GF 30%	
Specific gravity	—	D792	1.65	1.65	1.96	1.36	1.37	1.55	1.43	1.27	1.56	2.7
Water absorption (24 hrs. in 23℃ water)	%	D570	0.01	0.02	0.02	1.1	0.6	0.07	0.12	0.06	0.05	
Mold shrinkage Machine direction	%	D955	0.1	0.2	0.15	0.5	0.6	0.3	0.2	0.2	0.2	
Transverse direction	%	D955	0.69	0.75	0.55	0.8	0.9	1.0	0.5	0.3	0.9	
Tensile strength	MPa	D638	135	205	150	185	190	145	125	118	158	300
Elongation at break	%	D638	3.0	3.8	2.3	5.0	4.5	5.0	3.5	5.0	2.7	2.0
Flexural strength	MPa	D790	160	280	195	260	275	195	185	147	230	
Flexural modulus	GPa	D790	13.0	13.3	18.9	8.8	9.0	8.8	7.3	6.7	9.0	71.0
Izod impact	J/m	D256	75	155	120	125	85	90	157	98	101	
Heat deformation temperature 1.82MPa	℃	D648	270	>260	>260	215	255	217	149	142	224	
Linear thermal expansion Machine direction	X10^{-5}/k	D696	1.2	2.3	1.6	2.5	2.5	2.0	2.0	2.0	2.7	2.1
Dielectric strength	MV/m	D149	50	22	20	20	20	23	30	22	22	
Flammability class	—	UL94	V-0	V-0	V-0	HB equivalent	HB/0.8mm thick	HB	V-2	HB	HB	
Chemical resistance	—		◎	◎	◎	○	○	○	×	△	○	○

Note: These values are typical data for this product under specific test conditions and not intended for use as limiting specifications.

FIGURE A.2 Properties of SIVERAS® compared with other materials.

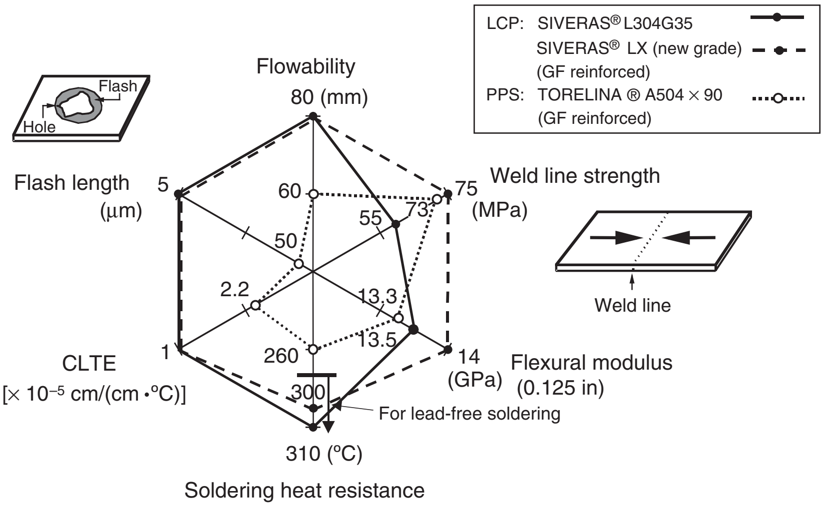


Figure A.3 Comparison of Toray SIVERAS® and PPS resin TORELINA®.

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Chapter 12

Polyamide-imide (PAI)

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Introduction

Polyamide-imides are thermoplastic amorphous polymers that possess exceptional mechanical, thermal, and chemical- and wear-resistant properties. They are inherently nonflammable, have outstanding electrical properties, and possess enormous temperature stability from cryogenic to 300°C. These properties place polyamide-imides at the top of the price and performance pyramid with polyketones and polyimides.

Polyamide-imides enjoy, as the name suggests, a positive synergy of properties from both polyamides and polyimides, such as flexibility, melt processability, elongation, dimensional stability, and toughness. Polyamide-imide polymers can be processed into a wide variety of forms, from injection- or compression-molded parts and ingots to coatings, films, fibers, and adhesives. Generally these articles reach their maximum properties with a subsequent thermal cure process.

History

With polyamide-imides sharing some of the best performance attributes of polyimides, they are considered a subset of this larger family. Polyimides were first developed in 1955 by Dupont [1–3]. The class of polyamide-imides was subsequently commercially developed in the early

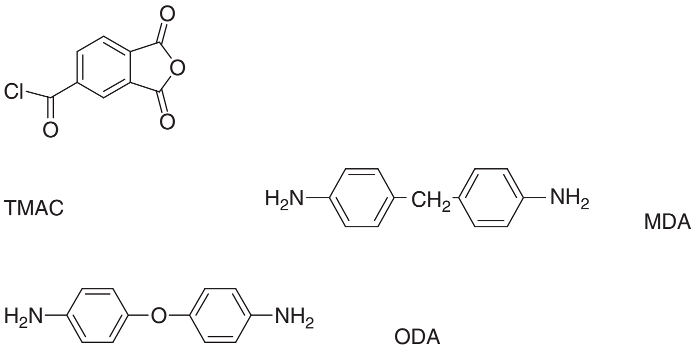

Figure 12.1 Polyamide-imide monomers.

1960s [4, 5] at Standard Oil of Indiana (Amoco)* and branded under the Torlon® trademark.

A large driving market factor for these first polyamide-imides was the need for a high-temperature-capable insulation for magnet wire. In early 1961, Amoco Chemicals Company started a project to develop high-temperature wire enamel with investigations into aromatic polyester imides and polyamide-imides. From that development, the polyamide-imide wire enamel products were based on *trimellitic anhydride chloride* (TMAC) and 4,4′-*methylenedianiline* (MDA) and also TMAC and 4,4′-*oxydianiline* (ODA) using the so-called acid chloride route (Fig. 12.1) and were sold in both solution and powder forms. This development filled a real need to have a readily soluble, lower-viscosity, lower-cost magnet wire enamel than the polypyromellitimide wire enamels that were on the market at the time, yet maintain high-temperature capabilities with a glass transition temperature of 280°C.

Following this wire enamel introduction, Amoco began development, in the mid-1970s, of melt processable polyamide-imide compounds for the injection molding and extrusion markets [6].

Also in this time frame, wire insulation producers began producing polyamide-imides using lower-cost isocyanate chemistry. This technology largely supplanted the acid chloride route for the wire enamel market.

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*At the time, Amoco Chemicals Company was a wholly owned subsidiary of Standard Oil Company (Indiana), which later changed its name to Amoco. Amoco Performance Products, Inc., was created with the purchase of Union Carbide's high-performance polymer and carbon fiber groups in 1985. BP inherited the polymers business in its merger with Amoco and then divested it to Solvay, where Torlon and the other high-performance polymers are now within the Solvay Advanced Polymers, LLC, business unit.

Polyamide-imide Polymerization Chemistry

There are currently two popular commercial methods to synthesize polyamide-imides. One is the acid chloride route, and the other is the isocyanate route. The synthesis method used will determine and limit to some extent the applications in which the resultant polymer is used. The chemistry of these two methods is outlined below.

Acid chloride route

The earliest and one of the most well-known routes to polyamide-imides is through the two step-process involving the condensation of an aromatic diamine and TMAC (Fig. 12.2) [7, 8]. Reaction of the anhydride portion of TMAC provides an intermediate amic acid (k_1). On the other end of the molecule, the acid chloride functionality reacts with aromatic amine to give the amide bond and hydrochloric acid (HCl) as a byproduct (k_2). In the commercial preparation of polyamide-imides, the solution polymerization is carried out in a dipolar, aprotic solvent such as *N-methylpyrrolidone* (NMP), *dimethylacetamide* (DMAC), *dimethylformamide* (DMF), or *dimethylsulfoxide* (DMSO) at temperatures between 20 and 60°C [9].

The presence of the byproduct HCl in the solution polymerization requires it to be neutralized in situ or removed by isolating and washing it from the resultant polymer formed. Organic bases such as tertiary amines (triethylamine) have been used in situ, along with ethylene or propylene oxide, as acid acceptors in the reaction solution [10].

The amic acid intermediate is stable and may be isolated as such. After the solution reaction is complete, the polymer is recovered via precipitation.

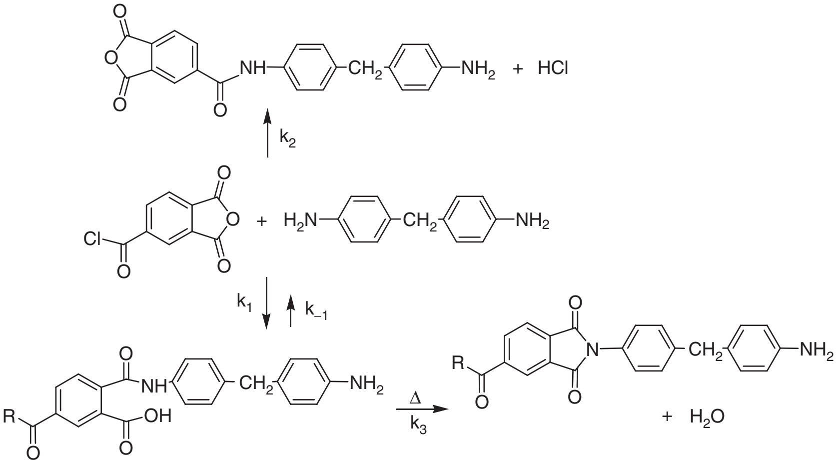


Figure 12.2 Acid chloride route.

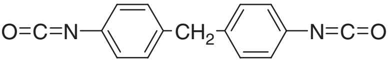


Figure 12.3 MDI.

With a high concentration of amic acid groups along the polymer backbone, the polymer at this stage can be formulated into aqueous solutions with the aid of a tertiary amine, which reacts to create the ammonium salt of the amic acid [11].

Further thermal treatment (k_3) of the polyamide-imide polymer increases the molecular weight and imidization level. In addition to thermal treatment, polyamide-imides can subsequently cyclize through chemical imidization. The chemical treatment is accomplished by using a tertiary amine and an anhydride; typically triethylamine and acetic anhydride are common, while other variants have also been used with success [12].

All polyamide-imides which are fabricated in some fashion, whether it is an injection-molded part, an extruded rod, or a thin coating, must be thermally cured in order for the material to reach its maximum properties. The cure schedule depends on the geometry and thickness of the part. Injection- and compression-molded parts require a longer postcure due to their inherent thickness and geometry, compared to polyamide-imide coatings, which are likely in the thickness range of 1 mil (25 μm) or less. The curing process further increases the molecular weight of the polymer, drives imidization of the amic acid, and induces cross-linking reactions. Once fully cured, polyamide-imide articles are no longer melt-processable or soluble. A general guide to cure schedules for polyamide-imide coatings and injection molded and compression-molded parts is indicated in the Processing section (see Table 12.8).

Isocyanate route

The other most popular method of synthesizing commercial PAI uses the so-called isocyanate route. This is the primary route to polyamide-imides which are then utilized as wire enamels or fibers. This PAI chemistry involves the reaction of a di-isocyanate, often 4,4′-*methylenediphenyldiisocyanate* (MDI) (Fig. 12.3) with *trimellitic anhydride* (TMA) (Fig. 12.4). To overcome the lower reactivity of the carboxylic acid functionality in

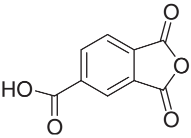


Figure 12.4 TMA.

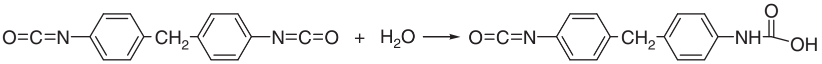


Figure 12.5 Formation of carbamic acid with water.

TMA versus the acid chloride in the previous route, the highly reactive MDI is used.

The reaction is thought to be catalyzed by a protic species. Water, as a residual impurity in the solvent, or alcohol or even the carboxylic acid proton from TMA, is often cited as the hydrogen source. One proposed mechanism is thought to be formation of the carbamic acid, with water, as shown in Fig. 12.5.

Reaction of the carbamic acid with the anhydride forms the mixed anhydride of *n*-acetylated carbamic acid and a carboxylic acid. This mixed anhydride decarboxylates to form the amic acid, releasing a molecule of carbon dioxide (Fig. 12.6).

The cyclization of the imide ring is thought to be promoted by the acylation of the acid with another isocyanate group, forming the reactive mixed anhydride. The amide nitrogen can then easily cyclize by reaction with the activated carbonyl of the mixed anhydride, releasing the carbamic acid (Fig. 12.7).

This unstable carbamic acid is then free to react with another anhydride or to decompose to the amine with concomitant release of carbon dioxide (Fig. 12.8).

By combining the reactions in Figs. 12.5 and 12.8, one can see that the isocyanate may ultimately end up as the amine in the presence of water (Fig. 12.9).

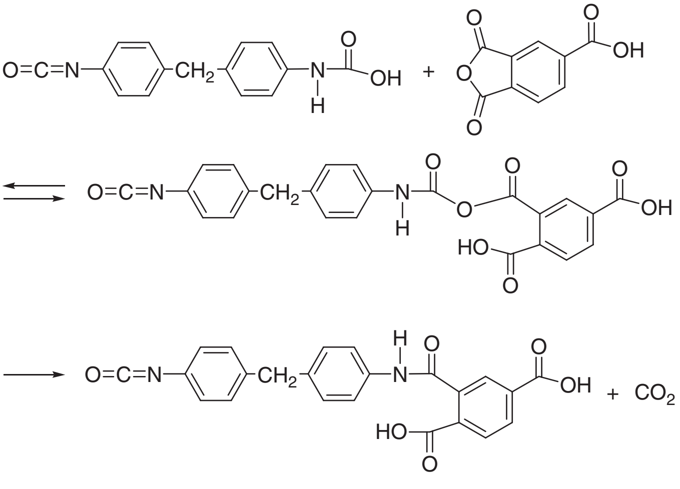


Figure 12.6 Reaction of carbamic acid with anhydride.

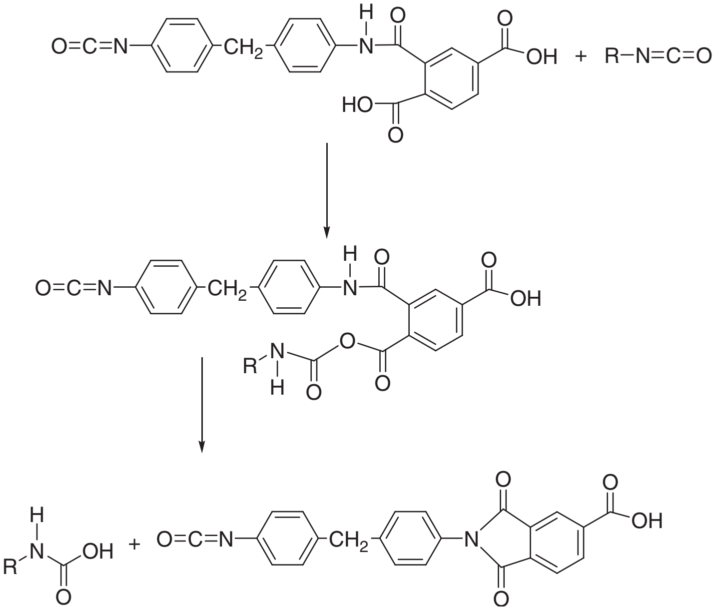


Figure 12.7 Cyclization of imide ring.

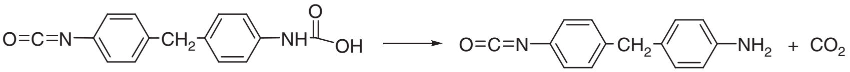


Figure 12.8 Carbamic acid decomposes to amine and carbon dioxide.

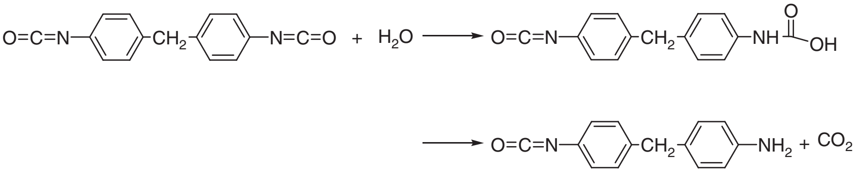


Figure 12.9 Isocyanate ends up as amine in presence of water.

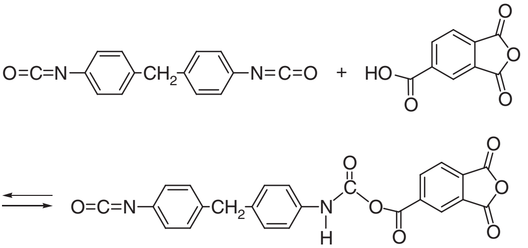


Figure 12.10 Monoacid reacts with isocyanate to form mixed anhydride.

The monoacid functionality of TMA reacts directly with the isocyanate functionality to give the mixed anhydride, again reducing to the amide bond with release of a molecule of CO_2 (Fig. 12.10).

In isocyanate chemistry many unintended side reactions can occur. The amine formed from the unstable carbamic acid can react with isocyanate, forming a urea. This secondary nitrogen urea or any other amide nitrogen may react further with another isocyanate, forming a cross-link at this new biuret functional group. The amine may also react with the anhydride on TMA, forming the amic acid. And, depending on temperature, the isocyanate may react with the solvent itself. All these side reactions and their influences on stoichiometry must be fully understood and controlled.

Commercially the isocyanate process is also done in a dipolar aprotic solvent, typically NMP. The isocyanate route is performed at higher temperatures to evolve CO_2 gases and promote imidization reactions. The reaction temperature is ramped over time to promote all the various reactions shown above. One typical profile starts the reaction at 80°C with the temperature increased at a rate of 30°C/h to 200°C over 4 h. Here the maximum CO_2 evolution occurs in the 120 to 130°C range, with no more evidence of isocyanate functional groups present [13].

The polyamide-imide achieved at the end of this process is a high-molecular-weight, fully imidized polymer in solvent with no condensation by-products, since the carbon dioxide gas is easily removed. This convenient form makes it especially beneficial for the manufacturer where the primary end use is wire enamel or another coating application. The solution viscosity is thus controlled by stoichiometry, monofunctional reagents, and polymer solids. The typical polymer solids level is 35 to 45% and it may be diluted further by the supplier or customer with diluents.

The polymer solution may also be spun into polyamide-imide fibers by using a wet or dry process. Fibers under the trade name Kermel® are manufactured in this manner, formerly by Rhodia.

As inferred from the reaction schemes shown above, there is the potential for many side reactions. These complex reactions lead to a polyamide-imide with potential branch points and a slightly irregular polymer backbone compared to the acid chloride route polyamide-imide. All the possible reactions are dependent on many parameters including the solvent, monomer concentration, purity of reagents, water content, and temperature reaction profile. Because of the slightly irregular backbone and branching which reduce thermal stability, isocyanate-based PAIs are not seen in melt-processable PAI compounds. Another reason is that MDI is often the di-isocyanate of choice. The methylene moiety is not stable at melt processing temperatures, leading to cross-linked material which does not flow well. In the acid chloride case, other diamines without methylene carbons, such as ODA, are used for the injection-molding grades.

Other polyamide-imide chemistries

Other direct one-pot syntheses are known and have been cited in the literature but are not practiced commercially. One example involves the formation of a diacid containing internal di-imide groups from the reaction of TMA and a diamine. The amide bond is then condensed in a second step in the same pot with additional diamine, using pyridine, triphenylphosphite, and lithium chloride in NMP [14]. This amide condensation may also be completed by the addition of a thionyl chloride/NMP complex to the diacid in the presence of an acid acceptor [15].

Alternatively, other methods use a di-isocyante, such as MDI, to react with the diacid-dimide [16]. This defined architecture allows microstructured polymers to be synthesized which can be useful in membrane and other specialty applications.

Most commercial PAIs, including the Torlon family, have glass transition temperatures in the range of 275 to 280°C. Lower and higher glass transition temperatures are possible by modifying the structure of the diamine or di-isocyanate. Incorporating more flexible units, such as monomers with ether bonds, will reduce the glass transition temperature T_g, while stiffer units, such as diaminodiphenylsulfone, will increase it [17].

Applications Using Polyamide-imides

Polyamide-imides have outstanding properties. Fortunately, they are commercially available in many different forms. Torlon polyamide-imide compounded grades can be processed via injection molding and extrusion into intricate parts and standard shapes and geometries. Coatings and adhesives may be formulated using Torlon polyamide-imide powders. Alternatively, polyamide-imide solutions manufactured via the isocyanate process may be used directly in coating applications, such as wire enamels and other industrial coatings. Because of their properties, polyamide-imide powders can be used as a toughening, wear-resistant, high-strength additive in other thermoplastics and fluoropolymer parts and systems. Individual parts may be easily machined from compression-molded or injection-molded ingots or extruded rod and plate stock.

Polyamide-imides, due to their high relative cost compared to common engineering plastics such as nylon and polycarbonate, are used when the application conditions require the property benefits of these materials and where lesser polymeric materials would fail. In addition to this, they have great strength-to-weight ratio, and polyamide-imide compounds are often used for metal replacements. Some of the unique areas where polyamide-imides are used are illustrated below.

Coatings

Fluorosurfacing. How do you answer the question, "If nothing sticks to *polytetrafluoroethylene* (PTFE), how does PTFE stick to the metal of your nonstick frying pan." The answer is often polyamide-imide. While other lower-cost, lower-performing high-temperature polymers such as *polyphenylsulfide* (PPS) and *polyethersulfone* (PES) are often used as fluoropolymer binders, polyamide-imides are recognized as the best-performing polymeric adhesive used in the high-temperature fluorosurfacing market. Cookware and bakeware coatings are well-known high-temperature nonstick applications. In addition, many other low-friction, abrasion-resistant, and high-temperature industrial coating applications use fluoropolymers in conjunction with high-temperature polymer binders. The polyamide-imide is formulated into the primer or first layer of a fluoropolymer coating. This layer provides the adherence to the metal substrate and to the subsequent fluoropolymer layers or to itself in a single-coat system. With a glass transition temperature of 280°C (536°F) and a decomposition onset temperature of over 450°C (842°F), it can readily handle the typical cookware temperatures. The high adhesive strength and high modulus of polyamide-imides resist scratching and gouging often seen with lower-priced nonstick cookware.

Friction and wear applications

A prime example of where polyamide-imides enjoy prominence is in friction and wear applications. This means not only in a system where the polymer components are meant to operate with low-friction and low-wear characteristics, but also in new applications such as brake pads and abrasion wheels, where the operating conditions require low wear with high friction, a truly demanding scenario. Polyamide-imides can achieve this due to their high softening temperature and retention of strength, stiffness, and compression properties at elevated temperatures.

High-speed bobbins. The critical component in today's commercial lockstitch sewing machine is the rotary hook and bobbin (Fig. 12.11). These parts traditionally have been manufactured out of stainless steel, which requires constant lubrication and stitch tension adjustments. Both can play havoc with operator productivity and stitch consistency, particularly with lighter-weight or delicate fabrics. Hooks and bobbin baskets made

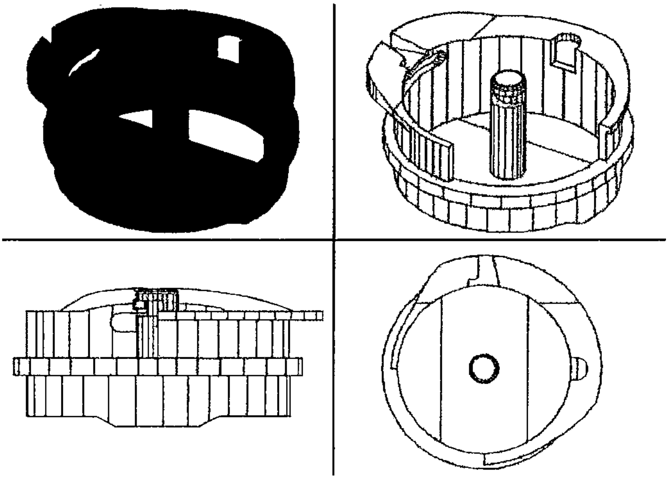


Figure 12.11 Polyamide-imide compounds are used in rotating industrial equipment.

from a polyamide-imide compounded with patent-pending additives [18] are able to withstand the high frictional heat which occurs in sewing machines that run at high speeds, 4000 to 9000 switches per minute, e.g., without bobbin lubrication. Hooks made from polyamide-imide don't stick or slip, and they need minimal adjustment. Unlike stainless-steel components, which have no flexibility, parts made from polyamide-imide have enough give to allow slight variances between upper and lower thread tensions, allowing the machines to be set at the lightest possible tension without losing stitch integrity.

Compressor vanes. Polyamide-imide compounds are being used in a number of rotating industrial equipment applications. One particular area of interest is in rotary vane compressors. Previously the vane materials were made from a phenolic composite construction. Although more expensive from a material of construction perspective, a polyamide-imide compound was chosen due to a dramatic extension in life and a lower lubrication requirement, both of which reduce maintenance and the overall operating cost of the compressor. In addition the compressors can operate at a higher discharge pressure due to polyamide-imide's higher-temperature capability.

Automotive transmission components: seal rings, thrust washers, check balls. Many automatic transmissions on the road these days contain multiple components manufactured from injection-moldable polyamide-imide compounds. Seal rings are placed on the transmission to prevent transmission oil from leaking out the shaft. The excellent friction and wear properties of polyamide-imides permit their use where rotational speeds averaging 3000 rpm are standard. They also must handle the resistance to many different automotive fluids at temperatures that reach 150°C. Polyamide-imide thrust washers can handle the cyclic compression and abrasive wear when placed against metal for the entire life of the vehicle. Valve body check balls must endure millions of cycles without fatigue or rupture, again at elevated temperatures and in harsh chemical environments. They must have the ability to seat against the orifice and provide a leakproof seal and then open without delay. Polyamide-imide compounds are one of the few materials that can handle these tough application requirements and still be a cost-effective part to manufacture due to injection-molding capability.

Race car suspension bushings. Due to their superior friction and wear properties, polyamide-imides are being incorporated in the suspensions of endurance race cars. Recently a race team upgraded its Ferrari to suspension bushings machined from extruded polyamide-imide tube. The switch was made because the factory bushing material wears out and has to be changed between every race. Worn bushings, which make car handling sloppy, are not an issue even in 24-h endurance races (Fig. 12.12).

Aerospace

The endurance benefits and performance characteristics of polyamide-imides qualify them to be an excellent replacement for metal in aerospace components. Inherent nonflammability, chemical resistance, and superb strength at elevated temperatures allow polyamide-imide compounds to be used in metal applications once unheard of for plastic materials. Neat resin, friction and wear, along with glass- and carbon-reinforced polyamide-imide compounds are incorporated in a variety of parts and locations in aerospace vehicles.

Aerospace composite adhesives. In addition to molded parts, polyamide-imides are used as the high-strength adhesives and polymer matrix in aerospace composites. One particular area is honeycomb composites [19]. The adhesives and polymer matrix are critical because the ultimate strength of the honeycomb is often directly dependent on the strength of the bond between the honeycomb layers. The polyamide-imide resin is dissolved in an appropriate solvent and applied to the honeycomb fabric, using a bonding technique to achieve the desired

Figure 12.12 Suspension bushings.

honeycomb structure. The planar honeycomb structure is manufactured to a rigid B-staged form, which can then be heated, postformed, shaped, and cured into its final state. Polyamide-imide powders are used here, because of their ease of formulation and usable viscosity.

Figure 12.13 Air return grill.

The final composite structures claim excellent chemical resistance, high strength, moderate ductility, and toughness.

Engine components. Parts fabricated from injection-molded fiber-reinforced polyamide-imides provide a lower-cost solution to previously machined metal pieces and maintain, due to low shrinkage, very tight tolerances which are required in these applications. Polyamide-imide compounds have replaced expensive titanium in air return grills for commercial aircraft engines (Fig. 12.13). The shroud on the interior of the aircraft engine, responsible for directing airflow, consists of an assembly of multiple polyamide-imide injection-molded pieces (Fig. 12.14).

Figure 12.14 Aircraft engine shroud.

Metal aircraft parts are easily converted to parts composed of polyamide-imide, because of the metal-like coefficient of thermal expansion of the filled compounds. The high modulus and low creep of polyamide-imides provide outstanding thread-holding ability for nonmetallic and thermally-isolating aerospace fastener mounts [20].

Clip nuts. Clip nuts for aircraft are configured to slide over an edge of a panel and align a screw and nut with a hole in the panel. They are used to mount devices to that panel and for attaching panels together. They require durability and high load capability, in addition to excellent corrosion resistance, a common pitfall of metal clip nuts. Clip nuts manufactured by the injection molding of a polyamide-imide resin enable a cost-effective and weight-saving metal replacement solution [21] (Fig. 12.15).

Semiconductors

Semiconductor manufacturing has some of the toughest material requirements of any industry. Materials used to hold and process wafers and the final IC chips during the manufacturing process are required to endure high plasma-etch temperatures and harsh chemical environments. The materials themselves must not introduce impurities into the manufacturing environment through outgassing or leaching of ionic molecules. Polyamide-imides, along with a number of other high-performance polymers, are utilized in this manufacturing segment because they are the only materials that can handle the difficult

Figure 12.15 Clip nuts.

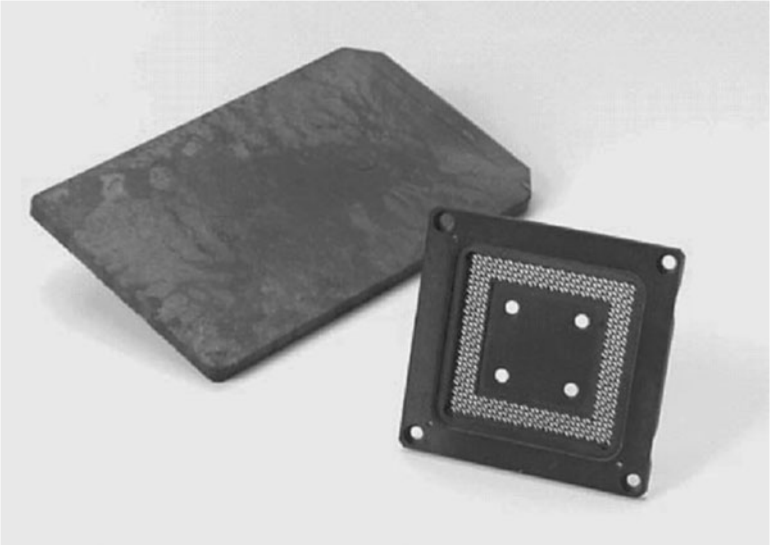


Figure 12.16 Electrical test sockets.

requirements. Polyamide-imide is utilized for semiconductor test sockets. These protect delicate devices during robotic handling and insertion into electrical test sockets (Fig. 12.16). Plus they maintain dimensional stability throughout the test sequence while providing necessary electrical isolation between the circuit pins.

Industrial

High-pressure hydraulic components. One industrial area where polyamide imides are exploited is in precision-machined poppets, seats, and spools in fluid power systems for agriculture and construction vehicles and equipment. These polymer parts are replacing metal, which tends to leak progressively over its service lifetime, because polyamide-imides have superior sealing capability and can handle the high operating pressure of 5000 psi (34 MPa). In addition to extension of the service life of the part, polyamide-imides enable significant system cost savings and weight reduction [22].

Commercial Polyamide-imides

The leading global provider of polyamide-imide powders and compounded resins is Solvay Advanced Polymers, LLC, with the resin under the registered trademark Torlon [23]. The major commercial grades are listed below.

Powder grades	Compounded grades
AI-10	4203L
AI-30	4301
AI-50	4275
4000T	4435
4000TF	5030
	7130

Torlon powders

Torlon AI-10 polyamide-imide is roughly 50% imidized and has a molecular weight optimal for specialty coating formulations. It is utilized in an extensive number of high-performance and high-temperature coatings and adhesives. Many of these are electrical and wire coatings, corrosion-resistant coatings, ablative coatings, nonstick cookware, and a variety of other industrial coatings. The use in these markets is due to its high glass transition temperature, adhesive strength, and thermal stability. Depending on the polymer solids level, its relatively low molecular weight provides a very usable solution viscosity and it may be dissolved in a number of solvents.

With the aid of a tertiary amine, Torlon AI-30 becomes the water-soluble analog of Torlon AI-10. The wet powder consists of 35% polymer solids, 63% water, and 2% NMP. It is made water-soluble by forming an ammonium salt with the amic acid groups on the polymer backbone. Torlon AI-30 aqueous-based solutions are environmentally friendly and allow the formulator to produce a high-performance coating or adhesive without needing a dipolar aprotic solvent such as NMP.

Both Torlon AI-10 and Torlon AI-30 are synthesized by using MDA as the primary diamine. Due to potential health consequences of exposure to MDA, OSHA has strict regulations concerning its handling and monitoring in the workplace. Because of their low molecular weights the residual levels of MDA in Torlon AI-10 and Torlon AI-30 are just above the OSHA threshold of 0.1 wt%, requiring these PAI powders to have the same environmental and monitoring controls. Recently Solvay Advanced Polymers, LLC, has introduced a new polyamide-imide powder grade based on MDA and TMAC, but without the OSHA handling and monitoring restrictions, due to its reduced residual MDA level. It has the same performance attributes as Torlon AI-10 and similar specifications.

Torlon AI-50 is another water-soluble polyamide-imide similar to Torlon AI-30 in solids composition and coating performance. Because of a slightly different polymer backbone, it also does not have the MDA handling restrictions, plus it has a lower viscosity at the same solids level compared to AI-30.

Torlon 4000T is greater than 90% imidized and has molecular weight ranges designed advantageously for compounded products which are utilized for injection-molding and extrusion processes. It is the neat resin powder utilized in the compounded grades discussed below. The diamines used in the synthesis of this resin provide flexibility, toughness, and melt processability. In addition, this polyamide-imide can be used in tough coating, adhesive, and additive applications. Torlon 4000TF is a fine-particle-size version of Torlon 4000T. It has a median particle size around 25 μm, and 95% of the powder is less than 75 μm. This defined particle size is advantageous in additive applications, compression moldings, powder coatings, and dispersions.

Torlon compounds

Torlon 4203L is an unreinforced, all-purpose grade, and it contains 3% titanium dioxide and 0.5% fluoropolymer. It has the best impact resistance and greatest elongation of all the Torlon compounds.

Torlon 4301 is one of three current friction and wear grades. This polyamide-imide resin is designed as a general-purpose, low-friction, and low-wear compound. The resin composition contains graphite and fluoropolymer. It is engineered to meet the needs of the bearing manufacturer with high strength, performance at elevated temperatures to 260°C, and excellent chemical resistance.

Torlon 4275 polyamide-imide resin is designed as a low-friction and low-wear compound, similar to Torlon 4301 resin with better performance at higher velocities and pressures up to 50,000 $\text{ft}\cdot\text{lb}/(\text{min}\cdot\text{in}^2)$. The resin composition contains graphite and fluoropolymer. Its high strength, performance at temperatures up to 260°C, and excellent chemical resistance make this grade an excellent choice for demanding rotating and sliding applications.

Torlon 4435 polyamide-imide resin is specifically designed to provide exceptionally low-wear performance in nonlubricated applications even at high *pressure and velocity* (PV) conditions greater than 50,000 $\text{ft}\cdot\text{lb}/(\text{min}\cdot\text{in})$. The low coefficient of thermal expansion provides the ability to meet close tolerances over a wide temperature range. Due to its electrically dissipative property, this grade may also be considered for antistatic functions.

There are two fiber-reinforced strength grades. Torlon 5030 is a 30% glass fiber reinforced polyamide-imide resin. The material exhibits high strength and stiffness, retention of stiffness at temperatures up to 260°C, and very low creep. Torlon 7130 is a polyamide-imide compound containing 30% carbon fiber reinforcement. This melt-processable, high-performance engineering thermoplastic has extraordinary strength and stiffness at temperatures up to 260°C. It has the best fatigue resistance of all the Torlon grades.

Other PAI producers

The majority of isocyanate-produced polyamide-imide solutions are consumed within the wire enamel marketplace, where Altana AG and Hitachi are known. Other producers with polyamide-imide solution products include Bayer Material Science with Resistherm®, while Huntsman has Rhodeftal®.

Due to the specialty nature and niche applications for polyamide-imide parts, many of these low-volume pieces are machined from preformed stock shapes. Toray, based in Japan, is producer of polyamide-imide resin that it converts to polyamide-imide parts and stock shapes, largely for the Asian markets. In the United States, Quadrant EPP supplies extruded Torlon polyamide-imide rod and plate stock as well as compression-molded ingots and shapes. Drake Plastics extrudes custom profiles in addition to standard shapes from Torlon resins. Injection-molded Torlon polyamide-imide stock shapes are available through Parkway Products.

Physical Properties

As seen from the application examples, polyamide-imides possess a unique blend of high-performance properties. An overview of polyamide-imide properties for compounded materials is shown in Table 12.1.

Mechanical properties

Polyamide-imides posses excellent mechanical properties over a broad temperature range that are virtually unmatched. The polymer chemistry responsible for this performance is the fully aromatic backbone, which offers stiffness, high-temperature capability, and thermal and oxidative resistance. Further stiffening the polymer backbone is the imide linkage driving the glass transition temperature to 280°C in its cured state. The amide and ether linkages provide processability, ductility, and toughness.

The room temperature tensile strength of an unfilled polyamide-imide is greater than 25,000 psi. Mechanical properties of polyamide-imides are higher than those of other related high-performance polymer compounds, especially at elevated temperatures (Figs. 12.17 and 12.18). Their mechanical properties at 204°C are greater than those of other engineering polymers at room temperature. Because of this, glass- or carbon-fiber reinforced polyamide-imides are utilized in critical metal replacement parts and demanding applications. At low strain levels, polyamide-imides behave as hookean solids with a very high modulus. At high strain levels, polyamide-imides do not yield, but instead rupture or break.

TABLE 12.1 Polyamide-imide Properties for Compounded Materials

Typical properties*, SI units	ASTM test method	Units	4203L	4301	4275	4435	5030	7130
Mechanical								
Tensile strength	D1708	MPa						
23°C			192	164	131	110	205	203
135°C			117	113	116	90	160	158
232°C			66	73	56	52	113	108
Tensile elongation	D1708	%						
23°C			15	7	7	6	7	6
135°C			21	20	15	4	15	14
232°C			22	17	17	3	12	11
Tensile modulus	D1708	GPa						
23°C			4.9	6.6	7.8	9.7	10.8	22.3
Flexural strength	D790	MPa						
23°C			244	219	212	152	338	355
135°C			174	165	157	129	251	263
232°C			120	113	111	91	184	177
Flexural modulus	D790	GPa						
23°C			5.0	6.9	7.3	14.8	11.7	16.5
135°C			3.9	5.5	5.6	11.2	10.7	15.6
232°C			3.6	4.5	5.1	10.3	9.9	13.1
Compressive strength	D695	MPa	220	170	120	138	260	250
Compressive modulus	D695	GPa	4.0	5.3	4.0	8.5	7.9	9.9
Shear strength	D732	MPa						
23°C			128	112	77	60	140	120
Izod impact strength (3.2 mm)	D256	J/m						
Notched			142	63	84	43	79	47
Unnotched			1062	404	250	219	504	340
Poisson's ratio			0.45	0.39	0.39	0.42	0.43	0.39

(*Continued*)

TABLE 12.1 Polyamide-imide Properties for Compounded Materials *(Continued)*

Typical properties*, SI units	ASTM test method	Units	4203L	4301	4275	4435	5030	7130
			Thermal					
Deflection temperature at 1.82 MPa	D648	°C	278	279	280	278	282	282
Coefficient of linear thermal expansion	D696	ppm/°C	30.6	25.2	25.2	14.4	16.2	9.0
Thermal conductivity	C177	W/(m·K)	0.26	0.54	0.65	0.80	0.37	0.53
Flammability	UL-94		94 V-0	94 V-0	94 V-0	94 V-0	94 V-0	94 V-0
Underwriters' Laboratories limiting oxygen index	D2863	%	45	44	45		51	52
			Electrical					
Dielectric constant	D150							
10^3 Hz			4.2	6.0	7.3		4.4	
10^6 Hz			3.9	5.4	6.6		4.2	
Dissipation factor	D150							
10^3 Hz			0.026	0.037	0.059		0.022	
10^6 Hz			0.031	0.042	0.063		0.050	
Volume resistivity	D257	Ω·cm	2×10^{17}	8×10^{15}	8×10^{15}	2×10^{7}	2×10^{17}	
Surface resistivity	D257	Ω	5×10^{18}	8×10^{17}	4×10^{17}	6×10^{6}	1×10^{18}	
Dielectric strength (1 mm)	D149	kV/mm	23.6				32.6	
			General					
Density	D792	g/cm^3	1.42	1.46	1.51	1.59	1.61	1.48
Hardness, rockwell E	D785		86	72	70	62	94	94
Water absorption, 24 h	D570	%	0.33	0.28	0.33	0.12	0.24	0.26

*Typical properties—actual properties of individual batches will vary within specification limits.

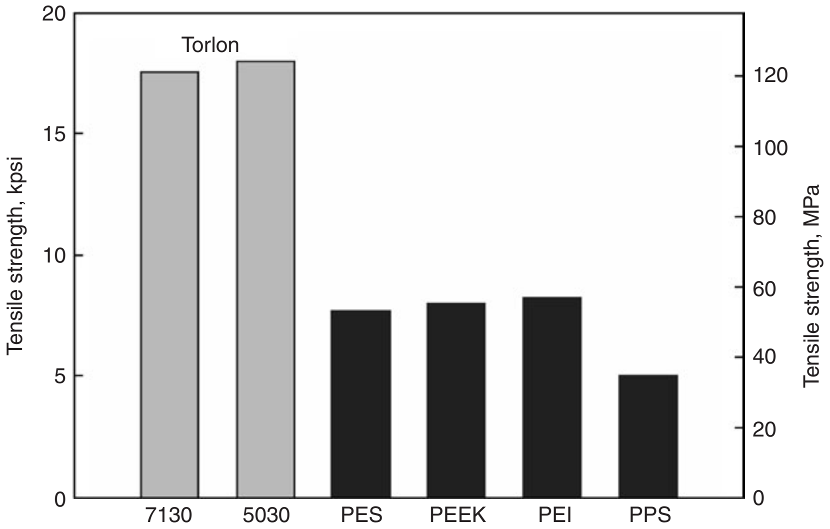


Figure 12.17 Tensile strengths of reinforced Torlon resins surpass competitive reinforced resins at 204 °C.

As noted before, polyamide-imide requires a thermal cure cycle to achieve its full properties. In its "green" or uncured state, polyamide-imide possesses significantly lower mechanical, chemical, and wear characteristics. During the cure cycle, molecular weight increases, the remaining amic acids cycle, and cross-linking reactions occur, rendering the polymer insoluble in solvents such as NMP and no longer melt-processable.

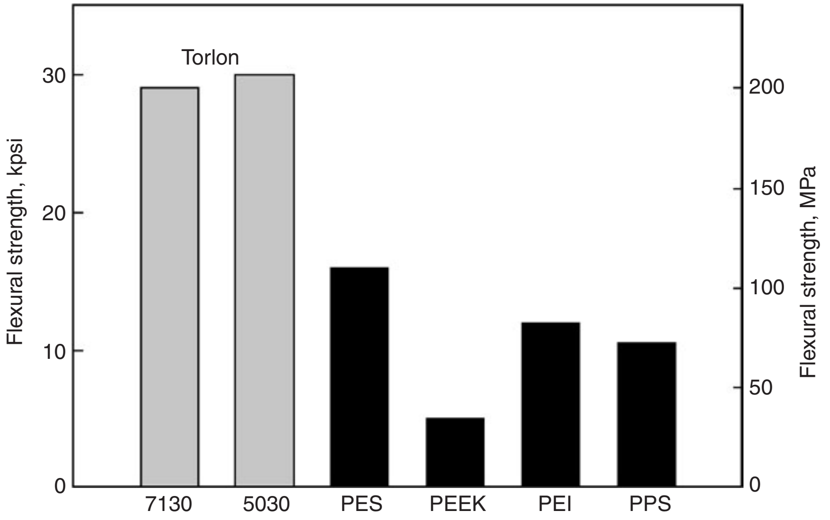


Figure 12.18 Flexural strengths of reinforced Torlon resins surpass competitive reinforced resins at 400°F (204°C).

Thermal stability

Polyamide-imides enjoy exceptional thermal stability with a decomposition onset at 500°C and 10% weight loss at 540°C. Long-term aging at high temperatures (250°C) shows only a 80 to 90% drop in tensile strength after 10,000 h (see Fig. 12.19). The UL *relative thermal index* (RTI) predicts 100,000 h of useful life at temperatures as high as 220°C.

Flammability

Polyamide-imides enjoy outstanding flame and fire resistance properties because of their inherent charring properties. Polyamide-imides are UL-94 certified V-0 at 1.2 mm. In FAA tests, both glass- and carbon-fiber filled polyamide-imides passed without igniting during vertical and horizontal flammability tests [24].

Chemical resistance

Polyamide-imides have a remarkable range of resistance against harsh chemicals. Polyamide-imides are virtually untouched by hydrocarbons, including the entire family of aromatic, aliphatic, chlorinated, and fluorinated solvents. Most acids have little effect on polyamide-imides. The material's weakness lies in its relatively poor resistance against strong bases such as concentrated hydroxides and strongly basic amines.

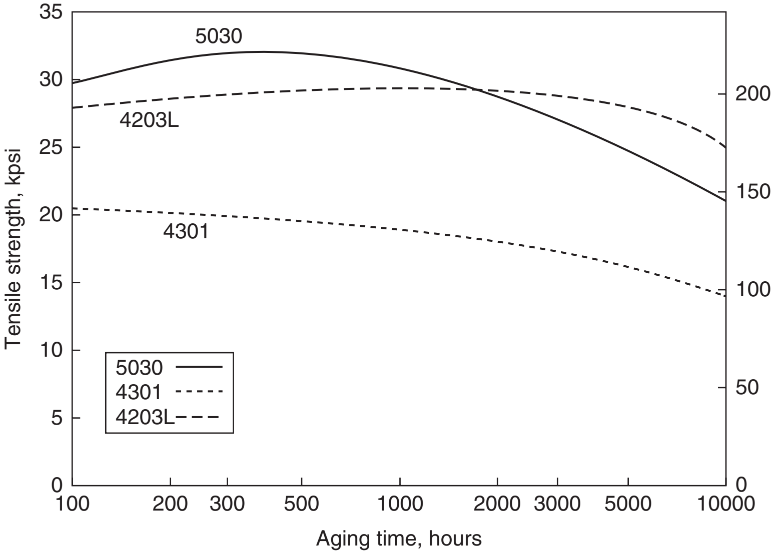


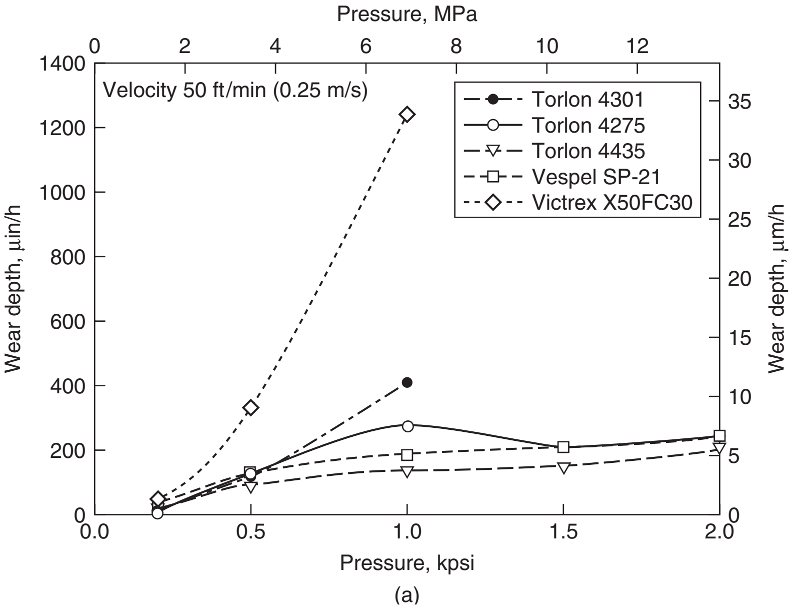
Figure 12.19 Torlon resins retain strength after thermal aging at 250°C.

Environmental resistance

Polyamide-imides possess very good environmental resistance to water, UV light, and radiation. Weather-Ometer tests, which exposed samples to cyclic light and water conditions, were performed on polyamide-imide bars for over 6000 h. Essentially no change in elongation or tensile strength was apparent. After a 1-Grad (10^9) dose of gamma radiation, polyamide-imide compounds show only a modest 5% drop in mechanical properties [25].

Wear properties

As seen from the preceding friction and wear applications, polyamide-imide compounds are a popular choice for these demanding applications. The graphs below (Fig. 12.20) show their performance against notable high-performance polymer families such as *polyetheretherketone* (PEEK) and polyimide. Having a high glass transition temperature approximately 130°C higher than PEEK, polyamide-imides enjoy a decided advantage. With their mechanical properties almost twice those of some polyimide compounds, polyamide-imide's combination of strength and thermal properties drives its accomplishment in this area.



(a)

Figure 12.20 (*a*) Wear resistance at low velocity; (*b*) wear resistance at high velocity.

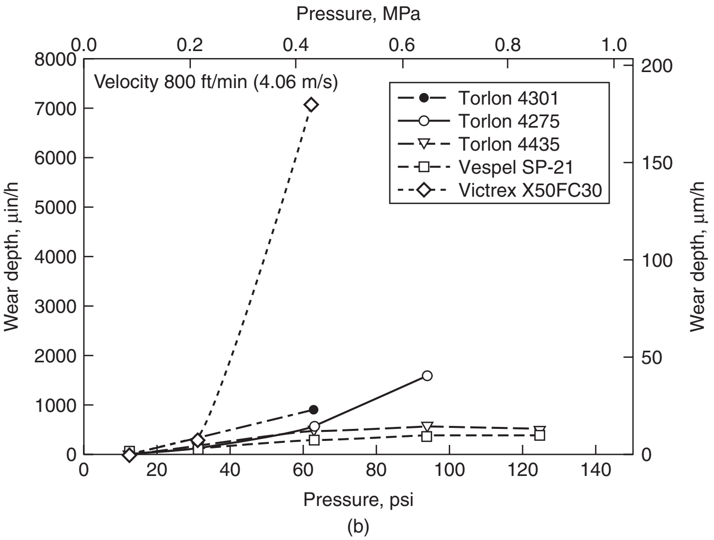


Figure 12.20 (*Continued*)

Processing

Adhesive and coating formulations

Most formulations for polyamide-imides start with a dipolar aprotic solvent such as NMP, DMAC, DMF, or DMSO and then diversify from there. To reduce the solution viscosity, diluents such as xylene and

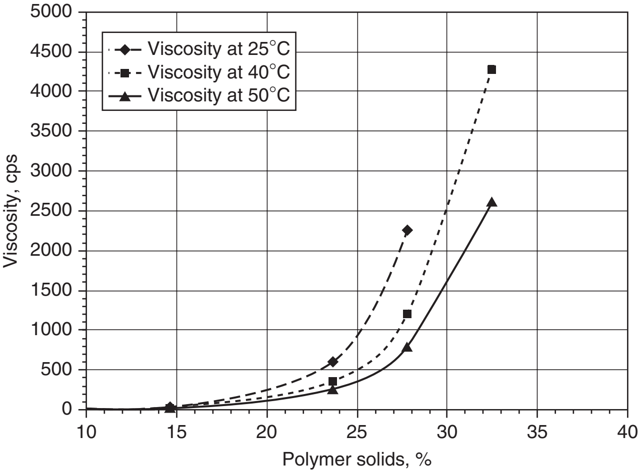


Figure 12.21 Al-10 solution viscosity in NMP.

TABLE 12.2 Diluents for PAI Polymer Solutions

Diluent	Percent of total solvent (maximum)
Aromatic hydrocarbons	40–50
Ethyl acetate	40–50
Acetone	60
Cyclohexanone	80

toluene are often employed. Because solution viscosity is such an important variable for formulators and applicators, different molecular weights of polyamide-imide powders are available. The starting solution viscosity will also depend on the percent polymer solids.

Torlon AI-10 polymer solutions

In Fig. 12.21, the solution viscosity is illustrated for Torlon AI-10 dissolved in NMP at various percent solids and measured at different temperatures. NMP is most commonly used due to its high solvency power, its low odor, and a relatively low level of toxicity. Diluents may be added up to the level provided in Table 12.2 to lower viscosity and formulation cost.

Alternatively, Torlon AI-10 powder may be formulated using a mixed organic aqueous system, where water is the major solvent component, as shown in Table 12.3 [26]. AI-10 is approximately 50% imidized along the polymer backbone. The remaining amic acid groups can form hydrophilic ammonium complexes, allowing a high portion of water in the formulation.

Alternatively, Torlon AI-30 and AI-50 are amenable to aqueous systems when formulated with a tertiary amine Table 12.4 [27]. Due to the very low degree of imidization compared to AI-10 or polyamide-imides produced in the isocyanate process, these polymers can form stable, low-viscosity solutions in water at low to moderate polymer solids. Generally the polymer solids are 5 to 15%, depending on the polyamide-imide used, and provide solutions with a viscosity in the range of 50 to 2000 cP.

Injection molding

By using standard injection-molding equipment and the right set points, polyamide-imide molding resins may be routinely processed. A short

TABLE 12.3 Torlon AI-10 in Mixed Organic Aqueous System

Torlon AI-10	15%
Water	50%
Diethylaminoethanol	4%
Triethylamine	2%
Furfuryl alcohol	18%
N-methylpyrrolidone	10%

TABLE 12.4 Aqueous Formulation of Torlon AI-30

AI-30	20 g
Dimethylaminoethanol	4 g
Water	76 g

reference guide is indicated in Table 12.5. It is critical to use modern injection-molding presses, which are the correct size. Torlon polyamide-imide compounds are still reactive, as evidenced by the need for an additional cure cycle. If the resin has excessive residence time in the hot equipment, the viscosity can increase, leading to flow problems, molding defects, and black specks. The shot size should conform to a minimum of 50% of the barrel size, but not to exceed 80%. The clamp tonnage should be a minimum of 6 tons/in^2 of the part area, while 12 tons/in^2 is recommended to improve dimensions at the part line.

As with any injection-molded polymer, mold design is critical to matching the characteristics of the polymer with desired part specifications. Due to the flow characteristics of polyamide-imides, the mold gates and vents need to be placed strategically, along with emphasis on smooth ejection. Steel selection is based on the length of the run, and mold plating is not necessary and is discouraged.

TABLE 12.5 Torlon Setup

	Torlon injection-molding setup table
Machine	Modern injection-molding press with microprocessor closed-loop controls
Shot size	50–80% of barrel capacity
Clamp tonnage	Minimum 6, recommend 12 tons/in^2 of projected part area
Screw design	1:1 to 1.5:1 compression, *L*/*D* of 18:1 to 24:1, smooth constant taper, no check ring
Tool design	Steel
Cavity	Prototype P-20 prehardened or S-7 (28–32 Rc) Production H-13 air-hardened (50–52 Rc)
Ejection	Smooth positive linear ejection with generous draft ($^1/_2$° to 1°) and polishing
Undercuts	These should be avoided due to brittle nature of polymer out of the mold. Movable in-mold features may be incorporated
	Shrinkage rates (molding and curing total)
Grade	Percent
4203L	0.60–0.85
4275	0.25–0.45
4301	0.35–0.60
4435	0.06–0.18
5030	0.1–0.15
7130	0.00–0.15

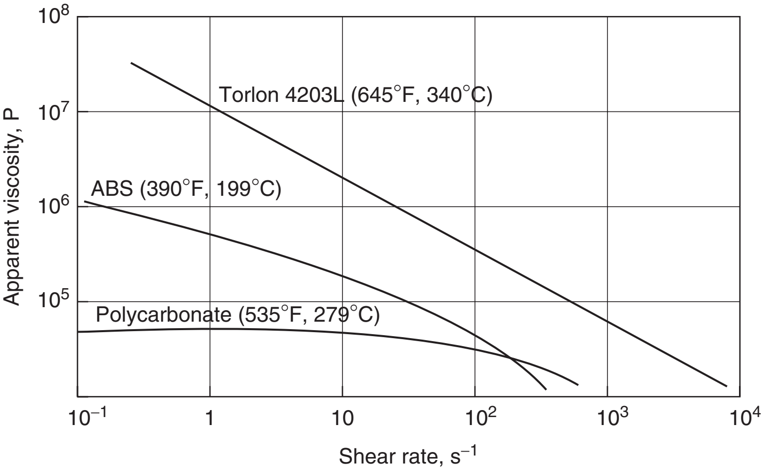


Figure 12.22 Apparent viscosity versus shear rate.

Polyamide-imides show typical shear thinning behavior. Due to the change in viscosity at different shear rates, it is important to injection-mold at proper speed and pressure. Figure 12.22 shows the viscosity–shear rate relationship between Torlon and other common polymers.

Thin wall sections and parts may require high injection speeds; however, care must be taken to avoid blistering at the gate, color change or degradation, splay or surface delamination, and gas burning at the knit lines or vents. High injection pressures are required to fill the entire mold; then during the hold period the pressure should drop from a high setting of 6 to 8 kpsi (41 to 55 MPa) for several seconds, to 3 to 5 kpsi (21 to 34 MPa) for the duration of the hold pressure sequence. This is intended to minimize or eliminate internal porosity or sink. Moderate backpressure, approximately 1 kpsi (6.9 MPa), and lower screw recovery speeds (50 to 100 rpm) are recommended in order to match the material's rheological behavior. The recommended barrel temperatures are shown in Table 12.6.

The total cycle time should be as short as possible, to reduce residence time in the barrel and mold. Excessive residence time will cause the polymer to increase in viscosity due to molecular weight growth, reducing flow. However, if the cycle time is too short, sprue breakage, sticking, warpage of the part, foaming, or blistering in thick sections may occur. Automatic operation is recommended to maintain a consistent cycle time. The recommended range for the surface temperature of the mold is 163 to 218°C. The mold should be insulated from the platen to minimize heat loss to the molding press.

TABLE 12.6 Recommended Barrel Temperatures*

Zone	Three-zone control	
	°F	°C
Feed	580	304
Middle	620	327
Front	650	343
Nozzle	700	371

*Actual temperature profile may vary depending on grade.

Compression molding

Polyamide-imide powders may be compression-molded into standard shapes and geometries. This operation produces parts that may be used as is or further machined into intricate parts. The mechanical properties of compression-molded parts are somewhat less than those of the corresponding injection-molded grades. The typical compression-molding operation uses a fine particle size of polyamide-imide powder. The powder material should have particles which are 100% less than 150 μm and 95% less than 75 μm. Polyamide-imide powders may also be used as an additive or adhesive binder in the sintering of other shapes based on PTFE powders, metal powders, or abrasive materials.

One example of the compression-molding process is outlined in Table 12.7 [28]. Polyamide-imide powder particles with a maximum particle size of 150 μm and a median particle size in the range of 10 to 50 μm are preheated in an oven for 1 to 24 h at 260 to 316°C. The purpose is to increase molecular weight and complete the imidization processes, both of which create water and can lead to voids in the compression-molded article. The compression-molding schedule depends on the size and geometry of the mold. A pressure-molding schedule for a 14.0 cm × 1.6 cm disk mold is shown in Table 12.8, where the mold temperature is set in the range of 315 to 329°C.

TABLE 12.7 Compression Molding Process

Step	Machine pressure, kN	Time, min	Part pressure, MPa
1	11.1	10	1.4
2	44.5	4	5.8
3	111.2	3	14.5
4	222.4	3	29.0
5	111.2	5	14.5

Cool to 260°C at 111.2 kN and then eject immediately.

TABLE 12.8 Polyimide-imide Cure Schedules

Coatings		
Torlon AI-10 (25 µm, 25% in NMP)		
Time, min	Temperature, °C	Temperature, °F
60	149	300
15	260	500
5	315	600
Molded parts		
Torlon injection-molded grades (4203L, 4301, 4275, 4435, 5030,7130) [29]	Parts with max. cross-sectional thickness of 0.3 in (7.6 mm)	
Days	Temperature, °C	Temperature, °F
1	149	300
1	191	375
1	204	400
1	218	425
1	232	450
1	243	470
1	252	485
10	260	500

Curing process

Polyamide-imide polymers require a thermal cure cycle to achieve maximum properties after they have been formed into the final article, whether it is a coating or injection-molded part. Polyamide-imides have relatively low molecular weight to facilitate melt processing or coating applications. The articles themselves, before cure, are actually weak, brittle, and poor in chemical and wear resistance, and they do not have optimum thermal resistance. The curing process involves heating the polyamide-imide material in a batch process such as a forced-air oven; or, in the case of coatings, they may cured in a continuous process due to the shorter time scale involved. The cure cycle is dependent on the thickness of the polyamide-imide article and its geometry. For parts the temperature cycle is ramped slowly upward to allow stress relaxation and diffusion of moisture, created in the curing reactions, out of the part. Different cure cycles may be required, depending on the application requirements.

During the curing process, the molecular weight of the polymer increases by chain extension, any remaining amic acids will imidize, and cross-links are created between the polymer chains. These reactions

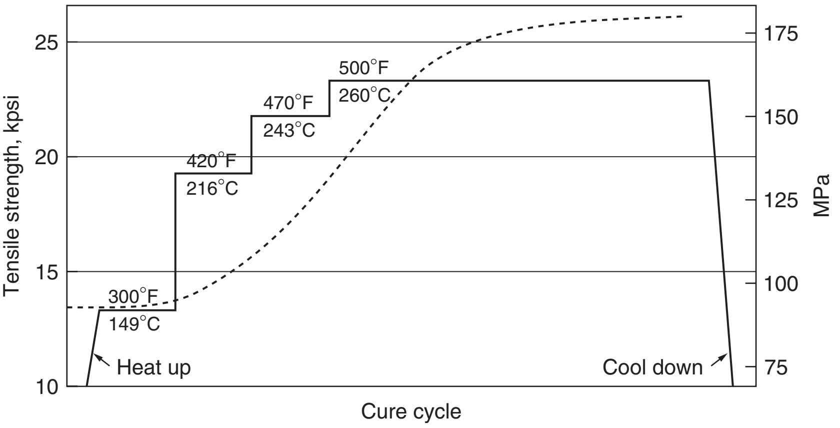


Figure 12.23 Cure versus tensile strength.

generate water, and its creation and diffusion during this cure process need to be managed to maintain dimensional stability and minimize void or blister formation. As these reactions occur, virtually all mechanical, chemical, and thermal properties are affected. Figures 12.23 through 12.25 show the changes that take place during the cure cycle. Strength and elongation in the part increase dramatically until the strength is approximately twice that of the uncured material. Uncured polyamide-imide is brittle, as shown in Fig. 12.25, but during cure the elongation goes from about 5% to about 15%, showing a tremendous increase in toughness.

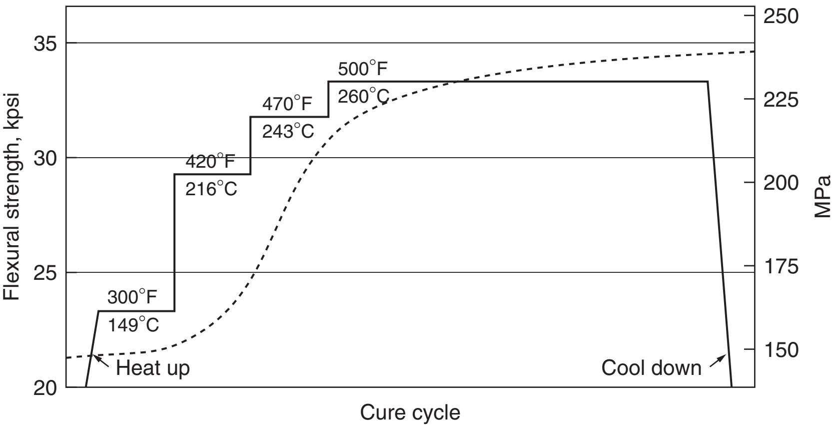


Figure 12.24 Cure versus flexural strength.

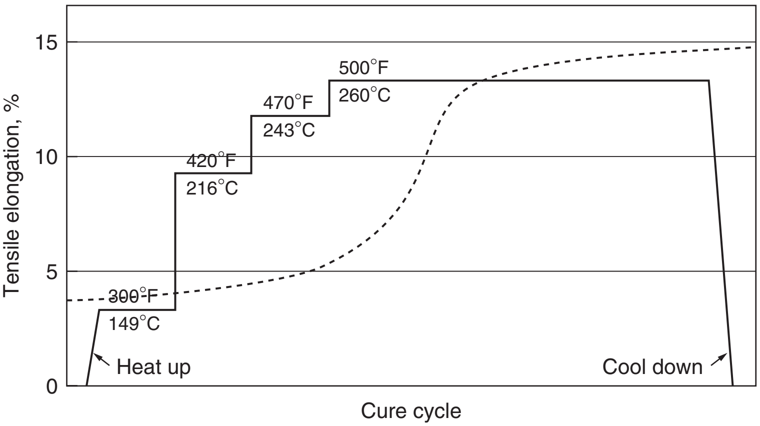


Figure 12.25 Cure versus elongation.

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Chapter 13

Polyarylethersulfones (PAES)

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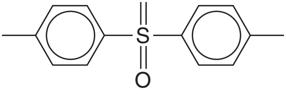
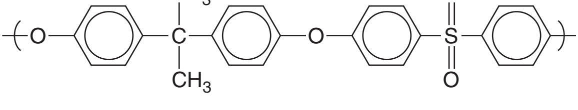
Overview

Polyarylethersulfones (PAES), also known as sulfone polymers or simply polysulfones, are a class of amorphous high-temperature, high-performance thermoplastic polymers. The polymers have an aromatic backbone structure comprised of phenyl rings, sulfone groups, and ether linkages, hence the name *polyarylethersulfones*. The *para*-linked diaryl sulfone moiety is the most distinguishing structural feature of a polyarylethersulfone:

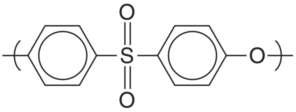


These polymers are a subclass of the larger family of engineering polymers known as polyarylethers that includes polyarylethersulfones, polyaryletherketones, and polyaryletherimides.

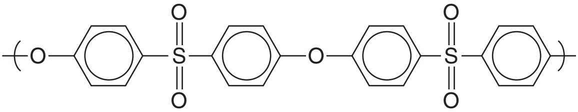
The first of the sulfone polymers was introduced commercially by Union Carbide Corp. in 1965 as Udel® Polysulfone, and it carries the following repeat unit structure:



It was produced by using the aromatic nucleophilic polycondensation reaction of bisphenol A with 4,4′-dichlorodiphenylsulfone, a process still used today by the commercial producers of this polymer. This polymer, known as *polysulfone* (PSF), has a glass transition temperature of about 185°C. It is the oldest and most widely utilized member of the family of sulfone polymers. Polysulfone and all the commercially available sulfone polymers are completely amorphous and transparent in their natural state. They have high glass transition temperatures T_g ranging from 185 to 265°C. The high heat resistance derived from the high T_g's, along with the high thermal oxidative resistance derived from the aromatic backbone structure, allows use of these polymers in demanding high-performance applications where high temperatures are encountered for long durations. In addition to the high-temperature capability, the sulfone polymers boast outstanding hydrolytic stability as another of their chief performance features. In the early 1980s, the second of the commercially important sulfone polymers, *polyethersulfone* (PES), was introduced by Imperial Chemical Industries in the United Kingdom. This polymer has the following repeat unit structure:



which is sometimes also depicted in the form



to reflect the polymer's chemical synthesis from the polycondensation of 4,4′-dichlorodiphenylsulfone and 4,4′-dihydroxydiphenylsulfone. This polymer extended the temperature capability of sulfone polymers by offering a glass transition temperature of 220°C.

In 1990, Amoco Performance Products, Inc., introduced an even higher-performance sulfone polymer derived from the condensation polymerization of 4,4′-dichlorodiphenylsulfone with 4,4′-dihydroxydiphenyl (also known as biphenol). This polymer, which came to be known as *polyphenylsulfone* (PPSF) and which was introduced commercially under the trade name Radel® R, has the following repeat unit structure:

It offered essentially the same 220°C T_g as that of PES but significantly superior performance attributes relative to both PSF and PES in terms of mechanical toughness, chemical resistance, and flammability resistance.

In 2005, Solvay Advanced Polymers, LLC, is in the early stages of commercial introduction of a next-generation sulfone polymer that extends the thermal capability even further. This new high-temperature sulfone polymer is being introduced as Supradel® HTS, and it offers a glass transition temperature of 265°C, the highest of any fully amorphous thermoplastic resin commercially available today. While it is a polyarylethersulfone in the general sense, the exact repeat unit structure of Supradel® HTS is not disclosed at this writing.

The commercial importance of sulfone polymers derives from their unique ability to offer a combination of performance features and attributes. Key among these performance features are the following:

1. High strength and stiffness even at elevated temperatures
2. High heat deflection temperatures and long-term use temperatures
3. Outstanding hydrolytic stability
4. Excellent resistance to acids and bases
5. Inherently good flammability resistance
6. Good dielectric properties over a broad temperature range
7. Good chemical resistance (relative to other amorphous plastics)
8. Transparency, low inherent color, and good colorability
9. Ease of melt fabrication
10. Ability to hold precise dimensional tolerances in injection molding
11. Safety for food and potable water contact

While many thermoplastics exist that offer high-temperature performance capability in some fashion, very few high-performance resins on the market offer the attributes listed above as a combination. In addition to the above list of features, PPSF offers supertoughness mechanical attributes, which include a high notched impact resistance on par with that of polycarbonate. There are four commercial producers of sulfone polymers today: BASF, Gharda Chemicals, Sumitomo Chemicals, and Solvay Advanced Polymers. The resin types offered by each of these suppliers along with trade names and some of the grade designations corresponding to the different resin types are listed in Table 13.1.

The rest of this chapter explores the synthesis processes of the sulfone polymers in general and discusses the property profiles of these polymers. The main areas of commercial applications of the sulfone polymers are also presented.

TABLE 13.1 Commercial Suppliers and Trade Names of Sulfone Polymers

Manufacturer	Resin type	Trade name	Selected grade designation
Solvay Advanced Polymers	PSF	Udel®	P-1700, P-3500, P-3700, P-3703
	PES	Radel® A	A-200, A-201, A-300, A-301, A-702, A-105
	PPSF	Radel® R	R-5000, R-5800, R-5500, R-5100
	HTS*	Supradel®	HTS-2600
BASF	PSF	Ultrason® S	S-1010, S-2010, S-3010, S-6010
	PES	Ultrason® E	E-1010, E-2010, E-3010, E-6010
Sumitomo Chemical	PES	Sumikaexcel®	3600, 4100, 4800, 5200, 5003
Gharda Chemical	PSF	Gatone® S	1200, 1300, 1400
	PES	Gatone®	3300, 3400, 3500, 3600
	PPSF	Gatone® P	4300, 4400, 4500

*HTS-2600 is a new ultrahigh-T_g sulfone polymer grade with a glass transition temperature of 265°C. The chemical structure of this polymer is not disclosed at this time.

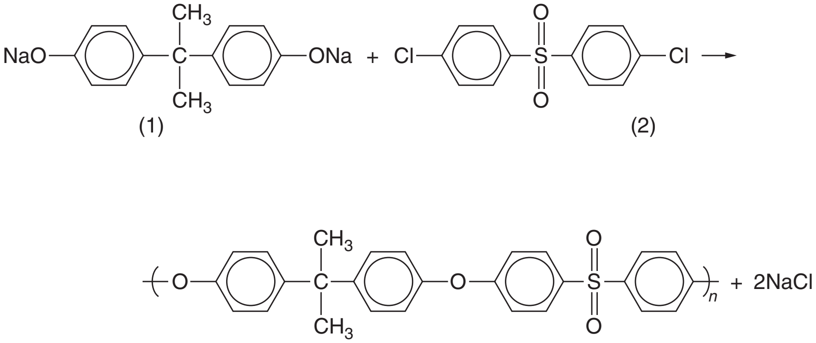
Synthesis Processes

Several polymerization routes can be employed for the synthesis of sulfone polymers. The synthesis route that is most practical and that is used almost exclusively today for the production of these polymers is the aromatic nucleophilic substitution polymerization route. This synthesis route involves the condensation polymerization of 4,4′-dihalodiphenylsulfone with a dihydroxy compound in the presence of a base to convert the phenolic hydroxyl group to a nucleophilic aromatic phenoxide group. The polymerization takes place in a dipolar aprotic solvent that will solvate all components of the reaction medium. This sulfone polymer chemistry was pioneered by Johnson and Farnham in the early 1960s [1, 2].

In the case of PSF, the aromatic nucleophilic displacement route involves a two-step process. In the first step, bisphenol A is converted to its dialkali salt analog by reacting bisphenol A with sodium hydroxide in a 1:2 stoichiometric ratio using *dimethylsulfoxide* (DMSO) as the reaction medium. A small amount of chlorobenzene is used in this step as part of the solvent system to distill off the water from the reaction medium, thereby maintaining anhydrous conditions.

The disodium salt of bisphenol A is next reacted with *dichlorodiphenylsulfone* (DCDPS) in the same DMSO medium, and again, a cosolvent such as chlorobenzene is utilized, both to enhance the solubility of the polymer in the reaction medium and to act as a distilling azeotropic agent for the water by-product of the polymerization. Keeping the polymerization medium anhydrous at all times is critical to the attainment of high polymer. Failure to do so can partially hydrolyze the DCDPS, forming 4-hydroxy-4′-chlorodiphenylsulfone, which biases the monomer stoichiometry from

1:1, thereby limiting the maximum attainable molecular weight. The PSF polymerization is carried out according to reaction 1 below

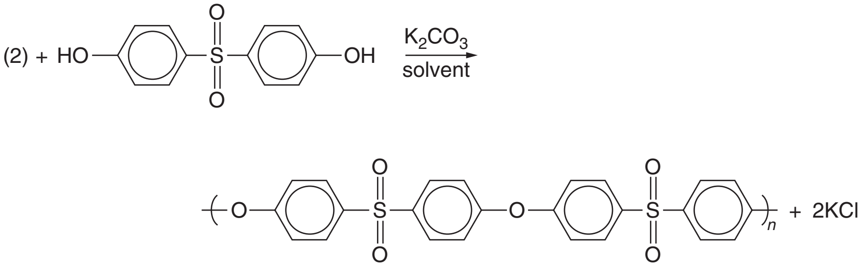


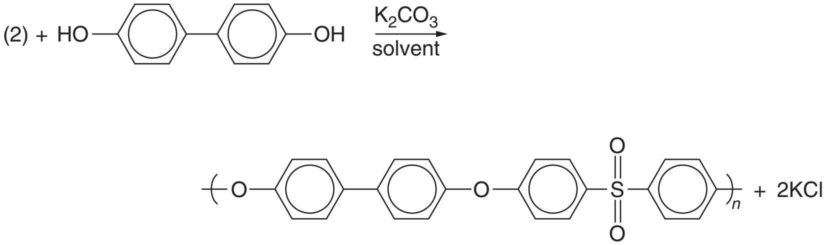
(1)

where the number of repeat units n is typically in the range of 40 to 60. The rate of the polymerization step is dependent on temperature. Typical temperatures to attain reasonable rates are in the range of 130 to 160°C. While the dichloride monomer is used in the commercial production of PSF, the 4,4′-difluorodiphenylsulfone can also be used as the starting sulfone monomer. The difluoride analog is actually more reactive, affording higher polymerization rates due to its stronger electron withdrawing character compared to the dichloride. However, the difluoride monomer is a far more expensive raw material than the dichloride, so the latter is the choice for commercial production. The difluoro analog is only used to produce sulfone polymers on a research scale due to its greater latitude in allowing high-molecular-weight polymer to be achieved. Another factor that contributes to the rate of the polymerization, as expected, is the purity of the monomers. The monomers should be of high purity in terms of being difunctional as well as having that functionality present in the 4 and 4′ positions. When the 3,4′-dichlorodiphenylsulfone is present in any significant concentration, it can effectively act as a monofunctional species, thereby arresting molecular-weight growth. This is so because of the poor electron withdrawing character (and hence poor reactivity) of the chlorine when in the *meta* position.

When the target PSF molecular weight is attained, the reaction medium is cooled by the addition of solvent to slow down the progress of the polymerization. A terminating agent such as chloromethane can then be injected into the reactor system to convert the active phenoxide groups to nonreactive methoxide. Alternatively, a monofunctional species such as a monohydroxy aromatic compound can be used to play the role of an end-capping agent. Excess dihalodiphenylsulfone monomer can also be used with similar effect to that of the monofunctional terminator. When the monofunctional or excess sulfone monomer is used as an end capper to achieve the target molecular weight, these reagents should be charged as part of the initial charge of reactants to the reactor system. The exact amounts of end-capping agent or excess DCDPS monomer can be calculated on the basis of Carothers' stoichiometric functionality equations that apply to an AA-BB type of condensation polymerization.

The polymerization of PES and PPSF proceeds in a similar manner to that of PSF, but unlike the two-step process described for PSF, the bisphenol S or the biphenol is now reacted directly with the DCDPS in the presence of a stoichiometric amount of base without the need for a separate first step to convert the bisphenol to its dialkali salt derivative. Another difference between the polymerizations of PES and PPSF as compared to the PSF synthesis process is the need for a higher-boiling-point solvent to handle the higher polymerization temperatures that are needed for these polymers. Suitable solvents for the production of PES and PPSF include NMP, dimethyl acetamide, diphenylsulfone, and sulfolane. A minor cosolvent such as chlorobenzene or toluene can again be used to help keep the reaction medium dehydrated. The most suitable base for use in PES and PPSF synthesis is potassium carbonate. Reactions 2 and 3 below depict the reaction scheme based on the use of potassium carbonate as base. Potassium chloride is produced as a by-product of the polymerization as a precipitate in the reaction medium. This salt precipitate can be removed from the reaction medium by using filtration or centrifugation to facilitate the recovery of the polymer in a pure state.





An alternative synthesis route for PES starts with the partial hydrolysis of DCDPS to form 4-hydroxy-4′-chlorodiphenylsulfone, followed by reacting this single difunctional polymer in the presence of potassium carbonate or potassium hydroxide to form PES [3]. While conceptually elegant, this route has not gained in commercial significance due to the complexity of the process and the inability to form the intermediate in sufficiently high yield and high purity to be of commercial viability.

Separation of the polymer from the solvent can be achieved by several means. Coagulation of the polymer by contacting the polymer solution with a nonsolvent can be used, followed by filtration, washing, and drying of the resin powder, which is subsequently melt-extruded through an extruder to form pellets. Another recovery method is the freeze-drying of the reaction medium, followed by extraction of the solvent from the polymer with a suitable low-boiling extraction solvent such as acetone. Both of these recovery schemes are amenable to commercial-scale production. Removal of the solvent by direct devolatilization in a vacuum-vented extruder is also possible, provided the solvent has good thermal stability and its boiling point is reasonably low.

The aromatic nucleophilic displacement chemistry described above is the most viable route for production of sulfone polymers on a commercial scale today. Other routes have been developed for the synthesis of sulfone polymers over the years, and these will be touched on briefly in this section for the sake of completeness.

A variation on the aromatic nucleophlic displacement chemistry described above employs the cuprous chloride catalyzed polycondensation of an aromatic dihydroxy compound with a divalent aromatic dibromo diaryl compound. This method has the advantage that the dibromo diaryl compound does not have to be activated by the sulfone group. This route can therefore be employed for copolymers and terpolymers that incorporate the sulfone moiety along with other non-sulfone-containing repeat units. This synthesis route is commonly known as the Ullmann synthesis [4].

One of the early and well-documented methods for producing polyarylethersulfones involves use of an electrophilic Friedel-Crafts polymerization process. First applied to PES, this synthesis route involved reacting bis(4-chlorosulfonylphenyl)ether in a 1:1 molar ratio with diphenylether [5–7]. Alternatively, a single-monomer Friedel-Crafts synthesis can be employed starting with 4-chlorosulfonyldiphenyl ether as the sole monomer. The Friedel-Crafts route to the production of sulfone polymers was used briefly on a commercial basis in the 1960s but was quickly abandoned due to a number of limitations. In addition to being operationally complex, this synthesis route yields polymers that are not always linear or *para*-linked.

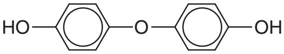
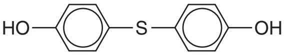
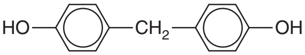
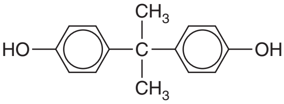
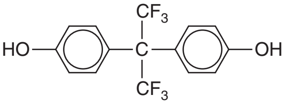
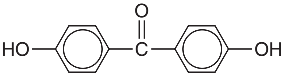
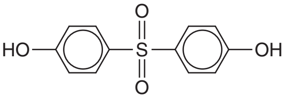
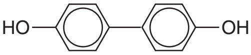
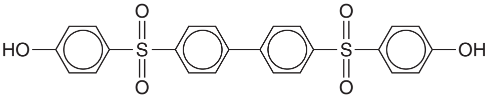
Nickel-catalyzed coupling of aromatic dihalides is a synthesis route that can be used to make sulfone polymers containing a phenyl-phenyl bond in their backbone, such as PPSF. This is a two-step synthesis that starts by forming an aromatic dichloride intermediate which carries the structural features desired in the polymer to be produced [8, 9]. Next this aromatic dichloride is self-reacted in the presence of Ni^0, triphenylphosphine, and zinc to form the polymer which contains biphenyl or terphenyl units as part of the backbone repeat unit [10, 11]. This synthesis method is documented in the literature as applied to the synthesis of PPSF.

Oxidative coupling of aromatic compounds via the Scholl reaction has been successfully applied to the synthesis of a polyarylethersulfone [12]. High-molecular-weight polymer was obtained by treating 4,4′-di(1-napthoxy)diphenylsulfone and 4,4′-di(napthoxy)benzophenone with ferric chloride. Equimolar amounts of the Lewis acid were used to effect the polymerization. This synthesis route is limited in scope and utility as it is only applicable to naphthoxy-based monomers and other systems that can undergo the Scholl reaction.

Properties

The three sulfone polymers that are most commonly used in commercial applications have several structural commonalities that account for the unique attributes of this family of resins. The key feature common to all three sulfone polymers is the resonant diaryl sulfone group. Because the sulfur is in its highest state of oxidation, the sulfone group is in the *para* position, and due to the high bond dissociation energies of the aromatic backbone, these polymers exhibit outstanding thermal stability and resistance to oxidation. This feature can be realized both during melt processing and in high-temperature end-use environments. Sulfone polymers can be melt-processed at temperatures up to 400°C without any significant degradation. They can be used in environments anywhere between 150 and 190°C continuously for extended periods. The ether linkage that is common to the sulfone polymers imparts chain flexibility, which allows for mechanical toughness and attractive melt rheological properties for thermoplastic fabrication. The chemical stability of the aromatic ether linkage and sulfone moieties contributes to the resistance to hydrolysis and chemical attack by acids and bases. Such behavior has allowed for the success of sulfone polymers in numerous medical and food service applications. The aromatic nature of the polymer backbones offers high strength and stiffness along with good ductility even at elevated use temperatures. Although the sulfone resins offer many common properties, they are quite different due to the variety of bisphenols that can be used to synthesize them. One particular change that can be made is in the glass transition of the material. A list of bisphenols and the T_g's of resulting polymers is shown in Table 13.2. The backbone structure of a polysulfone is very closely tied to its physical properties [13].

TABLE 13.2 Glass Transition Temperatures T_g of Polysulfones Produced from the Polycondensation of 4,4′-Dichlorodiphenylsulfone with Various Bisphenols*

Bisphenol	Structure	T_g, °C†
4,4′-Dihydroxydiphenyl oxide		170
4,4′-Dihydroxydiphenyl sulfide		175
4,4′-Dihydroxydiphenyl methane		180
2,2′-Bis(hydroxyphenyl)-propane		185
Hydroquinone		200
2,2′-Bis(hydroxyphenyl)-perfluoropropane		205
4,4′-Dihydroxydiphenyl phenone		205
4,4′-Dihydroxydiphenyl sulfone		220
4,4′-Dihydroxydiphenyl		220
1,4-Bis(4-hydroxyphenyl) benzene		250
4,4′-Bis(4″-hydroxybenzenesulfonyl) diphenyl		265

*Kwiatkowski et al. [11].

†Glass transition temperatures reported to nearest 5°C.

Physical properties

Because of the amorphous nature of polysulfones, they exhibit optical transparency. Even though they are transparent, they show a slight yellow-amber tint. This color is due to the high temperatures required for melt processing during both manufacturing and finished-article fabrication. PSF offers the lowest color and highest transmittance of visible light. The optical properties of all three commercially available polysulfones are given in Table 13.3 and are representative of resins in color ranges that are typical for commercially available grades. A great

TABLE 13.3 Physical and Thermal Properties of Polysulfone (PSF), Polyethersulfone (PES), and Polyphenylsulfone (PPSF)

Property	ASTM test method	PSF	PES	PPSF
Color		Light yellow	Light amber	Light amber
Clarity		Transparent	Transparent	Transparent
Haze,[a] %	D-1004	<7	<7	<7
Light transmittance,[b] %		80	70	70
Refractive index	D-1505	1.63	1.65	1.67
Density, g/cm^3	D-1505	1.24	1.37	1.29
Glass transition temperature,[c] °C		185	220	220
Heat deflection temperature,[d] °C	D-648	174	204	207
Continuous-service temperature,[e] °C		160	180	180
Coefficient of linear thermal expansion	D-696	5.1×10^{-5}	5.5×10^{-5}	5.5×10^{-5}
Specific heat at 23°C, J/(g·K)		1.00	1.12	1.17
Thermal conductivity, W/(m·K)	C-177	0.26	0.18	0.35
Water absorption, %				
In 24 h	D-570	0.22	0.61	0.37
At equilibrium	D-570	0.62	2.1	1.1
Mold shrinkage, cm/cm	D-955	0.005	0.006	0.006
Temperature at 10% TGA wt. loss[f]				
In nitrogen		512	547	550
In air		507	515	541

[a] As measured on 3.1-mm-thick specimens.

[b] Typical values—varies with color.

[c] Onset value as measured by differential scanning calorimetry.

[d] As measured on 3.1-mm-thick ASTM specimens under a load of 1.82 MPa.

[e] Practical maximum long-term use temperatures for PSF and PES based on UL-746 thermal rating data; value for PPSF is an *estimate*.

[f] Thermogravimetric analysis run at heating rate of 10°C/min and 20 mL/min gas (nitrogen or air) flow rate.

deal of progress has been made over the years toward minimizing the yellowness of the resins. As a result, the appearance of PSF is fast approaching the water-white character of polycarbonate. Another feature of the sulfone polymers is their high refractive index, which derives from the highly aromatic nature of the backbone. The refractive indices are substantially higher than those of other amorphous materials made from olefinic or other aliphatic backbones. The refractive indices of PSF, PES, and PPSF increase in the order PSF < PES < PPSF, following the order of increasing aromaticity in the polymer backbone. The high refractive index feature is of interest to some optical and optoelectronic lens applications as it allows higher light-bending power for a given lens curvature or thickness.

The amorphous character of polysulfones also contributes to minimal and isotropic shrinkages upon cooling during and after melt fabrication.

It also results in dimensional stability over the service life of a finished part that may be used in a variety of thermal environments. This excellent dimensional stability makes polysulfones an excellent choice for many structural, engineering, and particularly electronic applications.

One illustration of the variation of properties with backbone structure is that of moisture absorption. Because of the sulfone moiety, polysulfones are slightly hygroscopic. PES contains roughly twice the content of sulfone groups in its backbone relative to PSF and PPSF. Additionally, because PSF is synthesized from bisphenol A, it contains the hydrophobic isopropylidene unit. As a result, PES is the most hygroscopic of the three polysulfones while PSF is the least hygroscopic, as can be seen in Table 13.3. Minimizing the moisture absorption in a plastic material is generally desirable. One reason is that absorbed water expands the linear dimensions of polysulfones by about 0.010 to 0.012% for every 0.1 wt% of moisture absorbed. This change is quite small, but could be important in application designs where extremely tight tolerances on dimensions are required. Absorbed moisture can also slightly plasticize the resin, which can cause some lowering of the stiffness and strength if the plastic is in a hot and wet environment. This effect is also small and can be compensated for by part design considerations.

Mechanical properties

Polysulfones are rigid and tough with excellent strength and stiffness properties without reinforcement. Their strength and stiffness are quite high relative to those of amorphous plastics that contain aliphatic backbone structures. In addition, polysulfones are ductile and yield in a ductile fashion even at high deformation rates.

As with any other polymer family, the deformation mechanisms and resulting mechanical properties are closely tied to the subtle differences in backbone structure [13]. Polysulfones contain aryl groups that are connected in a linear (unbranched) and *para*-linked fashion. This arrangement imparts good strength and toughness as well as favorable processing attributes. Although all three polysulfones offer good toughness, PPSF offers superior toughness and impact resistance relative to PES and PSF. The ductility of polysulfones is tied to a second-order (β) transition that is observed in polysulfones under dynamic mechanical thermal analysis. The β transition occurs at around –100°C and is believed to be due to two mechanisms. The first involves 180° flips of aromatic units around the ether bond [14]. It is hypothesized that the second is a concerted motion of the sulfone group with complexed absorbed water [15]. The presence of water increases the magnitude of the β transition peak although the peak still exists in the absence of water. The effect of polysulfone backbone structure on the sub-T_g relaxations or second-order transitions has been discussed in detail [16].

TABLE 13.4 Typical Room Temperature Mechanical Properties of Polysulfone, Polyethersulfone, and Polyphenylsulfone

Property	ASTM test method	PSF	PES	PPSF
Tensile[a] (yield) strength, MPa[b]	D-638	70.3	83.0	70.0
Tensile modulus, GPa[c]	D-638	2.48	2.60	2.30
Elongation at yield, %	D-638	5.7	6.5	7.2
Elongation at break, %	D-638	75	40	90
Flexural strength, MPa	D-790	106	111	105
Flexural modulus, GPa	D-790	2.69	2.90	2.40
Compressive strength, MPa	D-695	96	100	99
Compressive modulus, GPa	D-695	2.58	2.68	1.73
Shear (yield) strength, MPa	D-732	41.4	50	62
Notched Izod impact, J/m[d]	D-256	69	85	694
Unnotched Izod impact	D-256	NB[e]	NB	NB
Tensile impact, (kJ/m^2)[f]	D-182	420	340	400
Poisson ratio, at 0.5% strain	—	0.37	0.39	0.42
Rockwell hardness	D-785	M69	M88	M86
Abrasion resistance,[g] mg/1000 cycles	D-1044	20	19	20

[a] Tensile, flexural, and impact properties based on 3.1-mm-thick ASTM specimens.
[b] To convert MPa to psi, multiply by 145.
[c] To convert GPa to psi, multiply by 145,000.
[d] To convert J/m to ft·lbf/in, divide by 53.38.
[e] No break.
[f] To convert kJ/m^2 to ft·lbf/in^2, divide by 2.10.
[g] Taber abrasion test using CS-17 wheel and 1000-g load for 1000 cycles.

NOTE: These and other properties reported throughout, as well as the summary of possible applications for these resins, are based on the best available information. Inclusion of the information is not intended to be taken as a recommendation for a particular use or as an endorsement of any particular material.

The room temperature mechanical properties of bisphenol-A, bisphenol-S, and biphenol-based polysulfones are given in Table 13.4. The tensile and flexural properties of these three polymers are fairly comparable with some subtle exceptions. Because PES is a more rigid molecule, the polymer exhibits higher strength and stiffness than do PSF and PPSF. The yield elongation for PPSF is higher than that of PES or PSF. One of the unique features of PPSF is its "supertough" behavior, which is exhibited by a high notched Izod impact strength. In addition, it is able to maintain much of this ductility, which assists with effective impact energy absorption and dissipation after exposure to prolonged heat and moisture.

The tensile and flexural properties can be enhanced by the addition of common fibrous reinforcing fillers such as chopped glass fiber or carbon fiber. Although these fillers offer an increase in strength and stiffness, such improvements can come with a reduction in impact resistance. Fortunately, glass-fiber-reinforced polysulfones still offer practical toughness. The ambient temperature mechanical properties for reinforced PSF, PES, and PPSF are presented in Table 13.5.

TABLE 13.5 Typical Physical and Mechanical Properties of Glass-Fiber-Reinforced (GR) Polysulfone, Polyethersulfone, and Polyphenylsulfone

		PSF			PES			PPSF
Property	ASTM-test method	10% GR	20% GR	30% GR	10% GR	20% GR	30% GR	30% GR
Tensile strength, Mpa[*]	D-638	77.9	96.5	108	86	105	126	120
Tensile modulus, GPa[†]	D-638	3.65	5.17	7.38	3.8	5.7	8.6	9.2
Tensile elongation, %	D-638	4.1	3.2	2.0	5.8	3.2	1.9	2.4
Flexural strength, MPa	D-790	128	148	154	145	162	179	173
Flexural modulus, GPa	D-790	3.79	5.52	7.58	4.1	5.2	8.1	8.0
Izod impact, J/m[‡]	D-256	64	69	74	48	59	75	75
Tensile impact, kJ/m^2[§]	D-1822	101	114	109	59	65	71	83
Heat deflection temp., °C	D-648	179	180	181	211	214	216	210
CLTE, mm/(mm·°C)	D-696	3.6	2.5	2.0	3.6	3.1	3.1	—
Specific gravity	D-1505	1.33	1.40	1.49	1.43	1.51	1.58	1.53
Mold shrinkage, mm/mm	D-955	0.004	0.003	0.002	0.005	0.004	0.003	0.003

[*] To convert MPa to psi, multiply by 145.
[†] To convert GPa to psi, multiply by 145,000.
[‡] To convert J/m to ft·lbf/in, divide by 53.38.
[§] To convert kJ/m^2 to ft·lbf/in^2, divide by 2.10.

The data mentioned previously in Table 13.4 give short-term mechanical properties under very simple loading conditions. These values are typical of commercially available PSF, PES, and PPSF of practical molecular weight. When one is considering a polymer for a particular end-use application, it is very important to also consider other service life factors such as creep and fatigue properties as well as temperature and other environmental factors.

Thermal properties

As mentioned previously, polysulfones offer excellent thermal stability and resistance to oxidation during manufacture and melt processing as well as in the end use. Polysulfones can be melt-processed at temperatures up to 400°C. Their excellent thermal stability is evidenced by their behavior during *thermogravimetric analysis* (TGA) in air. Figure 13.1 shows that all three commercial polysulfones must approach temperatures of 500°C prior to the occurrence of significant weight loss. Polysulfones are therefore very forgiving during melt processing. Outstanding thermal stability also allows for polysulfones to be used in a number of thermally aggressive environments such as those found in medical sterilization, food service, and electronics. The glass transition temperature of polysulfones produced via nucleophilic polycondensation can be tailored by the choice of the bisphenol, as shown in Table 13.2. The high glass transition temperature T_g is attributed to the rigid phenyl rings in the backbone.

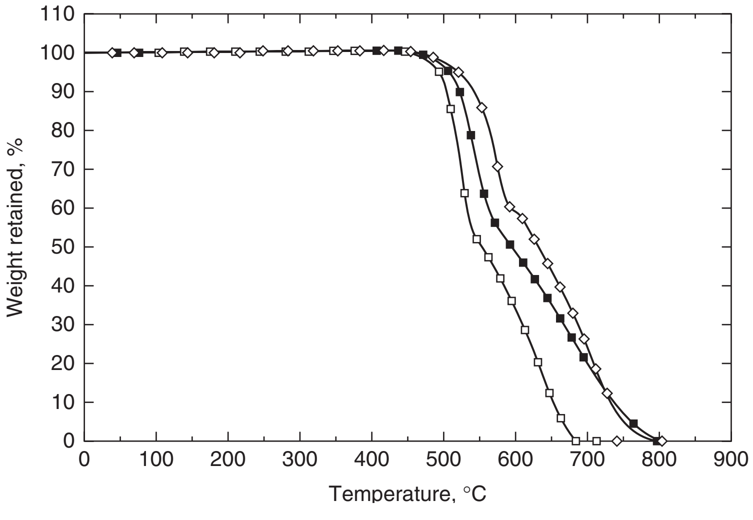


Figure 13.1 Thermogravimetric analysis curves in air for (□) PSF, (■) PES, and (◇)PPSF. TGA in nitrogen is at a heating rate of 10°C/min [17].

It is also attributed to the sulfone group. The strong dipole interactions and restricted rotation of the aromatic units relative to the other groups contribute to the rigidity of the molecule. Other connecting groups can result in either an increase or a decrease in the rigidity of the polymer chain and T_g, depending on the polarity and the conformational freedom imparted by those groups.

In addition to offering resistance to degradation at high temperatures, polysulfones maintain their mechanical properties at high temperatures without reinforcement. The effect of temperature on PSF tensile stress-strain behavior is shown in Fig. 13.2. It can be seen that the retention of useful properties extends to approximately 150°C for PSF. This useful temperature range approaches 180°C for PES and PPSF.

Flammability properties

Polysulfones exhibit excellent inherent flame resistance, which is critical in many end-use designs. The inherent burning resistance exceeds that of many engineering polymers. Due to the wholly aromatic nature of PES and PPSF, they exhibit outstanding flame retardance and they release very little heat and smoke during combustion. Flammability properties of PSF, PES, and PPSF are shown in Table 13.6. The flammability of all three sulfone polymers can be even further enhanced through the use of nonhalogen flame retardants. Such flame retardant–enhanced grades are available commercially.

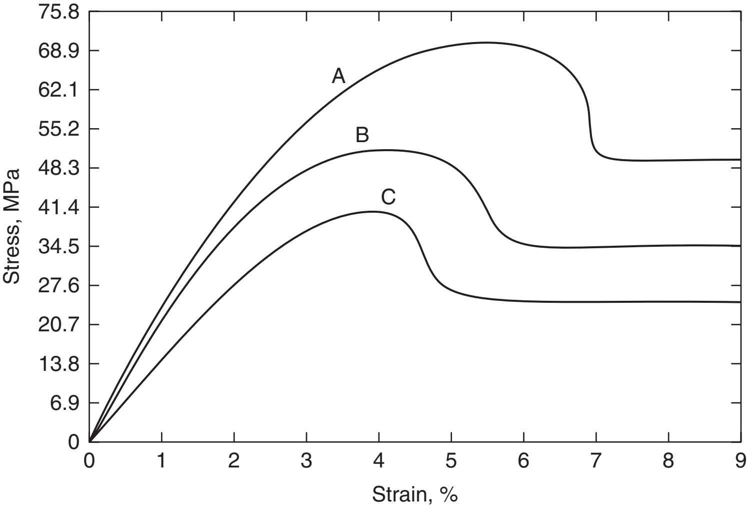


Figure 13.2 Tensile stress-strain curves for polysulfone showing yield behavior at (A) 20°C, (B) 99°C, and (C) 149°C. To convert MPa to psi, multiply by 145.

TABLE 13.6 Flammability and Burning Behavior of Polysulfone, Polyethersulfone, and Polyphenylsulfone

Property	Test method	PSF	PES	PPSF
Flammability rating	UL-94	V-0 at 6.1 mm	V-0 at 0.8 mm	V-0 at 0.8 mm
Limiting oxygen index	ASTM D-286	30.0	38.0	38.0
Smoke density*	ASTM E-662	90 at 1.5 mm	35 at 6.2 mm	30 at 6.2 mm†
Self-ignition temperature, °C	ASTM D-1929	621	502	—

*Specific optical density D_m at flaming condition.
†Thickness.

Electrical properties

Polysulfones exhibit excellent dielectric properties. They exhibit high dielectric breakdown strength and low dielectric constant. They also exhibit low dielectric loss. Because they are amorphous, the electrical properties such as dielectric constant and dissipation factor are stable across a wide temperature range. They are also stable over a wide frequency range. The desirable electrical properties in concert with attractive flammability properties have made polysulfones successful in many electrical and electronic insulation, business machine, and lighting applications. Polysulfone electrical properties can be found in Table 13.7.

Resistance to chemical environments

In general, amorphous plastics are susceptible to cracking by particular chemical environments when under stress. This behavior is called

TABLE 13.7 Electrical Properties of Polysulfone, Polyethersulfone, and Polyphenylsulfone

Property	ASTM test method	PSF	PES	PPSF
Dielectric strength, 3.2 mm,* kV/mm	D-149	16.6	15.5	14.6
Volume resistivity, Ω·cm	D-257	7×10^{16}	9×10^{16}	9×10^{15}
Dielectric constant at	D-150			
60 Hz		3.18	3.65	3.44
10^3 Hz		3.17	3.65	3.45
10^6 Hz		3.19	3.52	3.45
Dissipation factor at	D-150			
60 Hz		0.0008	0.0019	0.0006
10^3 Hz		0.0008	0.0023	—
10^6 Hz		0.0051	0.0048	0.0076

*Thickness.

environmental stress cracking, and the ability to withstand various environments is called *environmental stress crack resistance* (ESCR). The amount of susceptibility that a plastic exhibits to an environment depends on three important factors: temperature, amount of applied stress, and the concentration of the chemically aggressive medium. Because polysulfones are amorphous, they are vulnerable to some organic environments. This is due to greater ease of diffusion of aggressive solvents into the polymer, which in turn disrupts the electrostatic and dipole forces between the chain segments and facilitates chain disentanglement under applied stress. The potency of a stress cracking agent is related to the match between the solubility parameter of the solvent and that of the polymer. For example, PSF, which has a solubility parameter of $\delta = 21.8\ (\text{J/cm}^3)^{1/2}$, resists aliphatic hydrocarbons of lower δ and most alcohols of higher δ, but readily undergoes stress cracking by ketones that have δ values close to that of the polymer. For polysulfones, the most problematic solvents are aromatics, chlorinated hydrocarbons, ketones, and esters. The resistance of the commercially available polysulfones generally improves in the order PSF < PES < PPSF, as shown in Table 13.8.

The exact mechanism of environmental stress cracking is not fully understood, but it involves a weakening of secondary bonds between neighboring polymer chains due to solubility and diffusion of a chemical

TABLE 13.8 Resistance* of Natural (Unreinforced) Polysulfone, Polyethersulfone, and Polyphenylsulfone Resins to Various Chemical Environments[†]

	Ranking[‡]		
Environment	PSF	PES	PPSF
Aliphatic hydrocarbons	G	E	E
Aromatic hydrocarbons	P	P	F
Alcohols and glycols	G	E	E
Esters	P	P	F/P
Ketones	P	P	P
Chlorinated hydrocarbons	P	P	P
Aliphatic amines	E	E	E
Aromatic amines	P	P	F
Electrolyte solutions	E	E	E
Acids[§]	E	E	E
Bases	E	E	E
Ionic surfactants	E	E	E
Nonionic surfactants	F	G	G

[*] The above data are for comparative purposes only; actual resistance depends on many factors including stress, temperature, concentration, and exposure duration.

[†] Stress cracking resistance is substantially enhanced in the presence of reinforcement such as glass fibers.

[‡] Ranking codes: E = excellent; G = good; F = fair; P = poor.

[§] Nonoxidizing.

into the polymer. This behavior causes small crazes in the surface of the polymer. If many crazes are formed, then the stress within the polymer is reduced and cracking is prevented or delayed. If only a small number of crazes form upon exposure to an aggressive solvent, they grow and propagate into large cracks that can cause catastrophic failure of a finished article.

It is possible to improve the ESCR of polysulfones through the use of glass-fiber reinforcement or other fibrous reinforcement such as carbon fiber. This approach is quite successful as long as the solvent in question does not aggressively swell or dissolve the polymer.

In contrast to their response to some organic environments, polysulfones offer outstanding resistance to hydrolysis by hot aqueous environments such as boiling water. Resistance is also excellent toward mineral acids and alkalies, and salt solutions. This capability is often a key reason behind the selection of polysulfones over other engineering polymers such as polycarbonates, polyesters, polyamides, and polyetherimides [17].

Solubility

An understanding of the solubility of polysulfones is important for applications in which the polymer must be dissolved, such as in coatings and membrane applications. Solubility of the three commercial polysulfones follows the order PSF > PES > PPSF. All three polysulfones can be dissolved in a small number of highly polar solvents to form stable solutions at room temperature. NMP, DMAc, pyridine, and aniline are suitable solvents for polysulfones. Also 1,1,2-trichlorethane and 1,1,2,2-tetrachloroethane are suitable but are unattractive for health reasons. Because of the lower solubility parameter of PSF, it can also be dissolved in several less polar solvents such as *tetrahydrofuran* (THF), 1,4-dioxane, chloroform, dichloromethane, and chlorobenzene. Solvent choices for PES and PPSF are fewer because these polymers have a propensity to undergo solvent-induced crystallization in many solvents.

Radiation resistance

Polysulfones are resistant to many forms of electromagnetic radiation frequencies including microwave, visible, and infrared. They also show good resistance to X-rays, electron beams [18], and gamma rays [19, 20] under practical application conditions. Polysulfones have demonstrated an excellent fit in the area of microwave cookware due to microwave transparency and hydrolytic stability.

Polysulfones exhibit poor resistance to ultraviolet (UV) light, as do most aromatic polymers. The resins absorb heavily in the UV region, which causes degradation of the polymer chains on and directly beneath the surface of an exposed article. After brief exposure, discoloration occurs, and losses in mechanical properties can be realized after prolonged exposure. For this reason, extended exposure to sunlight is not recommended for neat polysulfones. The color shift exhibited by PPSF upon UV light exposure is greater than that of PES or PSF, but the retention of mechnical properties is greater for it, especially if the resin is pigmented to achieve an opaque composition. The higher tolerance to UV light found in PPSF is believed to be attributable to the inherently more ductile nature of PPSF relative to PES and PSF. Retention of mechanical integrity after UV light exposure can be improved substantially through the use of pigmentation and/or reinforcement. Black glass-reinforced formulations are UV-resistant. High loadings of carbon black can offer almost full protection of mechanical properties in unreinforced sulfone resins. Painting can also be used to achieve this end.

Applications

Sulfone-based polymers offer a number of features that make them attractive for a wide variety of applications. Several attributes of interest include excellent thermal stability, toughness, resistance to hydrolysis, inherent flame retardance, and clarity. PSF, PES, and PPSF exhibit many similar characteristics and therefore can be used interchangeably in a number of applications. In such cases, PSF is most commonly used due to its lower cost. There are applications that take advantage of the higher thermal performance or chemical resistance of PES. In addition, many applications are made possible by the excellent hydrolytic stability, chemical resistance, flame resistance, and supertough behavior of PPSF. Several application areas are described in some detail below.

Food service and food processing

The hydrolytic stability and heat resistance of PSF and PES make them suitable for use in a number of consumer and commercial food service items. Hydrolytic stability allows for repeated cleaning in dishwashers and for resistance to loss in properties due to the continual exposure to the hot liquids in foods. Heat resistance allows for containers to be used both for refrigerator storage and for microwave cooking and, in some cases, oven baking. Also, the sulfone resins in their natural state are very clean and safe from the standpoint of food contact. Many PSF, PES, and PPSF grades are available that are compliant with the U.S. Food and Drug Administration (FDA) requirements for repeated food contact. PES is used in baby bottles, where it offers the ability to endure repeated cleaning and sterilization without a loss in toughness. PES is also used as an adhesive binder in nonstick cookware coatings. PSF is used widely in coffee carafes, as shown in Fig. 13.3, and decanters for use with commercial

Figure 13.3 This coffee delivery system illustrates the use of polysulfone in food service applications.

coffee machines, where it can withstand exposure to hot coffee without staining and can be repeatedly cleaned. In addition, food service containers that must hold hot foods can be made from PSF. PSF offers unique attributes to milking equipment components. Not only is it less costly to mold PSF components than to machine metal components, but also these pieces can be repeatedly sterilized and are transparent. PPSF is used in commercial and institutional food service applications. One such area of use is steam table trays for restaurants and cafeterias. PPSF is an excellent alternative to stainless steel in this application and has been used successfully in it for more than 5 years. PPSF is also used as the material of construction in food service trays used in correctional institutions. One of the drivers there is the resistance of the PPSF to being broken into shards that can be used as makeshift weapons.

Functional plumbing

PSF and PPSF are used to replace machined metal in a number of plumbing applications ranging from fittings to faucet waterways. It is advantageous to manufacture such components from plastic because the various parts of one device can be consolidated in a mold design. In addition, an injection-molded part can be fabricated to close dimensional tolerances much faster than a machined metal part. Dimensional control and stability are critical to many plumbing applications. Sulfone polymers are very suitable for manufacturing hot potable-water plumbing components because of a number of key attributes in addition to the dimensional stability and control features just mentioned. These include hydrolytic stability, resistance to chlorine (that is present in trace levels in some municipal water supplies to prevent bacterial growth), resistance to corrosion and to lime scale or other mineral buildup (unlike most metals), and, last but not least, the excellent health and safety profile of these materials in contact with hot potable water.

PSF is used in water distribution manifolds for the reasons described above. *Glass-reinforced* (GR) PSF is used extensively in faucet mixing valve components, such as that shown in Fig. 13.4, for many of the same reasons cited. The mixing valve usually has a rather complex geometry, and its dimensional tolerance control is of utmost importance. Therefore machining it from brass or another metal is costly, plus the lime-scale buildup tendency of metals would render the mixing valve inoperative after a relatively short service life. PSF and PPSF have been used successfully in compression fittings applications for a number of years now. The key features for fitting uses are the excellent creep resistance and resistance to mineral buildup. Another advantage of sulfone resins over brass in fittings is that they offer better compatibility with *cross-linked polyethylene* (PEX) piping, thereby promoting greater longevity of the piping system overall. Reduced extractables over conventional materials such as brass are also possible for improved household water quality. PPSF is selected over PSF in fittings applications that involve a higher applied stress either from the internal hydrostatic stress or from the external load, and in cases where harsher conditions are generally present, such as a higher water

Figure 13.4 Glass-fiber-reinforced polysulfone was used in the thermostatic mixing valve of this MYM faucet.

Figure 13.5 These PPSF hot water fittings, designed by Wavin for use with cross-linked polyethylene-aluminum-cross-linked polyethylene composite pipe, are used in both household plumbing and radiator heating applications.

temperature. Examples of PPSF plumbing fittings are shown in Fig. 13.5. Blends of PPSF and PSF have also been used in plumbing component applications (see the “Blends and Alloys” section).

As a logical extension to plumbing applications, polysulfones are used in chemical processing equipment because of their very good resistance to some chemical environments along with the benefits mentioned above. Such uses are especially appropriate in industries involving aqueous streams, which can be acidic and highly corrosive to metals. Some of these applications include corrosion-resistant pipe, pump components, filter modules, support plates, and tower packing. Glass-filled grades are used in cases where chemical resistance requirements are more demanding.

Electrical and electronic applications

Polysulfones are used in quite a few electrical and electronic applications. They offer a very good fit in such applications because of their good dielectric strength, low dielectric constant and low dissipation, and excellent dimensional stability. PSF and PSF blends are used in a variety of electronic connectors because of flammability resistance, dimensional stability and warp resistance, and heat resistance. Good processability is also critical in this application in that tight dimensional tolerances are required for success in connector applications. For similar reasons, PES is used in *integrated circuit* (IC) burn-in sockets. Ease of insertion is also important in such applications. Dimensional stability is crucial in the use of carbon-fiber-filled PES in *electrostatic dissipative* (ESD) matrix trays that must hold integrated circuits to tight dimensional tolerances over the wide temperature ranges used in IC processing. The applications mentioned above comprise part designs that are often quite complex and require good resin flow to fill properly.

In addition to electrical connectors, PES and PPSF are used in fiber-optic connectors, shown in Fig. 13.6. Flammability resistance as well as resistance to chemically aggressive adhesives is necessary. Low loss and excellent dimensional stability are paramount to fiber-optic system efficiency.

Various sulfone polymers and blends are used in a number of business machine components ranging from printer sleds to ink jet cartridges. For ink jet cartridges, resistance to inks, ultrasonic weldability between components, heat resistance, and a good thermal expansion match to the mounted circuit are critical for proper operation of the cartridge.

PPSF offers unique toughness, chemical resistance, and electrical properties to magnetic wire insulation coatings. PPSF withstands high-temperature use to 200°C, exhibits low dissipation, and resists the insulating fluids that can be aggressive to a number of insulation materials. Wire insulation made from PPSF absorbs much less moisture than conventional materials, which facilitates drying and offers good abrasion resistance, thus allowing for efficient coil winding [21].

Circuit breaker housings are an area in which sulfone polymers are utilized. This is particularly true for housings that have to operate at a high temperature continuously or that have a potential for frequent high-temperature spikes. For such circuit breaker designs, a high continuous-use temperature and long-term resin oxidative stability are requirements. Glass-reinforced Radel® A PES has an Underwriters Laboratories (UL)

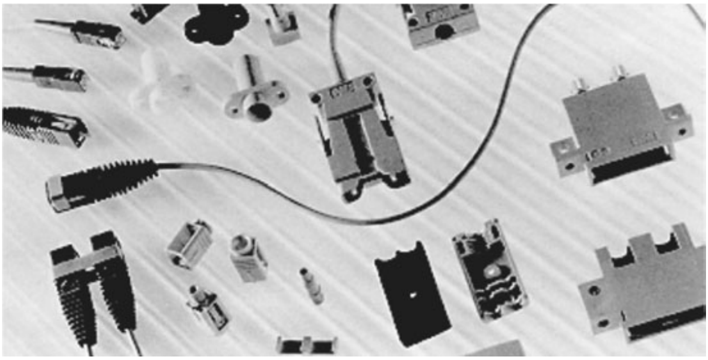


Figure 13.6 Polyethersulfone and polyphenylsulfone are used as fiber-optic connectors in view of their outstanding dimensional stability.

relative thermal index (RTI) of 190°C, which makes it suitable for the high-temperature segment of circuit breakers.

Transportation

The optimal combination of good electrical properties, toughness, dimensional stability, and flame retardance makes polysulfones suitable for several applications in the transportation industry. This industry is moving from thermosets such as bulk molding compounds and metal to thermoplastics in order to improve manufacturability, recyclability, and efficiency through component weight reduction. PSF and PES are commonly used in automotive fuses. In this application, electrical properties, dimensional stability (for reliability), high-temperature resistance, and transparency (to be able to see when a fuse fails) are important. Good flow is also important for the fuse overmolding process. PES is used in automotive headlamp reflectors, shown in Fig. 13.7. As in all lighting applications, flame retardance and high-temperature capability are important. High flow and toughness are important in the thin-walled reflector designs. Excellent mold surface replication and vacuum metallization capability are also critical for a mirror-like surface finish that is needed for optimum lumen output. PSF-based blends can also be used as interior automotive lamps for similar reasons. Glass-filled sulfone resins such as PES are used in motor starter housings by virtue of their heat resistance, dimensional stability, and inherent flame retardance.

Polysulfones are used in a number of aircraft interior applications as well. These applications, shown in Fig. 13.8, include passenger service

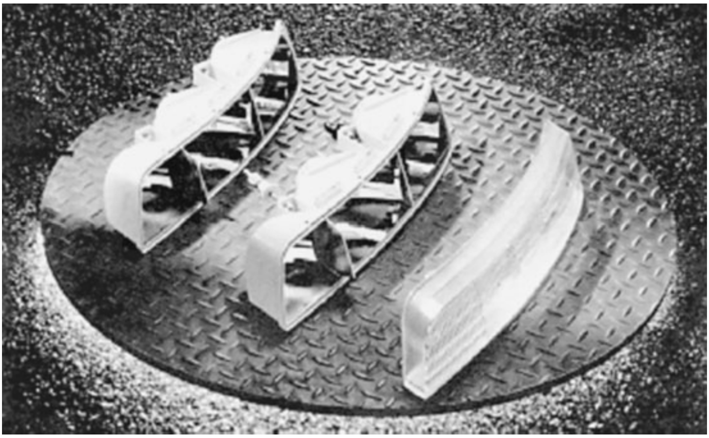


Figure 13.7 Polyethersulfone is used in automotive reflector applications because of its high-temperature capability and excellent high-gloss mold surface replication.

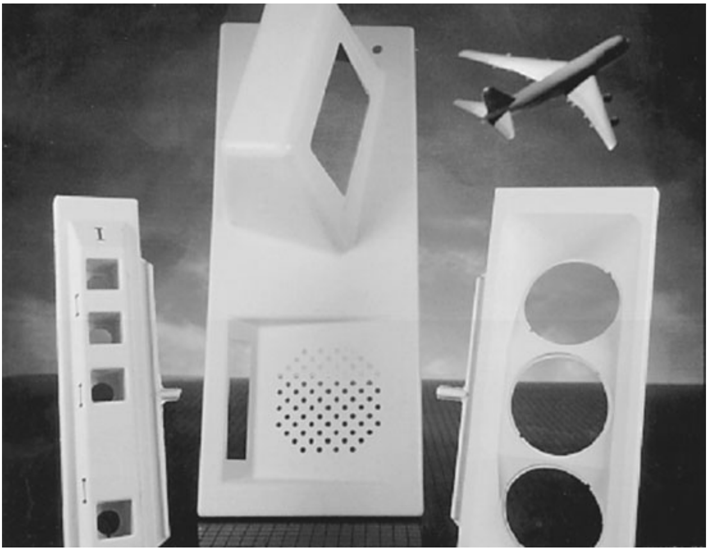


Figure 13.8 Outstanding flame and toughness properties allow polyphenylsulfone to be used in many aircraft interior components.

units, air return grills, and window frames. Extruded PPSF sheet is used in cockpit interiors and emergency exit doors. For these applications the most important attribute is low heat release during combustion. Sulfone-based polymers also offer low toxic gas emission during combustion. In addition, PPSF offers excellent impact resistance and good chemical resistance to aggressive cleaners, both features that contribute to durability during the life of an aircraft. PPSF offers good flow and low specific gravity, which enable the fabrication of lightweight parts that, in turn, contribute to the improved efficiency of aircraft.

Medical

The excellent hydrolytic stability of polysulfones makes them an ideal choice for use in a variety of medical and dental devices. The hydrolytic stability allows use in durable medical devices and components that have to be sterilized in a steam autoclave, sometimes hundreds of times over the life of the component. Such components include sterilization trays and cases, as well as parts of the surgical instruments themselves, such as the instrument handles. Traditionally, metals such as stainless steel have been used for this purpose. But metals are being replaced by thermoplastic materials. The use of plastics offers the ability to customize designs and colors as well as to mass-produce in a more economical fashion. For large parts, such as surgical instrument sterilization trays, the weight reduction is also an incentive for a switch to plastic. PPSF is generally regarded as the premier plastic material for durable sterilizable trays and devices. This is so because of its combination of impact strength, thermal stability, steam autoclave sterilizability, chemical resistance, and moldability in a variety of colors. PSF is also used in the same type of application but where the use conditions or the part longevity requirements are not as stringent. Polysulfones offer requisite FDA approvals and *U.S. Pharmacopoeia* (USP) class VI certifications for medical uses.

Because of its ability to be repeatedly sterilized and its excellent solution processing behavior and biocompatibility, PSF is widely used in membranes for hemodialysis. PSF is also used in laboratory animal cages because of its high transparency and low color, high strength and toughness, sterilizability, and ability to be molded into complex parts. PPSF is used in devices such as binocular opthalmoscopes and dental syringe guns. In both these applications, PPSF is an attractive material choice because it is sterilizable and offers good strength and chemical resistance.

Industrial

In addition to the market areas described above, other applications with similar requirements benefit from sulfone-based polymers. Many components that previously were made from metal now can be made from sulfone-based polymers. Because of the excellent hydrolytic stability, PSF and PPSF are used in fluid processing applications such as pump components, and because of their transparency these polymers are used in flowmeters and sight glasses. PSF use in dairy milking equipment is an example of this type of application. Milking components made from PSF are lighter in weight than their metal counterparts and are transparent. In addition, FDA approval, 3A, and National Sanitation Foundation (NSF) recognition make it a suitable choice.The features of PSF that make it suitable as a hemodialysis membrane material also make it suitable for gas separation membranes and water purification membranes [22–27]. PES can be used as a tower packing for various types of liquid separation units.

Recent Trends in Sulfone Polymer Applications and Some Application-specific Grades

The range of applications and utility of sulfone polymers continue to grow along with the awareness of the performance potential of these materials. One of the new and growing areas of sulfone polymer use is potable hot water applications, as alluded to previously. Sulfone polymers have been seen to deliver an unbeatable combination of properties for this application arena, which include hydrolytic stability, resistance to chlorine, resistance to lime-scale buildup, and excellent health and safety performance in contact with drinking water. The excellent burst pressure characteristics and long-term hydrostatic stress aging resistance of PPSF in particular have qualified this resin in plumbing fittings as an attractive alternative to brass, particularly in plumbing applications based on cross-linked polyethylene (PEX) piping.

A general recent trend for sulfone polymer use is an increased emphasis on appearance and aesthetics. In the 1970s and 1980s, most of the emphasis in the use of high-temperature engineering thermoplastics was on making the component or design concept work in a plastic material. The key to success was functional performance. In the 1990s, a shift began to occur as the design engineers gradually became accustomed to and comfortable with the functional aspects of sulfone polymers in high-performance applications. At the same time, the competitive environment surrounding the users of these materials necessitated that greater attention be paid to product differentiation through the use of bright colors or newer innovative designs with enhanced appeal to the consumer or end user. One such example is in the area of medical or dental applications, where high clarity and bright, clean colors elicit greater acceptance by both health care professionals and patients in the hospital. Historically, sulfone polymers have had a yellow or amber cast to them in their natural state, and this appearance has become less and less desirable in a hospital or other health care setting. To keep pace with the market trends in medical and other areas and to address the emerging needs, Solvay Advanced Polymers has introduced, over the past several years, high-clarity and clarified grades of the natural sulfone polymers. High-clarity polysulfone was introduced in 2004 for the first time under the grade names Udel® P-1700 HC and P-3700 HC. Similar grades have been introduced, based on polyethersulfone, such as the grade Radel® A-300 CL 128. In the same vein, brightly colored, transparent PPSF grades for durable medical component applications have been introduced recently as the Radel® R-5800 TR series.

The aircraft cabin interior is another area of plastics use where highly functional engineering performance is required alongside appealing aesthetics. PPSF has been used successfully in aircraft cabin interior components for over 15 years by virtue of the ability of this resin to combine an excellent resistance to burning and smoke emission with a broad range of colors to be formulated to suit different interior design needs. In this applications area, in recent years a greater emphasis has been placed on materials that provide added design flexibility, such as the ability to have transparent plastics with good clarity and light transmittance that also offer good inherent flame retardancy and low heat release characteristics. The Radel® R-7000 TR transparent series have been developed and introduced recently by Solvay Advanced Polymers to fill the emerging needs of commercial aircraft manufacturers that are looking to use transparent plastic components such as dividers, display case windows, and the like inside the aircraft cabin. The development of the clarified R-7000 TR PPSF grades has opened the door to such applications.

PPSF and PSF are both used in hot water fitting and related plumbing and hot water delivery system applications. In view of its superior mechanical toughness, PPSF is used where higher mechanical toughness and chemical resistance are needed or where the conditions of use are generally harsher. PSF, on the other hand, is a more economical plumbing fitting material. The introduction of Acudel® 22000, a blend of PPSF and PSF, by Solvay Advanced Polymers in 2000 allowed a mid-range grade that offers a cost-performance balance between PPSF and PSF. The Acudel® 22000 grade is finding many uses today in hot water delivery systems, particularly in fittings, where PSF may fall just short of specific intended capabilities. The Acudel® 22000 grade is also finding use in other applications where a mid-tier performance resin is needed that bridges the gap between PPSF and PSF.

In the realm of polyethersulfone (PES), an emerging area of application is in epoxy-based thermosetting formulations, to enhance the toughness of such formulations. Typically, in such uses, PES is dissolved in the prepolymer system, such as a B-stage epoxy, and then the system is thermally cured. This process allows the PES phase left behind to serve as ductile filler that enhances the level of energy dissipation when this modified epoxy is subjected to an impact load. Because of the generally low inherent compatibility between PES and the epoxy, it is desirable to introduce chemical groups into the PES that can chemically bind to the epoxy, thereby preventing or at least delaying phase separation of the PES upon thermal curing of the system. To address this need of thermosetting resin impact modification in the advanced composites arena and other areas in which higher thermoset mechanical performance is needed, Solvay introduced in 2003 the grade Radel® A-105, which is a hydroxyl-terminated, high-molecular-weight PES. The hydroxyl functionality at the ends of the polymer chains allows reactivity with the epoxide groups, thereby limiting phase separation of the PES from the epoxy system upon curing. The covalent bonding also allows more intimate mixing and more effective stress transfer between the epoxy and PES phases, leading to better toughening. The A-105 grade also has utility in the area of hot melt adhesives, where the hydroxyl functionality plays a role in improving the bonding with metallic or other substrates to form strong, thermally stable bonds between surfaces of dissimilar or like materials.

Glass-reinforced grades of PES offering higher stiffness, lower specific gravity, and lower water uptake than standard glass-reinforced PES grades are offered by Solvay under the trade names Radel® AG-340 and Radel® AG-360, corresponding to 20% and 30% glass reinforcement loading levels, respectively. These grades are suitable for electrical and electronic applications because of the lower moisture uptake and excellent dimensional stability, and for automotive under-the-hood or lighting component uses, where low specific gravity is important along with dimensional stability and high thermal capability.

The electronics industry continues to demand higher heat deflection temperature performance along with outstanding dimensional stability and control. This need is driven by a number of factors including the need for using lead-free solders in surface-mounted electronic circuit board applications. The lead-free solders have higher melting points than their lead-containing counterparts do, thereby necessitating higher-temperature plastics to withstand the infrared reflow temperatures required to flux the lead-free solder. These temperatures are typically in the range of 250 to 270°C. With the recent introduction by Solvay Advanced Polymers of Supradel® HTS, a thermoplastic sulfone polymer with a glass transtition of temperature of 265°C and a heat deflection temperature of 255°C, the electronics industry and other manufacturing technologies can extend the range of products and processes that take advantage of high-temperature amorphous resins such as sulfone polymers.

Blends and Alloys

Overview of sulfone polymer behavior in blends

The blending of two or more polymers to achieve products with intermediate or differentiated properties is nowadays commonplace and recognized as an attractive approach to economically develop new materials that are tailored to specific performance requirements. Polymer blend formulations based on sulfone polymers present some opportunities as well as challenges in this regard. The commercially available sulfone polymers PSF, PES, and PPSF are mutually immiscible in any combination. These polymers can be blended, however, to achieve blend properties that are intermediate in—and in some cases above—the expected average properties based on weight or volume fractions in the blend. Such binary blends form two-phase mixtures that are generally intimately dispersed with a well-defined and relatively stable morphology, allowing ease of fabrication of such blends. Some examples include PPSF/PSF blends [28–30], PPSF/PES blends [31], and PES/PSF blends [32]. Ternary blends of the three sulfone polymers have also been explored and are reported on in a U.S. patent [33].

Blends comprising a sulfone polymer with other engineering polymers pose a bigger challenge as the compatibility issues are more complicated. Miscible blends between sulfone polymers and polymers from other families of resins are extremely rare [34–41]. The blend of PPSF and PEI (e.g., Ultem® 1000) is a notable exception, as this blend system is miscible and transparent in all proportions [42]. Blending of sulfone polymers with most commodity-type polymers such as PE, PP, PVC, and styrenics is all but out of the question for a number of reasons; chief among them is the very poor polymer-polymer compatibility and interfacial adhesion between the phases. Furthermore, the poor thermal stability of the commodity polymers at temperatures that are required for effective melt processing of sulfone polymers severely limits viable blends based on sulfone polymers with aliphatic backbone resins.

Blends comprising sulfone polymers and other middle- to high-temperature engineering resins with at least a partially aromatic backbone structure are feasible in many cases. Such blends include sulfone polymer blends with polycarbonates, some polyesters, polyarylates, polyetherimides, and polyaryletherketones. Blends of PPSF with polyaryletherketones such as PEEK or PEK are particularly interesting as these blends form very finely dispersed systems with synergistic strength, impact, and environmental stress cracking resistance properties [43, 44].

Another area of possible interest in relation to sulfone polymer blends is the area of rubber modification for toughening of PSF to achieve supertoughness or enhanced ductility characteristics compared to unmodified polysulfone. Such supertough polysulfone formulations exhibit high notched impact strength values that are on par with those known for polycarbonate and PPSF. This area has been studied and reported on recently [45, 46].

Commercially available blends based on sulfone polymers

A number of sulfone polymer blends have become commercial products over the years. The most well-known group of such products is the PSF-based Mindel® series of resins (Table 13.9). These blends, which are supplied by Solvay Advanced Polymers, are based on PSF that is blended with mid-range engineering thermoplastics to provide tailored performance characteristics and somewhat improved economics over PSF alone. There are three main subdivisions of the Mindel® family of resins: Mindel® A, Mindel® B, and Mindel® S. The Mindel® A resin is designed to offer a polysulfone-type material for parts and components that need electroplatability metallization by using conventional plating techniques that are widely available for ABS resin. Decorative plumbing components are one of the areas in which Mindel® A resin is used. Mindel® B products contain a semicrystalline polymer component and are generally glass-reinforced products intended for applications requiring good chemical resistance, good dielectric and flammability resistance properties, along with long-term heat-aging capability. These products have found utility in electrical distribution and control applications, where

TABLE 13.9 Typical Properties of Mindel® Polysulfone-Based Alloys

Property	ASTM test method	Grade A-670	Grade B-322	Grade S-1000
Glass reinforcement level	—	None	22%	None
Tensile strength, MPa	D-638	50	103	65
Tensile modulus, GPa	D-638	2.1	8.6	2.4
Tensile yield elongation, %	D-638	4.0	—	5–6
Elongation at break, %	D-638	25	2.5	100
Flexural strength, MPa	D-790	83	159	97
Flexural modulus, GPa	D-790	2.2	6.2	2.63
Notched Izod impact, J/m	D-256	320	53	85
Tensile impact, kJ/m^2	D-1822	189	84	—
Heat deflection temperature, °C	D-648	149	160	149
Specific gravity	D-792	1.13	1.47	1.23
Water absorption [in 24 h], %	D-570	0.25	0.14	0.20
Mold shrinkage, %	D-955	0.66	0.3–0.5	0.7
Flammability rating	UL-94	None	V-0 at 0.8 mm	V-0 at 3.3 mm

they have replaced polyesters and nylons owing to their better dimensional stability and superior long-term heat-aging resistance. Mindel® S is a blend product designed to offer performance characteristics that bridge the gap between PSF and polycarbonate (PC). All in the Mindel® series of products are immiscible blends that are two-phase or multiphase; hence all are opaque products.

Blend products based on PES are also available commercially. The products Radel® AG-340 and AG-360 from Solvay are sold as 20% and 30% fiberglass-reinforced blend products based on PES being a majority component. These products offer performance profiles very similar to those of 20% and 30% glass-reinforced PES but with reduced specific gravity, slightly enhanced stiffness, and improved processability. These blends also offer attractive economics relative to glass-filled PES.

PPSF blends with PSF are sold commercially by Solvay under the trademark Acudel®. These blends are intended to bridge the performance gap between PSF and PPSF. They have been found to be particularly suitable for some plumbing component applications where higher toughness and slightly improved chemical resistance are needed compared to PSF [30, 47]. Another family of alloyed PPSF materials is the Radel® R-7300 and R-7400 series of products. These products were designed for use in commercial aircraft cabin interiors. They exhibit exceptionally low flammability and heat release characteristics to meet the *Federal Aviation Administration* (FAA) regulatory requirements for civil air transport. The resins also exhibit high melt flow properties, allowing use in thin and complex part geometries that are often required in this application.

Product Design

Design considerations for sulfone polymers are consistent with those of other thermoplastic polymers, particularly those of an amorphous nature. The ultimate goal is to create a design that meets the physical strength and other structural requirements of an application with a minimum amount of material while accounting for stresses caused by processing, assembly, thermal changes, and environmental factors. Because of the intertwined nature of design and fabrication, the part design is inseparable from the design of the fabrication tooling; both should be studied simultaneously. For part design, typical calculations for stress distribution within solid materials apply to designing with plastics. Parts can be made stiffer through the use of ribs, if necessary. For injection-molded applications, parts should be designed with the thinnest wall that offers sufficient structural strength to support expected loads, maintains deflection within acceptable levels, meets flammability and impact requirements, and offers sufficient clearance for adequate flow of the polymer. It is common for wall thicknesses to vary within a single part. In this case, it is important that the wall thickness taper gradually from thick to thin progressively away from the gate. Sharp transitions in wall thickness or at corners can create stress concentrations and possibly cause premature failure in a finished part. For this reason, corners should have generous radii.

Gates on injection-molding tooling should be very generous and ideally should approach 80% to 100% of the wall thickness of the part. This is so because of the relatively high melt viscosities and resistance of sulfone polymers in general to shear thinning. Failure to provide adequate gate cross-sectional area can result in excessive overheating of the melt and then resin degradation accompanied by outgassing—a phenomenon known as *shear burning*. This could cause cosmetic defects such as splay or bubbles in the molded parts and could potentially compromise mechanical performance during the service life. Runners should be full round or trapezoidal. In any 90° turns in runner systems, cold slug wells should be added. To assist with release of the part from the mold, parts are generally designed with a taper or draft in the direction of mold movement. Draft angles for polysulfones should be 0.5° to 1.0°. To allow for escape of any trapped volatiles, vents should be added at the end of runners and anticipated weld lines. Vents should have a land length of 0.80 to 0.120 in (2 to 3 mm) and should have depths up to 0.003 in (0.08 mm). As is the case with any thermoplastic polymer, ejector pins and stripper plates should be as large as possible to prevent deformation of the finished part. Weld lines should be avoided or minimized in injection-molding sulfone polymers, as the mechanical properties of the resin at weld lines are not as robust as the inherent properties of the material. If weld lines are unavoidable, then they should be located in areas of the part where the expected stress during part service is very low. For detailed guidelines on design and fabrication of sulfone polymers, the design guides available from sulfone resin manufacturers can be consulted [48, 49].

Fabrication

Polysulfones can be formed into finished articles via conventional thermoplastic processing techniques including injection molding, extrusion, film casting, and blow molding. Since the resins are soluble in some polar organic solvents, they also are amenable to solution processing to produce articles such as hollow fiber membranes and other forms, such as ultrathin films and coatings where melt processing may be difficult. The resins can be processed on conventional melt fabrication equipment used for thermoplastics as long as high-temperature capability approaching 400°C exists. As with most linear amorphous polymers, polysulfones are fully thermoplastic materials and readily flow at temperatures ≥150°C above their respective glass transition temperatures. The backbone structure is extremely thermally stable during melt processing, remaining unchanged even when subjected to several melt fabrication cycles.

Typical melt viscosity behavior as a function of shear rate is shown in Fig. 13.9 for polysulfones and some other polymers. As illustrated in these plots, the shear thinning characteristics of polysulfones are much more muted than they are for aliphatic backbone polymers, such as the polyethylene and polystyrene shown to illustrate this point. The rheological behavior of polysulfones is fundamentally more similar to that of polycarbonate.

Prior to melt processing, the resin must be dried to reduce the level of absorbed atmospheric moisture, which can be as high as 0.8 wt %. For injection-molding operations, moisture content below 0.05 wt % is appropriate; for extrusion applications such as film or sheet, the moisture level should not exceed 0.01 wt %. Although the presence of moisture in the melt does not adversely affect the molecular weight of the polymer, significant amounts present during melt processing cause bubbling and foaming, which lead to structural and appearance defects in the fabricated parts. Drying to the targeted 0.05 wt % moisture can be easily achieved in a circulating hot air oven or a dehumidifying hopper dryer in 3 to 4 h at 135 to 165°C. Drying temperatures can be increased up to 180°C for PES and PPSF, if it is desired to cut down on drying time.

Injection molding is the most common fabrication technique used in the plastics industry, particularly with high-performance polymers. Amorphous resins can be processed over a wide temperature range.

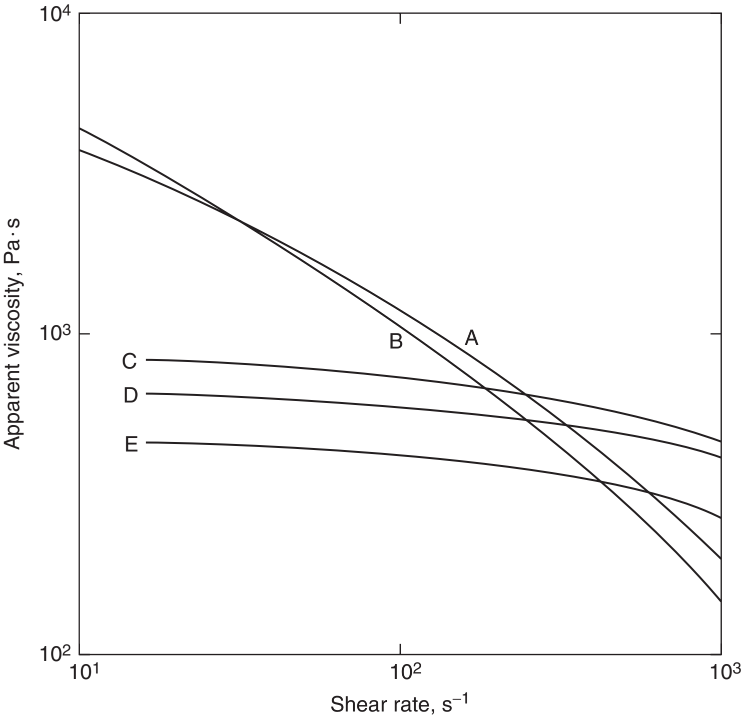


Figure 13.9 Melt viscosity dependence on shear rate for various polymers: (A) Low-density polyethylene at 210°C; (B) polystyrene at 200°C; (C) Udel® P-1700 (PSF) at 360°C and Radel® R-5000 (PPSF) at 380°C; (D), Lexan 104 polycarbonate at 315°C; and (E), Radel® A-300 (PES) at 380°C.

The polymer melt temperature for PSF injection molding can be in the range of 325 to 400°C depending on part thickness, length, complexity, and other factors. PES and PPSF are generally molded by using temperatures in the range of 360 to 400°C. For injection molding, a general-purpose amorphous screw offering an 18:1 to 22:1 length-to-diameter ratio and a 1.8:1 to 2.4:1 compression ratio gives good results. Mold temperatures suitable for PSF injection molding are in the range of 100 to 170°C; for PES and PPSF this range is 120 to 190°C. Lower mold temperatures can be used but are not recommended, as they can result in premature quenching of the polymer and ultimately unacceptably high levels of molded-in residual stresses in the parts. Because of the relatively high viscosities of polysulfones and the limited shear thinning they exhibit over the practical range of shear rates, generous sizing of runners and gates in mold design is recommended. The low rheological resin sensitivity to shear has the beneficial effect of resulting in parts that are low in molecular orientation, and hence are much more nearly isotropic than those molded from many other thermoplastics.

Polysulfones are easily processed by other fabrication techniques commonly used for thermoplastics, including extrusion, thermoforming, and blow molding. Extrusion into film, sheet, tubing, profiles, and coatings can be accomplished on conventional extrusion equipment with a metering screw of moderate depth having a 24:1 length-to-diameter ratio and a 2.5:1 compression ratio. Stock temperatures during extrusion of PSF, PES, and PPSF are in the range of 315 to 375°C depending on the resin viscosity and type of product being produced. A common fabrication technique is sheet extrusion followed by thermoforming. Prior to thermoforming, the sheet must be dry to prevent foaming. The surface temperatures required to produce the necessary sag are in the range of 230 to 260°C for PSF and 275 to 305°C for PES and PPSF. Blow molding of polysulfones is possible on most commercial blow-molding equipment, provided the equipment is capable of maintaining melt temperatures of 300 to 360°C.

Because of the excellent thermal stability of sulfone polymers, scrap from sprues, runners, sheet trim, and the like can be reground and reprocessed by blending with virgin resin. For successful use of regrind, the first and foremost consideration is to ensure resin cleanliness during regrinding and handling operations associated with it. Also the regrind ideally should be dried prior to reprocessing and should be blended with virgin resin in a ratio not exceeding 25% of the total mix, so as to limit the extent in quality variations of molded parts. Typically the main difference in molded parts resulting from regrind molding is a slightly higher color, as the sulfone resins tend to darken with each added melt processing cycle.

Once formed, parts made of polysulfones (particularly those produced by injection molding) can be annealed to reduce molded-in stress. Increased stiffness, dimensional stability, and resistance to creep during the service life of the part are generally enhanced if molded-in stresses are reduced. More importantly, the resistance of the part to environmental stress cracking or crazing is usually improved if molded-in stresses are minimized. Annealing can be easily accomplished in either an air oven or a glycerol bath. Typical time-temperature conditions for the proper annealing of polysulfones in an air oven are 30 min at 160 to 170°C for PSF and 30 min at 190 to 200°C for PES and PPSF. Time and temperature conditions for annealing in general should be as low as possible, to prevent significant reductions in resin toughness. Annealing at similar temperatures to those mentioned above by immersion in hot glycerol can be accomplished in 1 to 5 min. Because overannealing may result in a reduction of impact toughness, the use of conservative molding practices, most notably a hot mold and appropriate part and gating designs, to produce low-stress parts is preferred whenever contact with aggressive chemical environments is anticipated for the component during its service life. Solvent-induced stress cracking of molded parts with specific solvents can be used as a tool to ensure that the molded-in stresses in the part as molded are within acceptable levels or that the molded-in stresses have been eliminated by the annealing step employed [48, 49].

Secondary fabrication operations

Sulfone polymers are amenable to most postmelt fabrication operations. Because of their high glass transition temperatures and inherent toughness characteristics, the resins can be machined with conventional metalworking techniques such as drilling, tapping, sawing, turning, milling, and routing. They can also be polished to a high gloss. Cutting or machining oil is generally not required or recommended, but water can be used to reduce heat. Polysulfones can be joined by a variety of techniques. Joining polysulfones to themselves or to similar materials often employs ultrasonic welding, heat staking, or spin welding. Hot plate welding is also effective for this purpose. Solvent bonding can be used for self-bonding, but it is generally not recommended and should be used only as a last resort. Traditional adhesive bonding can be used, especially when polysulfone must be joined to a dissimilar material. Products manufactured from polysulfones can be easily finished and decorated by printing, painting, laser etching, or applying hot stamping patterns. Metallic patterns and finishes can be applied by vacuum deposition metallization and cathode sputtering, as well as flame and arc spraying.

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Chapter

14

Polycarbonates

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Introduction and Historical Background

Overview

Bisphenol A (BPA)–based *polycarbonate* (PC) is one of the most versatile and widely used engineering thermoplastics on the market. This amorphous material offers

- Outstanding impact strength—even at low temperatures
- Good mechanical properties over a broad temperature range
- Excellent dimensional stability, even at elevated temperatures
- Outstanding optical properties
- Low birefringence [for *compact disc* (CD) manufacture]
- Natural water-clear transparency
- Ability to be integrally colored to form transparent, translucent, or opaque parts in virtually any hue and a wide variety of special effects for parts with high aesthetics
- Amenability to plating, painting, and in-mold decoration
- Product purity and safety for food-contact and medical applications (many BPA-PC grades have agency compliance around the globe)

- Good thermal stability [*relative thermal index* (RTI) to 125°C]
- Good electrical insulating properties (although it can be made electroconductive via additives)
- Good ultraviolet (UV) stability and weatherability
- Very good flame retardance
- Good processability with fast cycle times

As such, polycarbonate is used in at least 27 major industry segments, ranging from telecommunications components, to eyewear, to health care devices, to optical storage discs. A more extensive description of markets and applications is provided later in this chapter.

Initially, just two major resin manufacturers—in North America and Europe—produced polycarbonate. The industry has since expanded to include a half-dozen other suppliers in Europe, Asia/Pacific, and North America. Currently, polycarbonate is produced on four continents. Demand for this versatile polymer has increased steadily since its commercial introduction in the early 1960s. Compounded annual growth rates typically average 10%.

Historical background

This chapter provides an overview of the properties, synthesis, methods of characterization and production, markets, and uses for polycarbonate and its blends. The chapter focuses primarily on the commercially significant aspects of polycarbonate development, manufacturing, and applications. For more in-depth information, the following excellent resources are recommended: Schnell; Vernaleken; Fox; Lapp; Serini; Clagett and Shafer; Freitag et al.; LeGrand and Bendler; and Brunelle and Korn [2–10, respectively].

The evolution of polycarbonate has been long and complex, with extensive fieldwork by many researchers. Discovery and development of polycarbonate, as with so many of the early polymer inventions of the 20th century, were affected by (and at times delayed by) a number of interlinked factors. Chief among these issues were the lack of perceived need for polymers with higher properties, a shortage of commercially available monomers, and an absence of processing equipment on which higher-viscosity, higher-temperature polymers could be processed. Hence, there was a span of more than half a century between publication of early findings and commercialization of viable forms of polycarbonate, much as there was with polyesters. In fact, polycarbonate resin evolved as a subset of general polyester chemistry, with developments in each polymer family helping to support advancements in the other [11–16].

Early developments in aliphatic polyesters. Lourenco first published descriptions of aliphatic polyesters [17] as reaction products from succinic acid and ethylene glycol in 1863. Thirty years later, Vorlander prepared polyesters by using fumaric and maleic acid and ethylene glycol [18]. In 1917, Hofmann introduced polymers made from adipic acid or methyl adipic acid, plus ethylene glycol or 1,2-propanediol for use as substitutes for natural fats and waxes [19]. These materials were nonstructural and of low molecular weight. Hence, they were later used in coatings and in polyurethanes by O. Bayer [20], but never found use in load-bearing applications.

Later, Carothers and colleagues [21–23] performed extensive studies on aliphatic and aliphatic-aromatic polyesters. They produced polyesters of malonic acid, succinic acid, adipic acid, sebacic acid, maleic acid, fumaric acid, and phthalic acid when reacted with ethylene glycol, 1,3-propane-diol, 1,6-hexanediol, and/or 1,10-decanediol. This work yielded low-melting, viscous liquids or microcrystalline waxlike solids with melting points below 100°C. This same group also prepared "superpolyesters" and "superpolycarbonates" that were then used as film and fiber formers. However, as with the earlier aliphatic polyesters, the melting points and thermal resistance of these products were low, and none of them has subsequently become a stand-alone, commercially significant polymer.

Early developments in aliphatic and aromatic polycarbonates. The first significant documentation of aromatic polycarbonates synthesis began with Einhorn [24]. He reacted hydroquinone, resorcinol, and catechol with phosgene in a pyridine solution, obtaining linear polymers from hydroquinone (an insoluble crystalline powder that melted above 280°C) and resorcinol (an amorphous material that melted with decomposition at 190 to 200°C), and a cyclic carbonate from catechol. Subsequent research was focused on finding more efficient preparation methods and on improving material properties [25].

In 1902, the same polymers that Einhorn had produced with his phosgene procedure were synthesized via a melt transesterification method developed by Bischoff and Hendenstroem [26] using *diphenyl carbonate* (DPC) as a phosgene equivalent synthon. However, interest in polycarbonates soon waned again due to the poor solubility and toughness of these early resins, the general challenges involved in processing them, and because of the limited methods of material characterization available at that time. No significant work in connection with aromatic polycarbonates was reported for the next 50 years.

Several decades later, in the early 1930s, work (and interest) once more revived on aliphatic polycarbonates when Carothers and van Natta were able to produce low-melting, low-molecular-weight, microcrystalline aliphatic polycarbonates via two different synthetic pathways [27]. The first method was the transesterification of aliphatic dihydroxylic compounds with diethyl carbonate. The second approach was via ring-opening polymerization of cyclic carbonates of aliphatic dihydroxylic compounds. Peterson then extended the transesterification work to yield low-melting, high-molecular-weight films and fibers from 1,6-hexanediol and dibutyl carbonate [28]. The first commercially viable polycarbonate was introduced in 1941 by the Pittsburgh Plate Glass (PPG) Company in the form of a liquid casting resin to surface-coat fiber for optical applications. This cross-linkable resin (called CR-39) was derived from the allyl ester of diethylene glycol carbonate. Further peroxide-initiated reactions were used to produce a scratch-resistant, water-clear transparent plastic.

Further developments in aromatic polyesters and polycarbonates. While research with aromatic polycarbonates was halted, activity did continue with aromatic acids and aliphatic diols or polyol polyesters.

The next step in the evolution of polycarbonates occurred as a result of continued reexamination of aromatic derivatives. The most significant work was the invention of polyethylene terephthalate by Whinfield and Dickson [29] in 1946.

Based on this work on aromatic polyesters, Schnell et al. [30] and Fox [31] independently prepared linear, high-melting, high-molecular-weight aromatic polycarbonates in 1953–1954 that were derived from 4,4′-dihydroxydiphenylalkane monomers. These aromatic polycarbonates could be prepared either (1) by a two-phase interfacial method (a modified Schotten-Baumann reaction) or (2) by a melt transesterification (monomers-as-solvent) process using diphenyl carbonate [32]. Versus earlier aliphatic polycarbonates, the aromatic polycarbonates were unique in that they could be made into water-clear (colorless) transparent structures that possessed excellent long-term mechanical properties.

Before these disclosures, polyesters and polycarbonates were generally thought to be either liquids or low-melting solids, although there are major differences between these two types of materials. Whinfield's aromatic polyesters exhibited limited solubility in common organic solvents, and they tended to crystallize, becoming translucent and brittle with a simultaneous loss of mechanical properties. In contrast, the aromatic polycarbonate resins were characterized by good solubility in organic solvents and retained their amorphous internal structure, transparency, and long-term mechanical properties after molding.

The excellent properties of the aromatic polycarbonates, particularly those based on 2,2-bis(4-hydroxyphenyl)propane (bisphenol A, or BPA), subsequently led to significant research into these materials by many organizations and a rush to develop commercial products. To date, the unique and commercially valuable properties of BPA polycarbonate have not been offset by any other commercially feasible aromatic diol. Hence, the commercial foundation for polycarbonate production has since been based on BPA-PC, although some copolymers with BPA-PC and other diols are also produced commercially.

By 1954, both Fox at General Electric Company (GE) and Schnell at Farbenfabriken Bayer AG (and their respective companies) recognized the unique properties of BPA-PC [33, 34]. Hence, the race for commercial development began. Bayer added polycarbonate production to an existing chemical plant in Uerdingen, Germany, producing commercial product by 1958. Mobay Chemical Company (New Martinsville, West Virginia, United States, now Bayer America) similarly expanded an existing plant to begin commercial production in early 1960. Unlike the other suppliers, GE started production by building a completely new plant in Mt. Vernon, Indiana, United States, and thus did not produce commercial products until late 1960.

The fact that there were multiple suppliers in various parts of the world producing polycarbonate actually boosted commercial sales of the material. Also, the fact that two major chemical companies had both made considerable investment in developing and producing this material helped build confidence in it and helped it to be specified in place of alternatives.

It is not surprising, given the concurrent research and commercialization efforts that were focused on bringing BPA-based polycarbonates to the market in the late 1950s, that a patent interference arose. Bayer was eventually awarded the first U.S. patents on BPA-based polycarbonates [35] and for the interfacial method of production. GE was issued a patent covering the melt transesterification production process [36].

By the mid-1960s, GE had pilot plants running both the DPC-based transesterification process and the pyridine solvent process. The pyridine process was replaced by the lime-slurry process, and the latter was run for several years in production during the later 1960s and early 1970s. The phosgene-based interfacial method was also being evaluated during this time. The company eventually switched all polycarbonate production to interfacial in the early 1970s. A similar pilot study conducted by Bayer led to the same conclusion. Hence, by the 1970s, all commercial BPA polycarbonate (BPA-PC) homopolymer was being produced by interfacial technology.

Interestingly, many decades after it was first developed and subsequently discarded, the original melt polymerization process is once again receiving attention and being reinvigorated. This has occurred for several reasons. First, methods have been developed that enable the production of very clean, water-clear transparent, and cost-effective polymer using the melt polymerization process. Specifically, certain inventions relating to the discoveries of the importance of avoiding certain critical monomer impurities, inventions in melt polymerization equipment, particular catalysts, and other technical advances have allowed such high-quality polycarbonates to be made by the melt polymerization process. Second, the solventless melt process is attractive because it helps polycarbonate production plants reduce the capital investment costs associated with polymer purification, solvent handling, and solvent recovery and recycling.

Homopolymer grades of polycarbonate can be made by either the melt or the interfacial process. The melt method, which is a continuous process, is better suited for large-volume production where process parameters are not changed often. The interfacial process can be used in either batch or continuous plants. With a batch interfacial plant, it is easier to switch between grades, and hence this method is more typically used in plants making multiple grades, especially lower-volume, specialty copolymer polycarbonates. In general, a number of parameters are reviewed to determine how a grade will be produced, including polymerization chemistry, polymer solubility, polymer thermal stability, and economics.

Chemistry of Polymerization

Reliable feedstock was key

The availability of bisphenol A, used in the epoxy industry, initially facilitated the commercialization of BPA polycarbonate. The commercial growth of polycarbonate is closely tied to the development of high-purity BPA. To achieve high-quality polycarbonates, the BPA feedstock used must be of the highest purity, or else both color and performance can be compromised. Thus, as polycarbonate customers have demanded lower color and more melt-stable resin at higher and higher processing conditions, the demand for higher-purity BPA has increased. This is especially true for resin prepared via the melt-polymerization process, where the polymer is often subjected to extended periods at elevated temperatures. For more in-depth information, the following excellent resource is recommended [37].

Early process successes and challenges

Fox discovered a method to make BPA-PC via transesterification of the BPA with diphenyl carbonate [38, 39]. Limitations in technology at that time, however, prevented scale-up and commercialization of a melt process to make PC. Instead, the solvent method was commercialized first.

The first solvent system that was scaled up used pyridine as both solvent and acid acceptor in a system reaction of BPA with phosgene and monofunctional phenol as a molecular weight regulator [40]. This process also met with challenges, since the cost, toxicity, and availability of the reaction solvent, pyridine, limited further growth.

Thus, the early process of choice for one of the major producers was the reaction of BPA, phosgene, and monohydric phenols in a methylene-chloride solution in contact with an aqueous solution of sodium hydroxide [41]. For this reaction, a tertiary alkyl amine was the preferred catalyst. Lime was used extensively as the acid acceptor in an alternative process preferred at the time by another major producer [42].

As would be expected, the manufacturing processes used to produce polycarbonate from BPA have evolved significantly since the early 1960s.

Various raw material suppliers around the globe have achieved significant production volumes. At present, both batch and continuous polymerization systems are in use. Early solution polymerization processes produced a highly variable resin. To yield a higher-purity polymer, a variety of purification processes were applied. One of the first resin isolation processes in use added a nonsolvent until the polymer precipitated out of solution—either partially or completely. Subsequently, numerous purification processes were explored, including filtration through beds or columns of natural or synthetic zeolites, charcoal, activated carbons, silica gels, or other adsorbents. Washing in plate columns or liquid-liquid centrifuges was used extensively to purify polycarbonate resin solutions. Extruder devolatilization, steam precipitation, nonsolvent precipitation, or gelling and crushing could then isolate the resin. Current methods for resin purification include decantation of the brine, acidification of the resin, and removal of the residual salts by water washes. Current methods for polymer isolation include steam precipitation, vacuum extrusion in a devolatilizing extruder, or gel crush. All these processes have a common goal: to yield very pure, water-clear transparent resin that maintains maximum properties and performance.

Reengineering the molecule

Polycarbonates based on BPA and terminated with monofunctional phenols are linear polymers that provide

- Inherent toughness
- Transparency
- Broad thermal performance
- Good electrical resistivity
- High refractive index
- Ease of colorability and compounding
- Good mechanical properties

Markets for polycarbonate materials are diverse, often large and global, and are treated in the next section. Polycarbonate has been successfully positioned to replace wood, metal, glass, and other lower-performing polymers.

These linear polymers, in various molecular weights and with various monofunctional phenol end groups, dominate commercial polycarbonate production and sales. However, these products do not meet all requirements, particularly for extrusion and extrusion blow-molding applications where there is a need for polycarbonates that provide nonnewtonian, shear-dependent, viscoelastic flow properties. These desirable flow properties are generally achieved via low-level addition of tri- and tetrafunctional monomers to the BPA, thereby creating a branched copolymer [43–44]. Extrusion blow-molded parts such as water bottles and other large hollow shapes [45] are made using these types of resins.

For applications calling for higher levels of thermal performance—especially where it is necessary to retain clarity and toughness—much work has been done to copolymerize difunctional aromatic carboxylic acids with BPA [46–47]. Others have taken the approach of including different structures of bisphenols.

BPA polycarbonates exhibit properties typical of aromatic polyesters with respect to flame resistance. Early on, flame resistance was enhanced in these materials by introducing tetrabromo BPA/BPA copolymers [48]. Although other, more sophisticated systems—particularly nonhalogenated ones—have since been discovered and commercialized, these brominated copolymers are still in use.

Commercial production of polycarbonate

Although there is an extensive volume of work on the polymerization of polycarbonate and polycarbonate copolymers, today there are only two basic commercial condensation processes used to produce the majority of commercial product: interfacial and melt transesterification. For a more in-depth review of these two processes as well as others that are not commercially significant, the following resource is recommended [49].

Interfacial polymerization process. The interfacial polymerization process is the oldest and most widely used of the commercial processes. Although different companies and even different manufacturing plants may have variations of the interfacial process, overall they are quite similar. Both batch and continuous interfacial processes have been practiced. The overall reaction (shown below in Fig. 14.1) involves the condensation of BPA with phosgene. A base, typically caustic, is used to scavenge the hydrochloric acid generated. The condensation is catalyzed with a tertiary amine and/or a phase transfer catalyst or both. The condensation is done in a two-phase medium such as methylene chloride and water. For a more in-depth discussion of the reaction mechanism, the reader is referred to the following sources [50–58].

The molecular weight, and therefore the melt viscosity, of the resulting polymer is controlled by the addition of a predetermined amount of

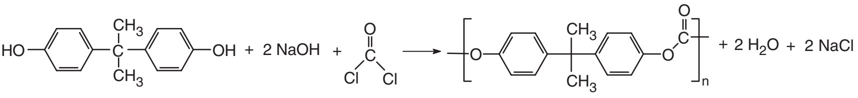

Figure 14.1 Interfacial polymerization process.

chain stopper. Typically, monophenols such as phenol, *p*-cumylphenol, *p*-tert-butylphenol, and octylphenol have been used. As will be described subsequently in the section entitled "General Properties of BPA-PC," retention of ductility as measured by notched Izod can be affected by the mobility of the end groups. Thus, for low-molecular-weight and high-melt flow grades, large bulky end groups are typically used.

Chloroformate processes [59] were developed as a variation on the interfacial process. These processes can be run continuously or in batches. An advantage of the process is that it can be run in such a fashion as to dramatically lower the diaryl carbonate levels. Diaryl carbonate molecules are formed from the reaction of two molecules of the mono-phenol end cap with a molecule of phosgene. High levels of diaryl carbonates in the resulting resin can cause plate-out on mold surfaces. This makes it harder to eject PC parts from a mold, potentially causes surface issues on aesthetically sensitive parts, and—in the case of compact discs—can lead to bad pit replication and rejection of parts, all of which increase the molder's downtime. In the chloroformate process, BPA is allowed to react with phosgene in an absence of (or at lower levels of) the amine condensation catalyst. The process generates chloroformate-terminated oligomers. After complete consumption of the phosgene, the addition and incorporation of the mono-phenol end cap ensure that no or low levels of diaryl carbonates will be formed. After incorporation of the end cap is complete, the condensation catalyst and additional caustic are added to complete the polymerization. The resin solution can be washed and isolated as discussed above (see "Early Process Successes and Challenges").

Melt transesterification process. The melt process, which was not used commercially until the late 1980s, has experienced a renaissance in the last 15 years. In the 1950s and 1960s, when the melt process was first studied for production of high-quality polycarbonate, it was hindered by the lack of both BPA feedstock having sufficient purity with respect to certain contaminants and melt reactors capable of processing high-viscosity polymer melts under high vacuum. By the 1980s, improved reactor designs and the commercial availability of BPA of sufficient purity—coupled with improved catalyst systems—helped the melt process finally become a commercial reality.

In the melt process, BPA is condensed with diphenyl carbonate at elevated temperature and reduced pressure. The reaction is base-catalyzed and is driven to high molecular weight by the removal of phenol under reduced pressure. The temperatures are steadily increased through the process such that the monomers, oligomers, and resultant polymer are maintained in a molten state. The reaction pressures are ramped from 760 to 200 torr in the initial stages of the reaction, and down to 0.1 to 1.0 torr

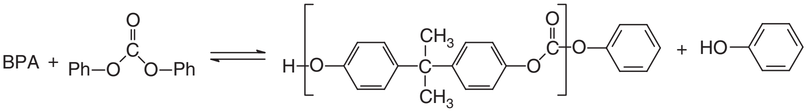

Figure 14.2 Melt transesterification process.

in the final stage. The molecular weight of the resin is controlled by the amount of phenol that is removed (Fig. 14.2).

A wide variety of catalysts have been studied and used with the melt process. Even today, the development of new and improved catalysts remains an extremely active topic of research. Catalyst systems other than alkali metal hydroxides (e.g., NaOH) have been investigated, including the salts of fluoride [60], carboxylates [61], phosphoniums [62], neutral amines [63], phosphates [64], and guanidine [65]. Many of the commercially effective catalysts are reported to be used in the concentration range of 10 to 250 ppb [66].

The mechanisms of the batch and semibatch processes have been reported [67–69]. The most recent work [70] indicates that efficient condensation polymerization necessitates proper maintenance of the ratio of reactive end groups. End-group dependence is particularly important during the later stages of the semibatch process. To compensate for loss of DPC from the melt during the low-pressure polycondensation stages, results indicate that addition of a slight excess of DPC is helpful. In fact, the benefits of using an excess of DPC have been known since the early 1960s [71–73].

There are significant differences between these two processes that may make one more advantageous than another in certain situations.

From a manufacturing standpoint, the interfacial process is capital-intensive to purify the resin solution, isolate and dry the resin, and recycle solvents and brine. With melt transesterification, because it is a solventless process, the only recycle streams that must be dealt with are those related to the recovery of phenol for reuse in the production of DPC. Hence, there is no need to invest in solvent recovery infrastructure with the melt process, and polymer purification units and dryers can likewise be avoided. However, these investments are somewhat diminished by the investment required for the preparation and purification of DPC.

From a product standpoint, the major benefit of the melt transesterification approach is that it produces resin with a most probable (thermodynamic) molecular weight distribution. Hence, under normal processing conditions, the anhydrous resin exhibits no tendency to change molecular weight or the *melt flow index* (MFI) (via redistribution).

Finally, the melt process also has the advantage of being able to produce resins with limited solubility in the typical solvents used in the interfacial process (e.g., biphenol). This feature—which has both manufacturing and product benefits—allows for production of a broader range of materials from the melt process since with the interfacial process if a material does not stay in solution, it is very difficult to make.

Interestingly, after more than half a century, the original two processes developed to produce polycarbonate are still in wide use and dominate the industry. Each process has its own unique balance of advantages and disadvantages. Although many products can be made from either process, each process can allow specific products to be produced that the other cannot. Both processes will be used for the foreseeable future, depending on the specific type of material being produced.

Polycarbonate Properties: General-Purpose and Application-Specific Grades

General BPA-PC properties

Bisphenol-A polycarbonate (BPA-PC) is a stiff-chain, aromatic, glassy amorphous polymer that has found wide use due to its high impact strength. As a clear, transparent polymer, it is commonly used as a high-quality replacement for inorganic glass and lower-performance transparent commodity plastics. BPA-PC is an engineering plastic, which by definition is a material that is used because of high property levels that yield engineering functionality, such as high tensile strength.

Amorphous polymers have no long-range order or crystallinity. A polymer is amorphous because the chain repeat units are incapable of close packing into a regular crystalline structure. This can be due either to irregular repeating units that simply will not pack well or to units for which the kinetics of local chain motions are too slow. Long-term thermal-aging studies have shown that BPA-PC can be thermally crystallized, but the rates are so slow that high-molecular-weight, thermally crystallized PC is not observed in practice. Diluents that provide sufficient chain mobility can also lead to solvent-induced crystallization at reasonable rates. Thus, it is reasonable to conclude that the amorphous nature of BPA-PC is due to low chain mobility in the melt. These very stiff chains cause very high viscosity in the melt, even at relatively low molecular weight. As a result, commercial grades of BPA-PC show very significant changes in properties as a function of viscosity. Properties are still commercially valuable, even at these low molecular weights, primarily because the critical molecular weight for chain entanglement is also very low for BPA-PC at 2400 g/mol [74].

Typical average molecular weights for BPA-PC are 18,000 to 36,000, when measured on an absolute molecular weight scale. Low molecular weight means that there are significantly more chain ends in BPA-PC than would be observed in most high-molecular-weight polymers.

The effective molecular weight for influencing physical properties is thus highly affected by the mobility of these chain ends. This can be controlled by the use of bulky end groups that restrict chain mobility in the solid state, but do not significantly affect chain mobility in the melt.

Properties of BPA-PC blends

The effects of BPA-PC molecular weight dominate the properties of blends that contain this material. Modifications are also made by blending with other polymers and the use of additives to achieve specific effects. These additives may be UV stabilizers, thermal stabilizers, flame retardants, mold release agents, fillers, colorants, impact modifiers, etc. Blends are made with

- *Acrylonitrile butadiene styrene* (ABS) for improved flow and modest improvements in chemical resistance
- Crystalline polyesters such as *polyethylene terephthalate* (PET) or *polybutylene terephthalate* (PBT) for significantly improved chemical resistance
- *Polyetherimides* (PEIs) for higher thermal performance
- Aliphatic-styrenic copolymers [e.g., *acrylonitrile styrene acrylate* (ASA)] for improved UV resistance
- Polyester-carbonates (PPC or PEC) for heat resistance while maintaining transparency

Blends of BPA-PC can be immiscible, semimiscible, or fully miscible. Most commercial blends are either compatible or have been compatibilized. An example of an immiscible compatible blend would be PC/ABS (commercial examples would be Cycoloy™ [75] and Bayblend® [76] resins). In this case, the ABS needs to be selected to be compatible with the BPA-PC phase. Examples of semimiscible compatible blends would include BPA-PC with either PET or PBT (a commercial example would be Xenoy™ [77] resin), with PBT showing greater partial miscibility than PET. Fully miscible blends would include examples such as BPA-PC with various cyclohexane dimethanol polyesters (a commercial example would be Xylex™ [78] resin). Miscibility or partial miscibility leads to T_g suppression and products with lower heat resistance. Compatibility without miscibility may lead to a slight depression in T_g, which may be due to slight miscibility.

Other polymers are also blended with BPA-PC to enhance properties. For example, blending with ABS will significantly enhance low-temperature impact and flow and also yield a modest improvement in chemical resistance. However, the greatest property loss from neat polycarbonate is in heat resistance, and the improvement in chemical resistance is less than what can be attained by blending with crystalline polymers, but it is achieved while maintaining all the advantages of fully amorphous polymer systems. The ABS will be present as a second phase of different refractive index, which will typically lead to significant light scattering from the phase boundaries, yielding an opaque material. Some of the characteristics of amorphous polymers that prove beneficial compared to their crystalline counterparts include low shrinkage, shrinkage consistency (due to elimination of variability in shrinkage caused by variations in crystallinity), and dimensional stability. PC/ABS is an immiscible blend. Blend morphology is controlled by the existing ABS morphology, mixing conditions, relative amounts of each material, viscosity ratios of the components, and the compatibility between phases. Normally, special grades of ABS are used to make PC/ABS blends. This is particularly critical since normal ABS stabilizers and additives are generally chemically incompatible with BPA-PC.

BPA-PC copolymers are often copolyester carbonates that include ester linkages mixed into the carbonate linkages. The monomers are added to achieve specific effects, such as UV resistance for the Lexan™ [79] SLX grades, or higher heat resistance as in the case of Lexan PPC 4701R or Makrolon® [80] APEC 1805 materials.

BPA-PC can also be blended with crystalline polyesters, such as PBT and PET. A commercial example of PC/polyester blends is the Xenoy blends. These polyesters are partially miscible with BPA-PC. PBT has higher miscibility with BPA-PC than does PET. On the other hand, PET has a higher T_g than PBT. Thus, PET blends have higher thermal resistance than PBT blends, both because of PET's higher T_g and because of the lower miscibility. Crystalline polymers typically have significantly improved chemical resistance compared to amorphous polymers. The largest property losses are in heat resistance at high loads and in dimensional stability. In some cases, there will also be significantly lower tensile properties, primarily due to large amounts of impact modifiers that may be used in these blends.

Polycarbonates also have the ability to transesterify with other polyesters. This leads to jumbling of the repeat units and is likely to lead to undesirable properties, such as low thermal resistance. In commercial products, such undesirable side reactions need to be controlled.

A critical caveat to the use of another material in conjunction with BPA-PC is the extreme sensitivity of BPA-PC to low-level additives that may function as degradation catalysts within the BPA-PC matrix. Some catalytic additives are effective degradation catalysts at parts-per-billion levels. Basic metal oxides/carboxylates, bases, and amines are classical examples of degradation catalysts for BPA-PC. Control of low-level impurities is an essential element in selection of any material for blending with BPA-PC. This means that special, higher-purity grades of raw materials may be required for BPA-PC blending. This explains many of the issues that arise when standard grades of additives are used with BPA-PC [81–89].

The effect of changing molecular weight on BPA-PC homopolymer is illustrated in Table 14.1 Melt flow varies from 3.5 to 66 for these grades. The corresponding molecular weight varies from 36,000 to 18,000. It is interesting to note the effect of molecular weight on various physical properties. It can be seen that tensile strength at yield is not sensitive to molecular weight in this region. Flexural modulus is only affected at the highest melt flows (low molecular weights). Heat resistance [as measured by *heat distortion temperature* (HDT)] is affected at the upper half of the melt flow range. Notched Izod impact at room temperature increases with decreasing melt flow until reaching the two lowest flow levels. In contrast, the notched Izod ductile-brittle transition temperature is sensitive to melt flow (and molecular weight) across the entire range of commercial products. This table illustrates the interaction between molecular weight and property performance in a simple fashion. Not all physical properties have the same dependence upon molecular weight.

Most of the properties given in Table 14.1 are relatively standard physical property measurements with standard methods referenced. The notched Izod ductile-brittle transition temperature is an approximate method to estimate the midpoint temperature at which notched Izod behavior shifts from fully ductile to fully brittle. It may be very sensitive to a variety of differences among samples. It is used here only for illustrative purposes to show the low-temperature impact capability limits as measured by this notched Izod test. Each user should determine the relevance of this small-scale laboratory impact test on small laboratory-molded parts to full-scale molded parts at end-use conditions for a given application.

Additional changes can be made by molecular architecture, such as by adding branching, as shown in Table 14.2.

New and specialty polycarbonate resins

Since the introduction of BPA polycarbonate homopolymer, researchers have continually sought to expand the usefulness of these materials via synthesis of new polycarbonate homo- and copolymers. This section will focus on the copolymers that are commercially available. For a more extensive examination of noncommercial, non-BPA polycarbonates, several excellent reviews may be found at [90–93]. Copolymer production generated by reactive blending, coextrusion, and/or compatibilizing materials (e.g., grafting) will also not be discussed. However, a historical overview of commercial alloys and blends may be found in a recent work by Utracki [94].

Polyestercarbonates and other high-heat polycarbonates. Increasing the thermal performance of BPA polycarbonates has long been a goal of

TABLE 14.1 Select Physical and Mechanical Properties for Various Types of Polycarbonate Based on Viscosity

	Tensile yield strength	Flexural modulus	HDT at 1.8 MPa, 3.2 mm	Notched Izod impact at 3.2 mm at 23°C	Notched Izod ductile-brittle transition temp.	Melt flow rate at 300°C/1.2-kg load	Commercial examples
Test standard	ASTM D-638	ASTM D-790	ASTM D-648	ASTM D-256		ASTM D-1238	
Units	MPa	MPa	°C	J/m	°C	g/10 min	
Very high-viscosity PC	62	2340	132	908	–30	3.5	Lexan 131 resin
High-viscosity PC	62	2340	132	908	–22	7	Lexan 101 resin
Standard-viscosity PC	62	2340	132	801	–15	10.5	Lexan 141 resin
High-flow PC (low viscosity)	62	2340	129	694	–5	17.5	Lexan 121 resin
Very high-flow PC	62	2310	127	641	5	25	Lexan HF1110 resin
Ultrahigh-flow PC	62	2250	120	550	15	66	Lexan OQ1030 resin

TABLE 14.2 Select Physical and Mechanical Properties for Various Types of Polycarbonate Based on Molecular Architecture and Blending

	Tensile yield strength	Flexural Modulus	HDT at 1.8 MPa, 3.2 mm	Notched Izod impact at 3.2 mm at 23°C	Notched Izod ductile-brittle transition temp.	Melt flow rate	At temp (°C)/ load (kg)	Commercial grade name examples
Test standard	ASTM D-638	ASTM D-790	ASTM D-648	ASTM D-256		ASTM D-1238		
Units	MPa	MPa	°C	J/m	°C	g/10 min		
Branched, high-viscosity PC	62	2340	132	748	–25	2.5	300/1.2	Lexan 151 resin
UV-resistant PC-polyester carbonate copolymer	65	2510	119	822	0	9	300/1.2	Lexan SLX1432 resin
High-heat polycarbonate copolymer	62	2330	160	< 300	>23°	10	330/2.16	Makrolon APEC 1805 resin
Aromatic polyester carbonate copolymer	66	2330	149	374	10	2	300/1.2	Lexan 4701R resin

researchers around the world. Only two polycarbonate-based copolymer resins have succeeded in becoming commercially significant: polyestercarbonates and copolycarbonates based on 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane. Even with the availability of these polymers, resin suppliers continue to pursue polycarbonates with higher heat deflection temperatures and improved ductility, low color, and improved color stability.

Aromatic polyestercarbonates (also called *polyphthalate carbonates*) derived from BPA and BPA phthalates have been commercially available since the early 1980s. These transparent resins offer an excellent combination of increased thermal performance coupled with good ductility (Fig. 14.3 and Table 14.3). Thus, they have found use in applications with higher thermal requirements than those in which traditional BPA-PC can perform, such as high-end headlight reflectors, automotive fuse bodies, fire helmets, and fire helmet face shields. Good thermal and mechanical properties, plus hydrolytic stability and agency compliance for short-term contact with skin, blood, and bodily fluids, have made this resin a good candidate for use in numerous steam-sterilizable medical devices.

Polyestercarbonates undergo a photo-Fries rearrangement when exposed to UV light. The *o*-hydroxybenzophenone that forms on the material's surface protects the part from further UV damage [95–97]. However, the rearranged product from the BPA arylate in polyestercarbonates can give rise to significant changes in the *yellowness index* (ΔYI). In some cases, such as lenses for automotive forward lighting, this shift can be noticeable.

Conventional BPA polycarbonates can be blended with polyestercarbonate resins to create miscible blends with a single T_g; they can also be blended with polyetherimides to yield immiscible blends with a fine-particle morphology. (See Chap. 8 in this book on thermoplastic polyetherimides for more details.)

These resins are typically prepared via an interfacial [100–104] or solution [105, 106] process by using BPA, isophthaloyl chloride, terephthaloyl chloride, and phosgene. Alternatively, they can be produced by using a melt process from BPA, diphenyl isophthalate, diphenyl terephthalate, and diphenyl carbonate [107, 108].

In the late 1980s, a new high-temperature copolycarbonate based on 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane [109–112] was

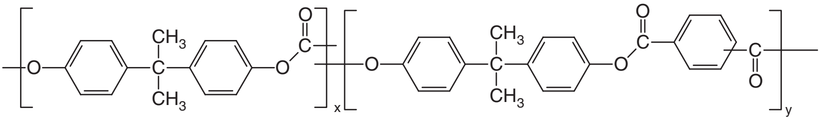

Figure 14.3 Aromatic polyestercarbonate (also known as polyphthalate carbonate).

TABLE 14.3 Properties of Commercial High-Heat Copolyestercarbonates and Copolycarbonates

Typical properties [98, 99]	Units *(Test method)*	Lexan 101 resin	Lexan PPC4501 resin	Lexan PPC4701 resin	Makrolon APEC DP9-9331 resin	Makrolon APEC DP9-9371 resin
Mechanical						
Tensile stress, yield	MPa *(ASTM D-638)*	62	65	66	64	69
Tensile stress, break	MPa *(ASTM D-638)*	69	71	78	66	57
Tensile strain, break	% *(ASTM D-638)*	135	122	78	90	70
Hardness, Rockwell M	— *(ASTM D-785)*	70	85	92	75	91
Hardness, Rockwell R	— *(ASTM D-785)*	118	122	127	125	127
Izod, notched, 23°C	J/m *(ASTM D-256)*	908	640	374	640	80
Thermal						
HDT, 1.84 MPa, 3.2 mm, unannealed	°C *(ASTM D-648)*	—	143	149	—	—
HDT, 1.84 MPa, 6.4 mm, unannealed	°C *(ASTM D-648)*	138	—	—	140	179
Physical						
MFR, 300°C/1.2 kgf	g/10 min *(ASTM D-1238)*	7	3	2	22	4
Specific gravity	— *(ASTM D-792)*	1.2	1.2	1.2	1.2	1.1
Optical						
Light transmission	% *(ASTM D-1003)*	88	85	85	88	88
Haze	% *(ASTM D-1003)*	1	1	1	1	1
Refractive index	— *(ASTM D-542)*	1.586	1.6	1.6	1.581	1.581

commercialized. This resin offered excellent transparency and low inherent color, plus improved melt flow compared to polyestercarbonates. A family of products offering a range of HDTs is available (Table 14.3). The toughness of these compositions varies with HDT. Medical-compliant, flame-retardant, UV-stabilized, and general-purpose grades are each available in this product family. Typical applications for such materials include

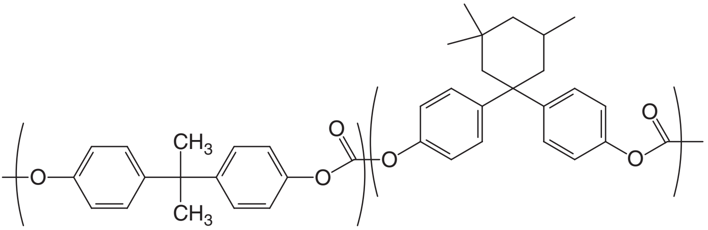

Figure 14.4 Copolycarbonate based on 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane.

automotive lenses and reflector light pipes, sterilizable medical devices, electrical equipment, and components for household appliances.

The copolymer (Fig. 14.4) is prepared from 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane **(1)** and bisphenol A. The cyclohexane containing bisphenol **(1)** is prepared by the condensation of phenol with 3,3,5-trimethylcyclohexanone and an acidic catalyst. The cyclohexanone can be prepared by the selective hydrogenation of isophorone [113, 114]. The T_g of the copolymers can be varied from 150°C (e.g., BPA homopolymer) to ~240°C [e.g., homopolymer of 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane]. And the resins can be prepared by either melt or interfacial processes. For increased ductility, terpolymers have been reported with a siloxane block [115]. For applications requiring low moisture absorption, the bisphenol **(1)** has been polymerized with bisphenol M (see the section "New Copolymers for Optical Storage Media").

High-melt flow copolycarbonates for thin-wall applications. Because of the ever-increasing number of applications that feature thinner walls and hence require materials with greater flow lengths, high-melt flow resin continues to fill an important need in both the design and processing communities. As with many polycarbonate applications, ductility combined with transparency is still the key requirement, even at these higher-melt flows. Typical applications include cell phones, cell phone windows, and refrigerator crisper trays. To date, several different approaches have been taken to achieve increased melt flow:

- Decrease of *molecular weight* (MW)
- Addition of plasticizers
- Addition of high-flow resins (see section "Typical Applications for Polymer Blends")
- Modification to the polymer backbone

The first commercially exploited approach was to decrease the molecular weight of the resins. This led to the development of BPA homopolymer products ranging in melt flow from ~65 g/10 min (for optical-disc grades) to 3 g/10 min (for extrusion-grade polycarbonate). For more information on these materials, see the "Polycarbonate Properties" section.

A second approach—the addition of low-MW plasticizers—has not been widely used. While this option does dramatically increase the melt flow, it also unfortunately decreases impact strength and retention of ductility.

Preparation of blends with a higher-flowing secondary or tertiary polymer is a third approach that has seen wide commercial use (see the section "Typical Applications for Polymer Blends"*)*. However, an unintended consequence of this tactic can be the loss of clarity.

To achieve a better balance between flow and ductility than can otherwise be obtained with the low-MW plasticizers approach, and to retain clarity often lost when blending with other high-flow resins, manufacturers have turned to a fourth option: modification of the polymer backbone itself. Polycarbonate chemistry and the process to produce it both lend themselves to incorporation of the following monomers or blocks to increase melt flow:

- Aliphatic diols [116, 117]
- Aliphatic diacids [118, 119]
- Aliphatic blocks [120–125]
- T_g-suppressing bisphenols (see the section on "New Copolymers for Optical Storage Media")
- Siloxane blocks (see the section "PC Siloxane Block Copolymers").

In this approach, the first four of the listed monomers or blocks rely on suppression of the T_g to improve melt flow. The fifth option relies on the ability of the impact-modified siloxane blocks to maintain ductility of the matrix at lower polymer MWs and thus higher flow. With the exception of aliphatic diols and aliphatic blocks, modifications of the polymer backbone with these monomers and blocks have found successful commercial use.

In the case of aliphatic diols, and for interfacial polymerizations, typically the diol is first prereacted with phosgene to form chloroformates [126, 127]. The chloroformates are then condensed with BPA in a standard interfacial process to yield the copolymer with a reduced T_g and increased melt flow (Fig. 14.5). Selection of the diol in the process is important. Diols containing beta hydrogens, which often readily crack at elevated processing temperatures, lead to melt instabilities. This potential for poor melt stability, coupled with complications of a two-step process, has limited commercial interest in this approach.

The second approach relies on the incorporation of aliphatic diacids into the polymer chain [128]. A wide variety of linear and branched diacids can

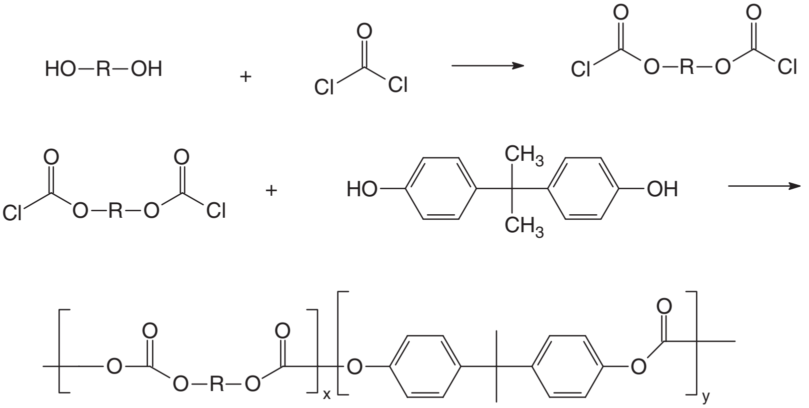

Figure 14.5 Formation of high-flow polycarbonates from diols.

be incorporated. These resins improve the flow-ductility balance while still maintaining transparency (Fig. 14.6).

For a given notched-Izod value, a higher melt flow can be obtained via use of a copolymer than with the corresponding BPA homopolymer (e.g., Lexan resins). For example, Lexan SP grades possess almost twice the melt flow index (MFI) of the BPA homopolymer resins at a 640 J/m (12 ft·lb/in) notched Izod. The tradeoff for the increased flow is a corresponding decrease in the *distortion temperature under load* (DTUL) of ~20°C, as shown in Fig. 14.7. These resins are being supplanted by the siloxane-BPA polycarbonate (see the section “PC Siloxane Block Copolymers”), which provide an even better balance of melt flow and ductility without a significant loss in heat performance.

Incorporation of alcohol- or carboxylic-terminated aliphatic block has also been used to produce resins with increased melt flow and good ductility [130–135]. In most cases, the synthesis of the copolymer has been similar to that described for diol and diacids. Although a good balance of melt

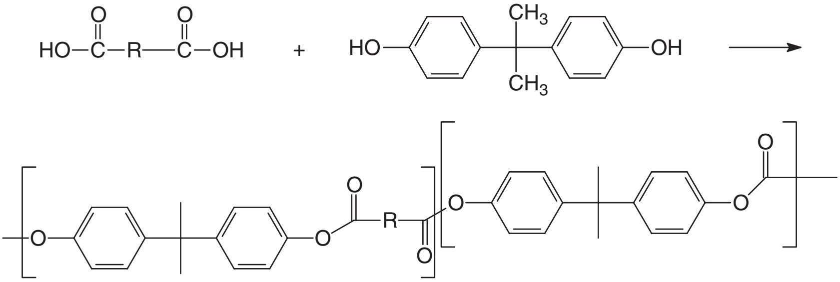

Figure 14.6 Formation of high-flow polycarbonates from diacids.

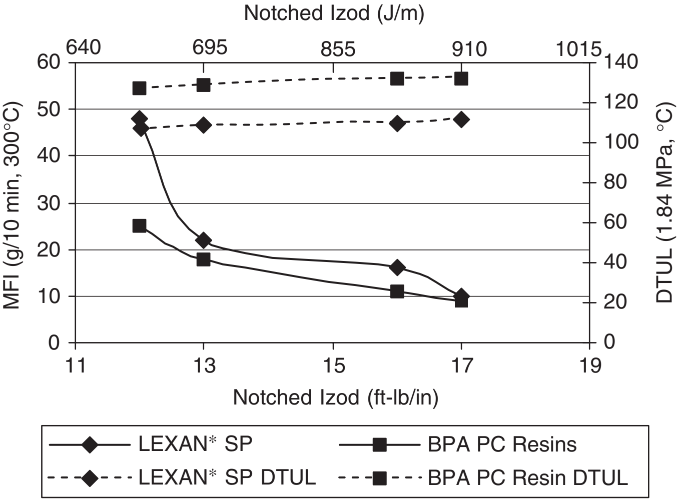

Figure 14.7 Comparison of copolyestercarbonate resins vs. polycarbonate homopolymer resins [129].

flow and ductility has been obtained in many cases, other factors such as a readily available, low-cost monomer source have inhibited commercialization.

The use of siloxane block copolymers to improve the balance between melt flow and ductility is covered in the next section, "PC Siloxane Block Copolymers." The use of a T_g-suppressing bisphenol to improve melt processability is covered in the section "New Copolymers for Optical Storage Media."

PC-siloxane block copolymers. Block copolymers based on polycarbonate and *polydimethylsiloxane* (PDMS) were first prepared by Vaughn in the 1960s [136, 137]. The two synthetic methods described by Vaughn have become the basis for the commercial technologies previously used to manufacture PC-siloxane copolymers. Both involve reaction of bisphenol-A and phosgene with a dimethylsiloxane comonomer that is terminated with a phenolic functional group. The latter is prepared either via reaction of a chloro-terminated siloxane (Fig. 14.8) with excess BPA—excess BPA is used to minimize oligomerization due to reaction of both phenolic groups on the same BPA—or via the hydrosilation reaction of a hydride-terminated siloxane (Fig. 14.9) with a phenolic compound bearing an allyl functional group [the latter most commonly either 2-allyl phenol [138] or the commercially available natural product, eugenol (2-methoxy-4-allyl phenol)] [139]. Once converted to a bisphenol structure, these siloxane intermediates can then be incorporated into the PC copolymer by simply

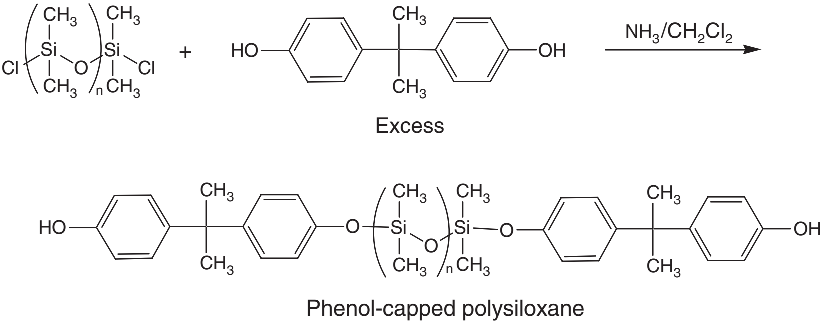

Figure 14.8 Production of a siloxane intermediate via reaction of a chloro-terminated siloxane with excess BPA.

coreacting them with BPA in the conventional interfacial reaction process used to make BPA-PC homopolymer (Fig. 14.10).

Depending on the composition of the PC-siloxane copolymer (e.g., siloxane block length and weight percent of siloxane), the resulting materials will be either flexible *thermoplastic elastomers* (TPEs) or phase-separated rigid thermoplastics. Typical elastomeric copolymers contain 40 to 70 wt % siloxane and with a *degree of polymerization* (DP) of the siloxane blocks between 10 and 20 [140, 141]. Thermoplastic copolymers contain a lower weight percent of siloxane (typically 2 to 8%), with a DP value of the siloxane blocks in the range of 20 to 100 [142]. In their elastomeric form, the copolymers have found uses in varied applications such as impact modifiers for thermoplastic resins [143] and adhesive layers in PC and PC-glass security laminates [144]. In the form of rigid thermoplastics, these materials have found wide utility as injection-molding resins due to their exceptional combination of thermal stability, impact strength under severe-use conditions (i.e., low temperatures and weathering), and flame

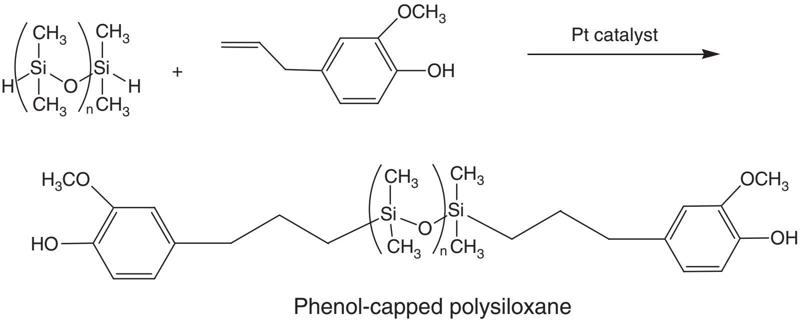

Figure 14.9 Production of a siloxane intermediate via hydrosilation reaction of a hydride-terminated siloxane.

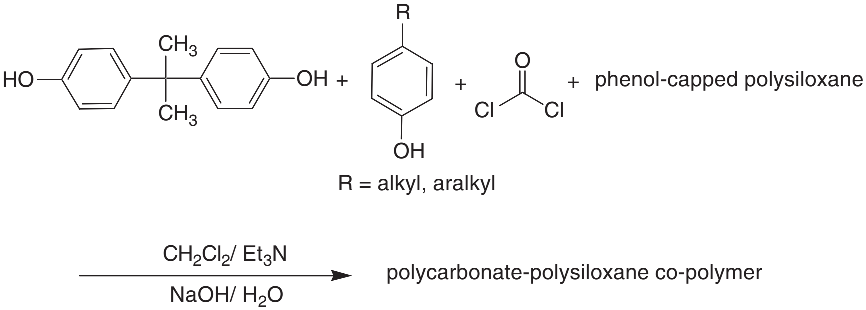

Figure 14.10 Incorporation of siloxane intermediate into PC copolymer via coreaction with BPA using interfacial reaction process.

retardancy [145, 148]. Typical applications for the latter include protective helmets, outdoor postal boxes, and cell phone housings.

Reaction process conditions as well as copolymer composition variables are critical when one is determining the overall structure of the polymer backbone of PC-siloxanes, and thus the microphase structure and ultimately the properties of the material, most notably transparency. Reaction process conditions are critical because—owing to differences in both solubility and reactivity between BPA and the phenolic end-capped siloxanes under the usual interfacial-reaction conditions (Figs. 14.8 to 14.10)—the BPA and the siloxanes oligomerize at different rates, with the end result being formation of polymer chains high in siloxane content along with polymer chains substantially free of siloxane. The final composition exhibits, to a significant extent, the characteristics of a polymer blend between two essentially incompatible polymers (most notably, opacity) [149–153].

Recent improvements to the reaction process have overcome the problems caused by reactivity differences between BPA and the functionalized siloxanes and now allow production of transparent, thermoplastic PC-siloxane copolymers suitable for a variety of injection-molding applications. The process improvements [154, 155] involve, essentially, preformation of chloroformate end-group BPA-PC oligomers in the interfacial reaction prior to addition of the phenol-capped siloxane. Alternatively [156–158], the chloroformate of the siloxane can be preformed in a tubular reactor before reaction with BPA or BPA oligomers. Careful control of the molecular weight of the PC oligomers results in control of the PC block length in the final copolymer, and thus the distance between siloxane blocks. The more uniform, random incorporation of the siloxane results in a single homogeneous copolymer that exhibits morphology with more uniform, smaller siloxane domains, which, in turn, yields an essentially transparent composition.

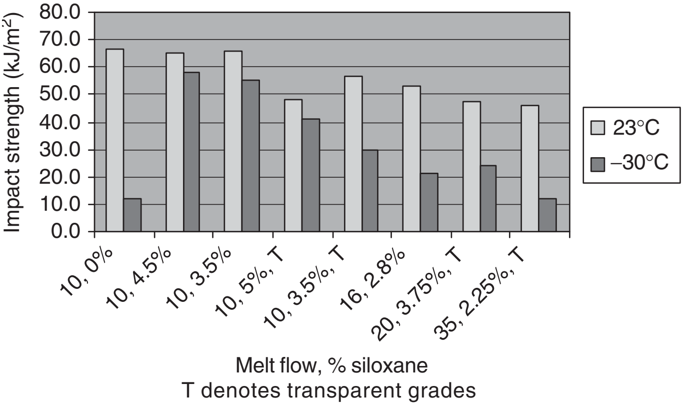

Figure 14.11 Iso Izod impact strength for PC-siloxane grades—*temperature study.*

The commercial value of PC-siloxane resins is based primarily on the enhanced impact strength these copolymers exhibit compared to PC homopolymers under severe (i.e., embrittling) end-use conditions. Frequently, the superiority of the PC-siloxane resins is demonstrated by impact testing at low temperatures. Figure 14.11 displays Izod impact data measured at room temperature and –30°C that clearly demonstrate this performance advantage.

Polymers may also be embrittled by part design variables. In Figs. 14.12 and 14.13, the embrittling effects of sharper notch radius and of increased part thickness on various materials are shown. Again, the PC-siloxane resins are shown to be superior to PC homopolymers in this regard.

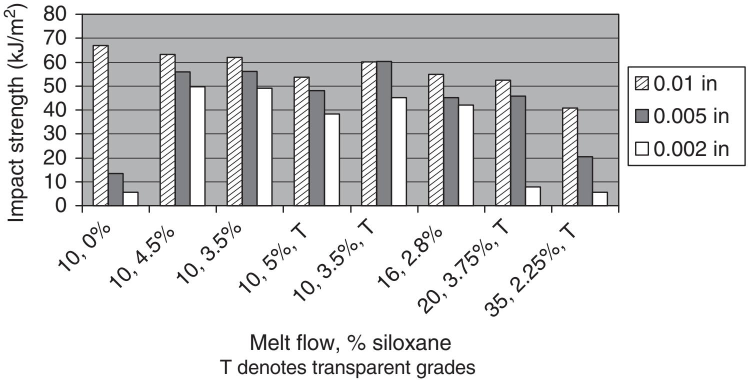

Figure 14.12 Iso Izod impact strength for PC-siloxane grades—*notch radius study.*

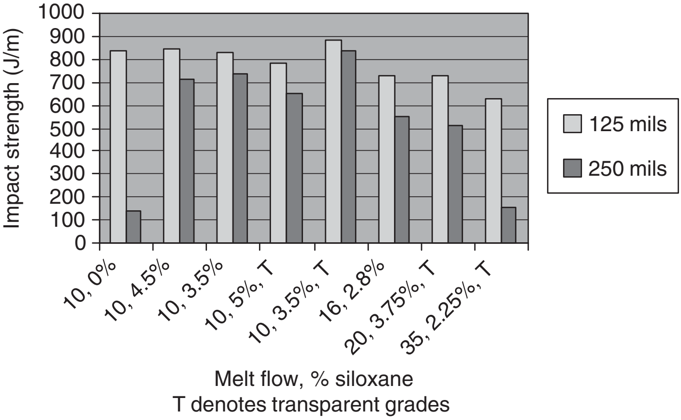

Figure 14.13 Iso Izod impact strength for PC-siloxane grades—*part thickness study.*

Biphenol copolycarbonates. Efforts to further improve polycarbonate's toughness, chemical resistance, and flame-retardant properties have led to the development of biphenol-containing copolymers with polycarbonate (Fig. 14.14).

Because of limited solubility and differing monomer reactivity, melt polymerization may be the process of choice for creating biphenol-based copolymers [159–163], but these copolymers can be prepared by interfacial processes as well [164]. Under appropriate polymerization conditions, transparent resins can be obtained by using up to ~50 mol % of biphenol [165]. Copolymers with more than 60 mol % biphenol will exhibit liquid crystalline behavior [166].

The addition of biphenol to BPA-PC improves low-temperature impact strength, increases the critical thickness at which the ductile-brittle transition occurs, and increases the impact retention after heat-aging [167–173]. While BPA polycarbonate homopolymer has higher room temperature impact strength, the material becomes brittle below –10°C.

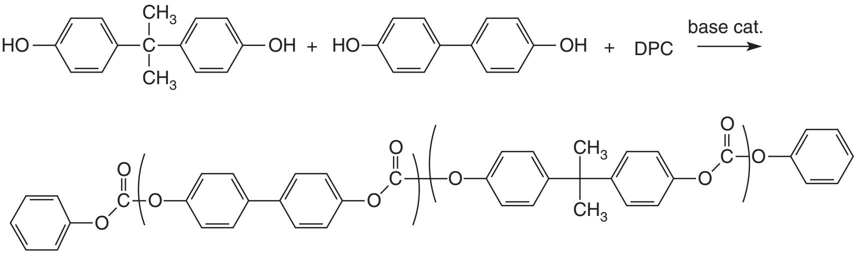

Figure 14.14 Melt preparation of biphenol-containing polycarbonates.

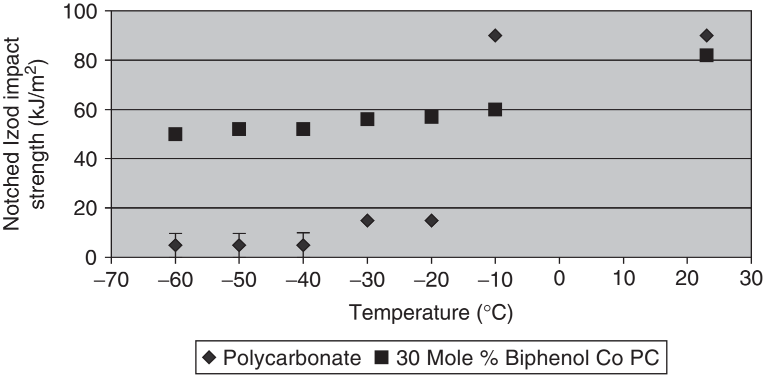

Figure 14.15 Low-temperature ductility of 30% biphenol copolymers.

The 30 mol % biphenol-containing copolymer maintains its ductility down to –60°C (Fig. 14.15) [174].

The optimum level of biphenol in the composition for improved low-temperature impact appears to fall in the range of 26 to 34 mol % (Fig. 14.16). The improved ductility of these copolymers appears to be related to a combination of the presence of biphenol-carbonate-rich microdomains (10 to 20 µm) and the low rotational-energy barrier around the biphenyl units in the polymer chain [175]. In addition to low-temperature ductility, the resins maintain a higher percentage of their notched Izod impact strength after heat-aging compared to standard BPA polycarbonate [176–182].

When compared to BPA homopolymer, these transparent copolymers also show improvement in

- Flame retardance [UL® [183] 94 tests increasing from HB to V-2 at 3.0 mm (0.12 in)]
- Limiting oxygen index (increasing from 28 to 35.9)

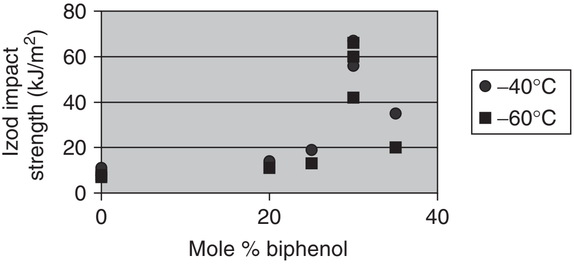

Figure 14.16 Izod impact strength as a function of biphenol content.

- Stress-crack resistance to hydrocarbons such as ASTM Fuel C (toluene/isooctane 50/50)
- Hydrolytic stability in boiling water

UV-resistant polycarbonate copolymers. Polycarbonates are used in a wide range of applications due to their excellent optical, thermal, mechanical, and impact properties. However, when exposed long-term to ultraviolet (UV) light, polycarbonates are susceptible to photodegradation, resulting in discoloration (increased yellowness), loss in transmission or gloss, and reduction in mechanical properties [184, 185]. The susceptibility of the polycarbonate backbone to degradation upon extended exposure to high-intensity UV radiation has limited its use in some uncoated or unpainted outdoor applications [186]. The common methods of protecting polycarbonate against photodegradation include addition of low-molecular-weight UV absorbers, application of UV protective coatings, and the proper selection of pigments [187]. Both bulk additive and coating technologies are limited by the amount of UV additives that can be introduced without affecting other properties, and by their rate of loss or degradation of these additives during extended weathering. Bulk additive *UV absorber* (UVA) technology is inefficient because the photochemical processes are mostly limited to the surface of the exposed part, whereas the majority of the UV absorber is deep within the part. In addition to being inefficient, the use of high loadings of low-molecular-weight UVAs can have deleterious effects on physical properties and, at times, resin color, because these UVAs are often slightly yellow themselves.

Polyarylates of resorcinol have good weatherability properties and provide protection against photochemical yellowing [188–190]. When irradiated by UV light, the resorcinol arylates undergo a photo-Fries rearrangement to form high levels of *o*-hydroxybenzophenone units at the polymer surface (Fig. 14.17), where they act as efficient UV absorbers. The photo-Fries rearrangement provides an in situ self-protection mechanism with a virtually infinite supply of UVAs, which are incorporated in the polymer chain.

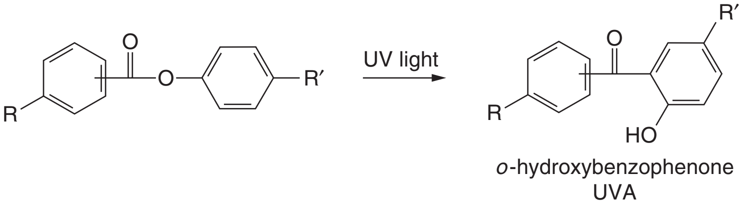

Figure 14.17 Formation of UVA via the photo-Fries rearrangement.

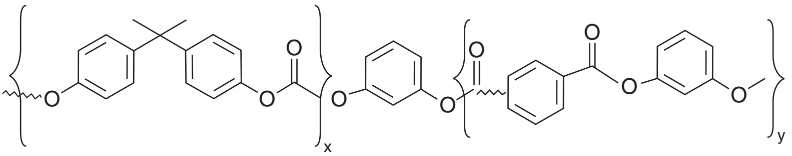

Figure 14.18 ITR block copolymer.

By using this concept, resorcinol poly(ester carbonate)s were developed and introduced under the trade name Lexan SLX grades. The block copolymers of *I*so- and *T*erephthalate esters of *R*esorcinol (ITR) and BPA polycarbonate can be prepared by melt, solution, or interfacial reactions [191]. The properties of these resins are controlled by adjusting the percentage of resorcinol phthalate to BPA carbonate (Fig. 14.18).

Compositions have been prepared with polymers having high, medium, and low levels of resorcinol phthalate along with BPA polycarbonate homopolymer (Table 14.4). Like polycarbonate, the ITR resins show an excellent balance in physical and thermal properties. With increasing ITR content, the resins show an increase in tensile strengths and moduli, but—although still high—slightly decreasing HDTs and notched Izod values.

TABLE 14.4 Physical Properties of ITR Copolymers [192]

Property	Units	ASTM method	No ITR, PC control	Low ITR	Medium ITR	High ITR
		Mechanical				
Tensile strength, yield, Type I, 0.125 in	MPa	D-638	62.4	64.7	70.3	73.8
Tensile elongation, yield, type I, 0.125 in	%	D-638	6.2	6.3	6.2	6.3
Tensile elongation, break, type I, 0.125 in	%	D-638	115	126	106	89
Flexural strength, yield, type I, 0.125 in	MPa	D-790	101	105	112	115
Tensile modulus, 0.125 in	MPa	D-790	2317	2434	2530	2627
Izod, notched, 23°C	J/m ft·lb/in.	D-256 D-256	910 17	905 17	530 10	470 9
		Thermal				
HDT, 0.45 MPa, 3.2 mm, unannealed	°C	D-648	138	135	127	127
HDT, 1.84 MPa, 3.2 mm, unannealed	°C	D-648	127	123	116	113
		Physical				
MFR, 300°C, 1.2 kgf	g /10 min	D-1238	10.8	10.0	6.9	6.8

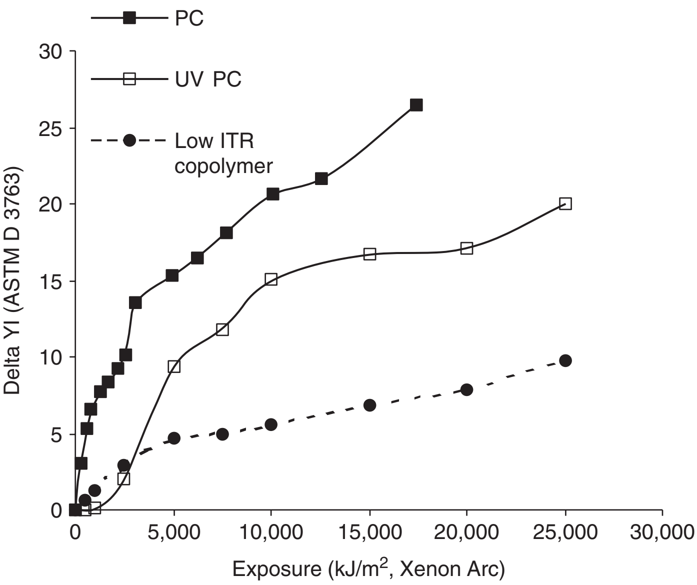

Figure 14.19 Color change during xenon arc weathering of transparent ITR resin formulations [195].

For transparent applications such as utility meter covers and sight glasses, hurricane windows, light lenses, and windscreens, the term *weatherability* is mainly related to the parts' ability to retain color, transparency, and good mechanical properties upon outdoor exposure. Figure 14.19 shows the change in yellowness index (ΔYI, ASTM E313-73, D-1925) as a function of exposure energy in xenon arc (CIRA/soda lime inner and outer filters) testing [193] of three materials: standard polycarbonate (PC), polycarbonate stabilized with low-molecular-weight UVA (UV-PC), and a low-ITR copolymer [194]. The advantage of the ITR resin in retaining color is clearly seen compared to standard PC and the UV-PC grade. After about 3000 kJ (~1 year) of exposure, the photo-Fries products at the surface screen the UV radiation, and the rate of discoloration is dramatically reduced. The enhanced performance of the ITR resins is also seen in the change in light transmission (Δ %T) and haze (Δ %H) for the same samples (Fig. 14.20). The ITR copolymer has minimal changes in both %T and %H, while the UV-stabilized polycarbonate control sample loses about 7% of its light transmission, and its haze increases up to 70% after the equivalent of more than 8 yr of Florida exposure. The new UV-resistant copolymers not only demonstrate great retention of their optical properties, but also retain most of their mechanical integrity. After 10,000 kJ of exposure, the copolymers still exhibit ductile failures in instrumented

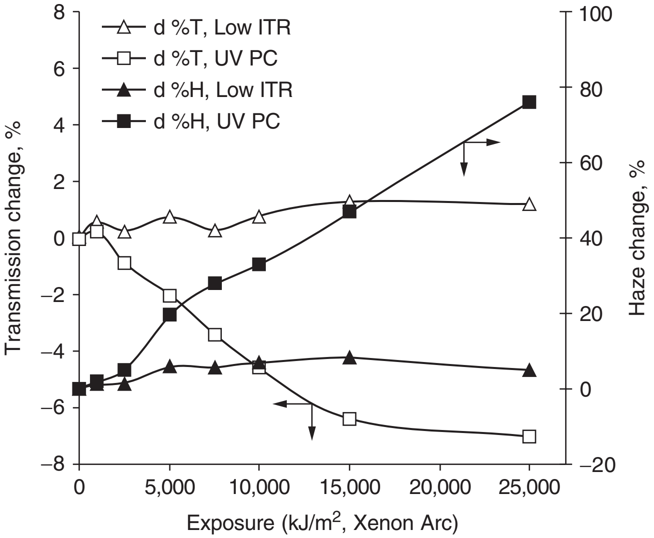

Figure 14.20 Change in light transmission (Δ%T) and haze (Δ%H) during xenon arc weathering [196].

impact tests (ASTM D-3763), whereas the UV-stabilized PC grade exhibits brittle failures after 5000 kJ.

Transparent ITR formulations are also used in refractors for *high-intensity-discharge* (HID) lamps. The refractors have to be able to withstand the combination of intense light (UV and visible) and heat. In addition, for many applications, such as vandal-resistant refractors, high impact strength is also required. The improved color stability of low- and medium-ITR resins over standard PC and UV-stabilized PC homopolymer is shown in tests with a sample surface temperature of 105 ± 3°C and a 400-W metal-halide lamp (Fig. 14.21).

In opaque applications, such as parts for automobiles, agricultural and construction equipment, and boats and personal watercraft, *weatherability* typically means retention of the gloss, color, and physical properties of the resin. Adding and increasing ITR levels will increase the gloss retention of opaque yellow resins upon weathering [199]. For polycarbonate, the gloss remains relatively constant for ~2500 kJ/m^2 and then drops to almost zero, whereas the pigmented ITR resins retain much of their initial gloss (Fig. 14.22). The CIELAB color shift (ΔE) of three samples is less than 2.5 at 6000 kJ (or ~2 yr equivalent exposure to Florida sun).

A comparison of the gloss retention of the ITR-containing resins compared to gel-coated fiberglass typically used in outdoors applications is shown in Fig. 14.23. The data indicate that the ITR-containing resins maintain at least as much of, if not more than, their gloss

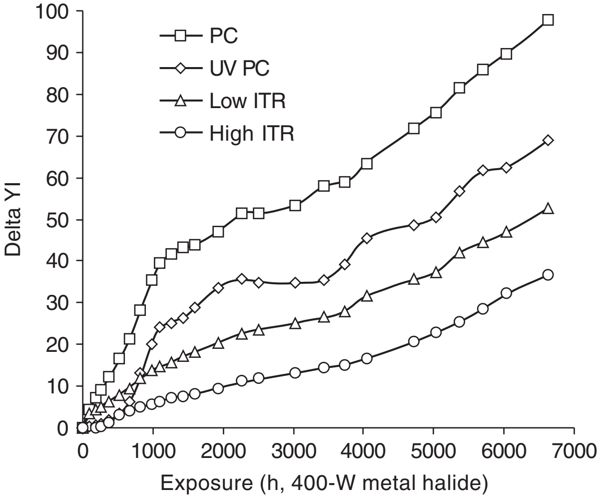

Figure 14.21 Change in yellowness index (ΔYI) during exposure to metal-halide lamp [197].

as the fiberglass parts. In fact, under these test conditions, the black gel-coated fiberglass shows a significant loss in gloss at 6000 kJ (~2 yr equivalent exposure to south Florida sun), whereas both the low- and medium-ITR resins have retained a high percentage of their initial gloss. Thus, the ITR copolymers not only can potentially provide the weatherability of gel-coated fiberglass, but also offer the higher productivity associated

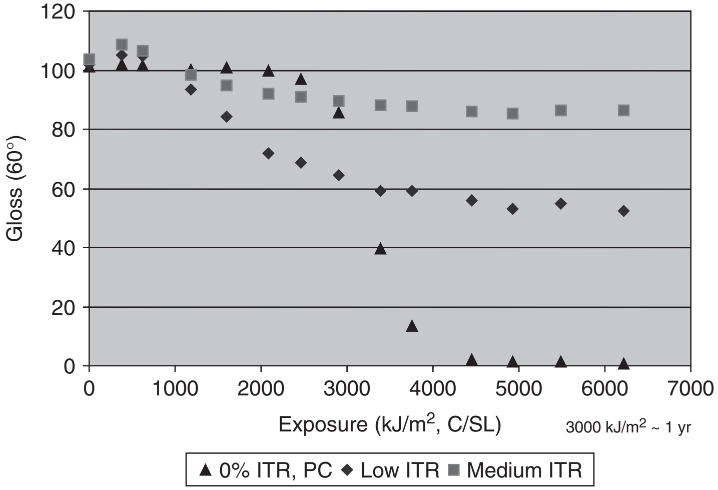

Figure 14.22 Gloss retention of yellow-pigmented, opaque ITR copolymers [198].

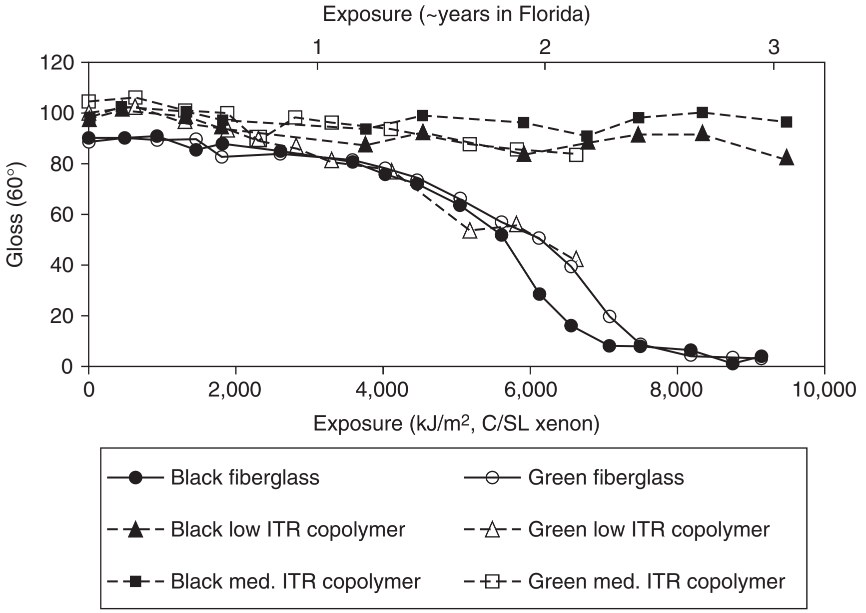

Figure 14.23 Gloss retention of ITR-containing resins compared to gel-coated fiberglass.

with the injection-molding processes. In addition, the ITR copolymers can be extruded into sheet stock (or a cap layer) for thermoforming applications. A comparison of data in Figs. 14.22 and 14.23 shows that the percentage of gloss retention is color-specific.

Often resins used in outdoor applications may come in contact with various chemicals and solvents. The low- and medium-ITR compositions were found to be more resistant to staining from a wide variety of agents than standard polycarbonate alone on samples with no residual or applied stress, as shown in Table 14.5. With hot motor oil, a slight stain was observed with the standard polycarbonate sample. And with unleaded

TABLE 14.5 Stain Resistance of ITR-Containing Resins

Agent	Agent temp, °C	PC	Low ITR	Med ITR
Ethylene glycol coolant/ water, 50/50	82	OK	OK	OK
Motor oil	135	Slight stain	OK	OK
Hydraulic fluid	135	OK	OK	OK
Diesel fuel	23	OK	OK	OK
Unleaded gas	23	Slight stain	OK	OK
Armor All [200]	23	OK	OK	OK
Brake fluid	23	Stains	Slight stain	OK

gasoline, the standard polycarbonate resin exhibited a 5% loss in gloss value as well as staining. No staining was observed on any of the ITR-containing compositions when exposed to these chemicals. As with all applications in which contact with chemicals or solvents may occur, it is imperative that the end user test the resin for suitability for the application and under potential exposure conditions.

These copolymers, containing a high level of ITR, have also been commercialized in a highly weather-resistant film that has the appearance of a paint film. The film is available in transparent and opaque colors. In addition, the film can be made with a metallic look. The film can be used with *in-mold-decoration* (IMD) (see the section "Processing Polycarbonates") molding processes to produce class A automotive exterior parts. Because the film contains very high levels of the ITR resin, it has an excellent balance of scratch resistance, weatherability, chemical resistance, and thermal performance.

New copolymers for optical storage media. A family of copolymers [201, 202] has been developed based on the bisphenol of TMC [1,1-bis(4-hydroxyphenyl)-3, 3,5-trimethylcyclohexane] and bisphenol M [4,4-(metaphenylene diisopropyl) diphenol]. These materials have a unique combination of good melt processability, low moisture absorption, and a T_g of >120°C (248°F), all of which are necessary properties for substrates used for high-density magnetooptical storage discs (Fig. 14.24). The substrate for these discs needs to have excellent transparency, thermal resistance, low birefringence, low moisture absorption, and low hydrolytic expansion coefficient, plus be able to provide good replication of the pits and grooves on the mold surface. Once metallized, if these discs have been prepared from substrate resins that absorb more than 0.2% moisture, then they will tend to warp

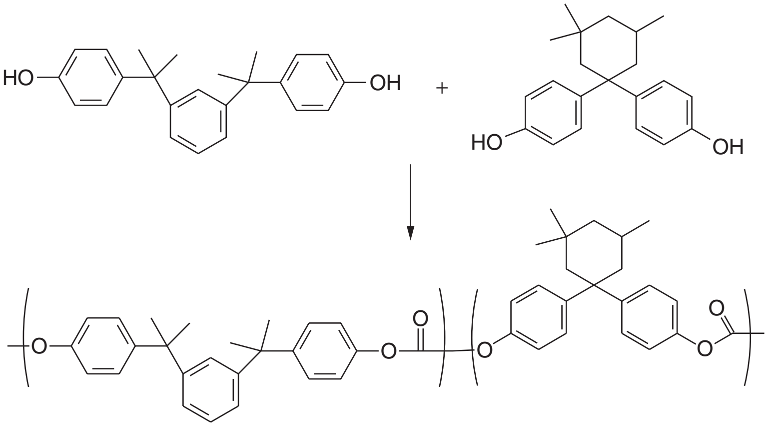

Figure 14.24 Copolycarbonates for optical data storage applications.

to such an extent that they will cause an unacceptable number of tracking errors. Increasing the number of bisphenol M carbonate units in the composition leads to a decrease in moisture absorption (and hence in disc warpage or deflection), plus also decreases the T_g of the resins (Table 14.6).

Control of the TMC bisphenol carbonate level (~20 to 80 mol %) in the polymer chain is used to obtain the appropriate T_g [125 to 150°C (257 to 302°F)] to balance the melt processability with the HDT requirements. Advantageously, both monomers contribute to the greater hydrolytic stability and lower birefringence relative to BPA-PC. That is, both TMC-PC homopolymer and BPM-PC homopolymer have lower moisture expansion and lower birefringence than BPA-PC. But compositions with high levels of TMC bisphenol carbonate could not be molded into discs with low birefringence because of their high T_g and high melt viscosities. Discs from BPA homopolymer had unacceptably high water absorption.

Applications Using Polycarbonates

When it comes to commercial use, common thinking is that most materials can be categorized as either commodity products, where huge volumes are consumed in a few mass-market applications, or specialty products, where use is confined to a larger number of small-volume, niche applications and the material often carries a significant price premium. In such a situation, the *80:20 rule* generally applies. That is, a relatively small number of applications account for 80% of the material's total market volume. The remainder is consumed by a broader number of applications, none of which accounts for more than 20% of the material's total market use. This applies to plastics as well as to metals, wood products, dimensional stone, concrete, and other materials of construction. Whether the polymer is polyethylene (widely used in garbage bags, film, and packaging) or polyethylene terephthalate [(PET) primarily used for bottles and fiber], or polyvinyl chloride [(PVC) which is heavily consumed for pipe, siding, and window lineals], a relatively small number of applications account for most of the resin's sales [205].

Polycarbonate, however, may prove an exception to this type of categorization. No single application category accounts for more than 10% of this polymer family's total market volume. Polycarbonate, copolycarbonates, and polycarbonate blends have essentially evolved as moderate-volume, specialty engineering thermoplastics serving a broad range of niche markets. In fact, most major resin suppliers producing polycarbonate offer at least 500 grades commercially. This unusual situation can likely be explained by several factors.

First, polycarbonate offers a broad palette of physical, mechanical, and aesthetic properties, allowing it to serve many different types of applications requiring quite different properties. Its performance profile offers

TABLE 14.6 Low Moisture-Absorbing Copolymers for Use as Optical Disc Substrates*[203–204]

Ratio of constituents	Units	Properties of Copolymers						
TMC biphenol		50	40	60	100	50	0	10
Bisphenol M/BPA		50	60	40	0	50	100	90
Resin properties								
T_g	°C/°F	147/297	135/275	133/271	232/450	189/372	143/289	115/239
Water absorption	wt %	0.15	0.12	0.16	0.30	0.30	0.31	0.14
MFR [280°C (536°F), 2.16 kg (4.76 lb)]	g/min	70	90	68	No data available	4.5	65	100
Disc properties								
Stress optical coefficient	cm^2/dyn	3.90×10^{-12}	4.00×10^{-12}	3.80×10^{-12}	†	6.70×10^{-12}	8.20×10^{-12}	4.60×10^{-12}
Retardation‡	nm	20	24	20	†	61	68	45
Disc deflection or warpage	mm/in	0.20/0.008	0.15/0.006	0.20/0.008	†	0.35/0.014	0.40/0.016	No data available

*Data obtained from U.S. Patent 5,633,060 (1997).

†Melt viscosity too high to mold a disc.

‡Measured with an ellipsometer at an incident angle of 30°.

broader applicability than either higher-volume commodity resins or specialty niche resins. Of course, polycarbonate's broad performance, while useful in a larger number of application areas than most other polymers, is not capable of solving all issues in every market segment.

Second, polycarbonate resins can easily be modified, blended, and tailored to meet market demands in many different arenas.

Third, because polycarbonate has acquired a unique status as a broadly based specialty polymer, it sells in higher volume and therefore offers a more attractive price position than would normally be expected of a specialty material.

Thus, polycarbonate can be challenging to categorize by market or application since many of its uses are highly technical and focused in a large number of niche segments. Perhaps an easier way to categorize applications in polycarbonate is to differentiate by key properties that help make the polymer commercially successful. A list of the "top 10" most useful properties would include

- Transparency
- Toughness
- Stiffness and strength
- Dimensional stability
- Moldability
- Facility to paint, decorate, and finish (via secondary operations)
- High aesthetics
- Inherent flame retardancy
- Thermal stability
- Agency approval for certain medical and food-contact uses for certain grades

While any one or two of these properties can be met by other polymer systems, it would be difficult to find a single family of materials that can provide all these properties simultaneously. Hence, the more of these properties that are required for a given application, the more that polycarbonate becomes the obvious material of choice.

Water-clear transparency is probably the single unique and most important attribute of polycarbonate. It is of such importance because there are very few transparent polymers—especially with high optical properties. The vast majority of polymers are opaque, with a few families providing degrees of translucency. And while it is certainly true that polycarbonate is of interest in applications other than those requiring clarity, it is also true that approximately one-half of all the polycarbonate sold is formulated to be transparent. The remainder is shared between opaque and translucent applications.

By first segregating polycarbonates into transparent and opaque applications and then reviewing other combinations of properties—in conjunction with transparency or opacity—that make this resin appropriate for a given application, its breadth of use begins to become clearer in the sections below. Then, by subsequently looking at blends of polycarbonate and other polymers, some unique applications will also be covered.

Typical applications for transparent grades

Two of polycarbonate's premier attributes are toughness and transparency. There are relatively few polymers (or other materials) that offer both of these properties—especially when combined with other polycarbonate attributes such as lightweight strength and high levels of impact resistance. Applications where this combination of properties is required include

- Compact discs
- CD-ROMs
- Refrigerator crisper trays
- Lighting fixtures
- Automotive headlamps
- Prescription eyewear
- Blow-molded 5-gal water bottles
- Safety face shields and glasses
- Aircraft windows
- Bullet-resistant glazing
- Architectural window glazing
- Automotive moon roofs and sunroofs
- Automotive side window glazing
- Aircraft jet canopies

Another property combination offered by polycarbonate is transparency with inherent, nonhalogenated flame retardancy. There are many applications where it is desirable to be able to "see" electrical connections, or where transparency helps make an application less obtrusive, such as telephone connector jacks. Still other applications exist where it is beneficial to have a window in an enclosure to be able to observe what is happening inside a device. Especially in applications where transparency, flame retardancy, and lightweight impact strength are needed, polycarbonate is an ideal replacement for glass and lower-performing or higher-cost transparent polymers.

A combination of weatherability and break resistance, along with transparency, helps polycarbonate penetrate numerous applications such as automotive and outdoor light lenses, backlit and unlit signs, and architectural glazing. The material's excellent outdoor-weathering performance, impact strength, and low mass help reduce breakage while lowering cost and weight.

Polycarbonate's ability to provide high thermal performance, resistance to steam and ethylene oxide (EtO) sterilization, biological nonreactivity, and clarity has led to its use in thousands of different types of disposable medical devices, including Leur fittings, valves, blood bowls, dialysis tube holders, bottles, and containers of various sizes and shapes. Dimensional stability, strength, and ductility are also helpful attributes in such applications. Polycarbonate is not recommended for long-term contact with body tissues or fluids, or for implantation in the human body. Medical plastics are among the most highly regulated polymers, and they must be compliant with numerous global regulations. In the United States, Food and Drug Administration (FDA) and *U.S. Pharmacopeia* (USP) class VI recognition are usually necessary. Compliance with Tripartite Guidelines and with the *International Organization for Standardization* (ISO) 10993 requirements has become nearly a global requirement. In general, medical polymers have more restrictions in terms of the types and levels of stabilizers, additives, and colorants that may be used. These additives tend to be more costly (since they are more specialized and "cleaner" than those used for standard grades), causing medical grades of polycarbonate and other polymers to carry a price premium. Additionally, with medical grades, it is not uncommon for one or more properties to be somewhat lower than those offered by a standard offset, again owing to these restrictions.

Among medical-grade polycarbonates, a special subsection of products is designed to withstand gamma (γ) irradiation. Due to the high energy of γ radiation, virtually every structural unit in a polymer backbone is susceptible to reaction. Hence, polymers designed to survive γ irradiation must provide various pathways to dissipate the absorbed energy. First-generation γ-resistant grades of polycarbonate were introduced in the 1980s and based on various low-molecular-weight, radical-scavenging stabilizers. Next-generation technology, introduced in the 1990s, was more complex and incorporated high levels of multiple types of additives and/or miscible polymer blends.

Still another important area of use for transparent polycarbonates is in food-contact applications. This category shares similarities with the medical market in that it requires agency approvals and has restrictions on allowable stabilizers, additives, and colorants, yet it also differs in many important ways. Food-contact regulations govern the type and amount of low-molecular-weight species that can be extracted from the polymer under test conditions designed to simulate short-term and extended food-contact situations. Materials are approved for contact with certain classes of foods (e.g., fats, fluids, acids, dry goods) under specified temperature ranges and other end-use conditions. Typically, polycarbonate does very well in such tests under most conditions. Unlike in medical situations, almost all uses of polycarbonate in food-contact applications are permanent, not single-use (disposable). Typical food-contact applications for transparent polycarbonate include measuring cups, salt and pepper shakers, bowls, dispensers, containers, glassware, and goblets. In most cases, food containers made of glass that are used at temperatures below 121°C (250°F) can be converted to polycarbonate. It is often common to cross-qualify a new grade of polycarbonate for both medical and food-contact applications.

A further specialization within the food-contact arena is for bottled water—both large, refillable, and reusable bottles and small, single-use containers. In fact, bottled water is a sizable global application for polycarbonate. It has very specific requirements that are often stricter than those for conventional food-contact applications. In the United States, containers for bottled water not only require FDA food-contact approval but also must comply with the *International Bottled Water Association* (IBWA) requirements, with particular emphasis on the presence of formulation ingredients that could leach out and affect the taste of the water. Small water bottles are made from many types of plastics, including polyethylene terephthalate, but the larger 19-L (5-gal) containers are almost always blow-molded from polycarbonate. The high strength of polycarbonate allows for lighter containers, and its resistance to breakage increases bottle life over PET. Standard linear polycarbonate homopolymer lacks sufficient melt strength to blow-mold these large containers, so a branched form with higher melt strength and melt fluidity at high shear rates allows a good parison to be extruded or injection stretch blow-molded. These formulations are also designed to provide minimal melt fluidity at low shear rates, so the parison will maintain its dimensions while hanging, but can still be blown out easily to form the container's final dimensions.

Typical applications for opaque grades

Aside from clarity, the same combination of properties that helps polycarbonate succeed in transparent applications also helps these materials be selected for a large number of applications where opacity is not an issue. Since most polymers are naturally opaque, there is potentially a greater pool of viable competitors for each opaque application. Nonetheless, there are still numerous situations in which polycarbonate's other attributes make it the material of choice.

Where clarity is not an issue, polycarbonate's next most important property is very high impact resistance and ductility for a rigid polymer. While its initial properties in this area are already excellent, it can be improved even further with modifiers, extending the properties to thick-wall sections, lower-temperature conditions, and high-strain-rate applications. The excellent ductility of the starting matrix means that much lower levels of impact modifiers can be used—on the order of 20 to 40% less than with competitive polymers—to achieve comparable performance. This is a distinct advantage for polycarbonate because many of the tradeoffs usually associated with the use of impact modifiers can be avoided or minimized, such as reduced strength, modulus, and hardness, owing to the low T_g of the modifiers and reduced flame retardancy, since most of these rubbery additives are quite flammable. Other properties that can be negatively affected by the need to add high levels of impact modifiers include viscosity, melt fracture, shear sensitivity, high-temperature melt stability, surface appearance, colorability, weatherability, and the ability to perform secondary finishing operations (e.g., painting or plating). Fortunately, polycarbonate suffers less property degradation than other thermoplastics, owing to the lower levels of impact modifiers needed to achieve the required performance.

Hence, a great many applications for opaque polycarbonate make use of impact-modified products, including

- Automotive components (e.g., instrument panels and airbag deployment doors)
- Safety products (e.g., hardhats, protective earmuffs)
- Athletic gear (e.g., football, baseball, and motorcycle helmets, and supports, braces, and pad reinforcements)
- Communications devices [e.g., pay phones, housings for laptops, *portable data assistants* (PDAs), cell phones, and other multifunctional converged communications devices]

Interestingly, chemical resistance of polycarbonate can often be improved through the use of marginally compatible impact modifiers. This is so because the impact modifiers lower the yield stress of the polymer, allowing ductile yielding, rather than crazing or brittle crack propagation, to occur during chemical attack. Since some of these materials are prone to delamination during processing, they are usually restricted to conversion via low-stress processes such as extrusion, thermoforming, or low-shear-rate injection molding. They are commonly used to produce food service trays and containers for commercial food operations for hospitals, airplanes, hotels, prisons, and schools. When products based on miscible blends are combined, an even higher level of chemical resistance is possible. Such grades are generally used to make food preparation utensils and containers for the housewares market.

Glass-filled (GF) grades of opaque polycarbonate are frequently used to make housings for small equipment, handheld power tools, electric motors, and small appliances. Glass reinforcement provides greater dimensional stability, rigidity, and flame retardancy, but the loading level must be balanced between achieving a higher modulus and a resultant loss in impact strength. At higher loading levels of glass, improved flow and impact strength are often achieved by using polycarbonate copolymers rather than homopolymer matrices. Use of aliphatic segments increases flow without loss of impact (see the section "High-Melt Flow Copolycarbonates for Thin-Wall Applications"). And the surface appearance of these GF copolymer products improves, since the copolymer prevents glass fibers from being forced to the part surface during molding.

A subset of GF opaque polycarbonate materials is that for structural foamed components for applications such as the housings for *automated-teller machines* (ATMs). The engineering structural foam process is used to injection-mold very large, thick-cross-section parts with rigid cellular walls that are significantly lighter than their solid counterparts would be. Foaming, which can be accomplished with chemical blowing agents or gas, reduces mass while maintaining stiffness and impact in low-stress, lower-weight, and lower-cost parts.

Excellent aesthetic properties with high impact strength are another reason that opaque polycarbonate is commonly specified for applications. Since the resin has no significant base color or opacity of its own, it can be subsequently colored to just about any possible endpoint, allowing hues (e.g., high-chroma colors) to be achieved that can only be produced in clear, glassy polymers. Similarly, a wide variety of special-effects packages can be readily used in polycarbonate to create faux stone, wood, metal, and other special effects. Common applications where high aesthetics, coupled with impact strength, make polycarbonate the material of choice include backlit and unlit outdoor signage and high-gloss, class A automotive exterior appliqués, positioned between pillars and window glass. UV hardcoats help enhance long-term weatherability.

Flame-retardant (FR) applications are also an important area of use for opaque grades of polycarbonate. When the final product is opaque, a wider range of FR additives (many capable of providing higher levels of flame retardancy) are available than can be used with transparent grades. Key applications for FR opaque grades include housings and chassis for business equipment, components for aircraft interiors, and connectors and housings for electrical devices. Polycarbonate provides flammability resistance, ductility, thermal performance, and low cost compared to competitive systems.

Specialty grades of polycarbonate are used in wear applications (e.g., computer keyboards) where higher thermal performance is needed, coupled with a low coefficient of friction.

In applications requiring higher thermal performance, a polyestercarbonate copolymer has been developed with an HDT that is 28°C (50°F) higher than that of standard polycarbonate homopolymers (see the section "Polyestercarbonates and Other High-Heat Polycarbonates"). The most common use of this material occurs in automotive headlamp applications, where the copolymer forms the metallized reflector, and in animal cages that require repeated autoclave sterilization.

Typical applications for polymer blends

Producing polymer blends is another major area of use for polycarbonate materials. The most important commercial families include

- Polycarbonate/acrylonitrile-butadiene-styrene (ABS) blends
- Polycarbonate/acrylonitrile-styrene-acrylate (ASA) blends
- Polycarbonate/polyetherimide (PEI) blends

Each of these families has been created to fill performance or cost targets around polycarbonate that are more effectively met via a polymer blend approach.

Polycarbonate has long been blended with partially miscible, crystallizable thermoplastic polyesters, such as *polybutylene terephthalate* (PBT) and polyethylene terephthalate, to create alloys that feature improved chemical resistance while maintaining much of polycarbonate's inherent impact strength. These products are heavily targeted toward automotive exterior-body components where both impact strength and resistance to gasoline and other aromatic hydrocarbons are required. The largest-volume applications have been in bumper systems, although these materials have also been used in vertical body panels and cladding. PC/PBT blends—both weatherable (molded-in color) versions and grades that were subsequently primed and painted—have been injection-molded for front and rear bumper systems globally for decades. Similar blow-molding grades have been used on vehicles in Asia and North America. Still other polycarbonate/polyester blends are used in lawn and garden equipment and weatherable automotive-exterior components, such as mirror housings.

Polycarbonate/ABS blends are used as a lower-cost, slightly lower-performing option in very price-sensitive segments where thermal requirements are somewhat lower than those of standard polycarbonate. Two basic formulations of PC/ABS blends are generally used: flame-retardant (FR) and non-flame-retardant grades.

Flame-retardant PC/ABS blends are widely used for housings for computer and business machines, portable computer housings, handheld scanners, and battery packs. FR versions usually use nonhalogenated, low-molecular-weight systems that provide dramatically increased flow to fill out complex geometries in thin walls. As would be expected, the heat distortion temperature values of these blends tend to be significantly lower than those of neat polycarbonate.

Non-FR grades of PC/ABS blends are primarily used in automotive components (e.g., interior-trim panels, knee bolsters, and nonstructural interior filler panels) where cost is an issue and thermal requirements do not necessitate use of a more expensive polymer such as PC, but ductility is important.

A desire for enhanced weatherability coupled with excellent physical properties led to the development of formulations using PC and ASA. Primary segments that use these blends include automotive and construction, particularly for exterior applications where reduced gloss is preferred. In the automotive arena, exterior-trim pieces, appliqués, and mirror scalps and housings are commonly molded in PC/ASA blends. In construction, lineals for premium window systems—particularly those in dark or high-chroma colors requiring higher thermal performance than vinyl—are the most common use. Polycarbonate contributes higher strength and better physical properties to the blend, while ASA contributes higher resistance to UV degradation.

For applications where polycarbonate homopolymers or copolymers lack sufficient thermal performance, blends with polyetherimide (PEI) are often used. PEI, which also contributes excellent flammability and low smoke generation to the alloy, may be combined with either straight polycarbonate or polycarbonate blends, depending on what other properties are required. The most common uses are found in light reflectors for automotive headlamps, components for aircraft interiors (especially wall and ceiling panels), and food-contact applications for microwave-to-table cookware.

Polycarbonate Part Design

Polycarbonate resin's exceptional impact strength, transparency, and practical toughness establish it as a premier material for a variety of very demanding applications across diverse industries.

Design calculations used with polycarbonate resin are no different from those for any other thermoplastic material. Physical properties of all thermoplastics are dependent on the expected temperature and stress levels as defined by the application's end-use environment. Standard engineering calculations can be used to predict part performance for polycarbonates. It is important to take into account the notch sensitivity inherent to all engineering thermoplastics. As with many types of plastics, polycarbonates may show reduced hydrolytic stability under some exposure conditions, depending on the specific test method used.

In general, polycarbonate exhibits excellent mechanical property retention over a wide temperature range with only slight loss of strength and stiffness through elevated temperatures up to 120 to140°C. However, as temperatures decrease, polycarbonate (just like all materials) becomes slightly stiffer and slightly more brittle. At sufficiently low temperatures, polycarbonate will become more brittle upon impact. The temperature at which this occurs is called the *ductile-brittle transition temperature*. As with all engineering plastics, this transition is very dependent on the molecular weight of polycarbonate used, the effect of degradation through processing, and the design of the component, as well as the specific test method used.

The ductile-brittle transition temperature of each part molded of polycarbonate resin may indicate the overall robustness of that part and may give indications as to the longevity of the part in the end-use environment. The lower the ductile-brittle transition temperature, the more robustly the component may perform and the longer the part may last, assuming proper design and processing.

Another aspect that affects impact performance is design. As with all engineering materials, the larger the designed radii that are present within an application, the greater the likelihood that the part will behave in a ductile manner upon impact (Fig. 14.25). Sharper radii concentrate

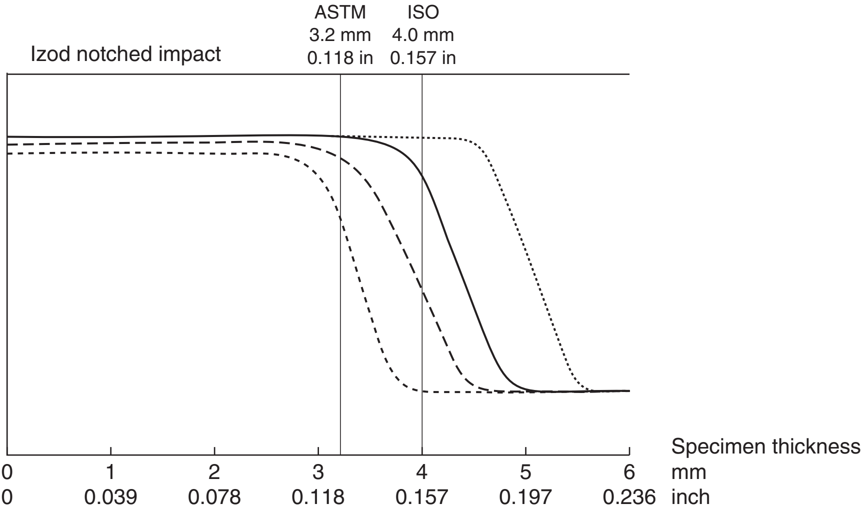

Figure 14.25 Effect of design radii on Izod impact strength of generic polycarbonate samples [206].

the deformation in a smaller region, thus effectively increasing the strain rate, which can lead to lower fracture energy at failure. Larger radii will spread the deformation out over a greater area, which may result in a more ductile performance.

Typically, resin suppliers will recommend the highest-molecular-weight grade available to provide the most robust solution for a given set of application requirements. In addition to higher-molecular-weight neat resins, newer product offerings include siloxane-based polycarbonate copolymers, which can provide enhanced ductility at very low temperatures as well as lower notch sensitivity (see the section “PC-Siloxane Block Copolymers”). These very robust copolymers are typically used in high-performance environments where standard polycarbonate would not provide sufficient properties, such as high-fatigue mobile phone covers continuously exposed to skin oils; vandal-resistant industrial items including postal box and automated teller machines; and high-performance personal protection equipment, such as hockey masks.

Processing Polycarbonate

The wide variety of applications in which polycarbonate materials are used demonstrates the inherent versatility of this family of polymers to be designed into parts of varying size and geometry, to provide a range of physical and mechanical performance, and to be amenable to different means of manufacturing. To obtain parts as divergent as large extruded sheet for barrel-vaulted skylights, blow-molded bottles, intricate medical components, and optical storage discs, rheology is a critical property for selecting polycarbonate grades in terms of both part and process design.

Polycarbonate processes

Injection molding. It is possible to injection-mold polycarbonate with as little as 35 N/mm^2 clamping force, but more commonly used pressures fall between 40 and 50 N/mm^2. For complex, thin-wall components requiring fast injection speeds, combined with high injection pressures, a clamping force of up to 80 N/mm^2 is required. Careful attention to the right tool and equipment combination is critical for such complex thin-wall parts.

When one is injection-molding polycarbonate, it is important not to subject the melt to long residence times as this can cause material degradation and a subsequent drop in properties. The ideal maximum residence time is between 6 and 12 min, depending on the selected melt temperature. When one is processing standard polycarbonate grades on the upper limit of the melt temperature range, it is recommended that the shot size be 60 to 80% of the barrel capacity to minimize residence time.

The fastest possible injection speed is desirable due to polycarbonate’s fast setup times, especially when glass-reinforced grades are used.

However, care must be taken to reduce overly excessive shear stresses that may be present, typically at gates and sharp corners. Adequate venting is essential when a fast injection speed is selected. High mold temperatures are desirable for optimum flow, minimum molded-in stress, and optimal surface appearance. For the greatest machine productivity, polycarbonate grades with mold release are used to reduce the amount of ejection force required to remove parts from mold cavities. Recent efforts with siloxane copolymers of polycarbonate have shown productivity improvements due to the reduction in surface friction. This allows for ejection at higher part temperatures due to reduced ejection forces.

Standard injection-molding guidelines should be followed to maximize the quality and productivity that can be achieved while using versatile polycarbonate resins.

Extrusion and blow-molding. For lineal or larger parts, extrusion processes are typically used with polycarbonate. While the melt strength of polycarbonate is not as high as that of other high-melt-strength resins such as *ultra-high-molecular-weight polyethylene* (UHMWPE) or acrylonitrile-butadiene-styrene, large complex parts can be readily produced. To increase the melt strength, special branched grades have been developed that facilitate large part blow-molding and the extrusion of complex profiles (see the section "Reengineering the Molecule"). Since the viscosity, and therefore melt strength, of polycarbonate varies greatly with melt temperature, care must be taken to minimize the in-process fluctuations of processing temperatures. This applies equally to extruded sheet stock, film, and fiber and shapes.

In-mold decoration. With the broadening use of polycarbonate-based resins in consumer items such as mobile phone handsets and external automotive panels, the need for rapid, paint-free part decoration is beginning to be met via in-mold decorating solutions. In this process, a decorative film is placed in the cavity side of an injection-molding tool, the tool closes, and a resin substrate is injected behind the film for rigidity. Due to the broad performance capabilities represented by the various copolymers and blends of polycarbonate, the choices of film and substrate can meet a variety of unique product requirements while still providing the adhesion needed between the two materials. Typically, choices for the decorative film are driven by color, texture, and weatherability requirements, while the substrate resin is chosen primarily for processability in order to adequately fill the part without damaging the film.

Process controls

Viscosity. Polycarbonate resins are available in a wide range of viscosities, as shown in Fig. 14.26. These are obtained by producing grades with

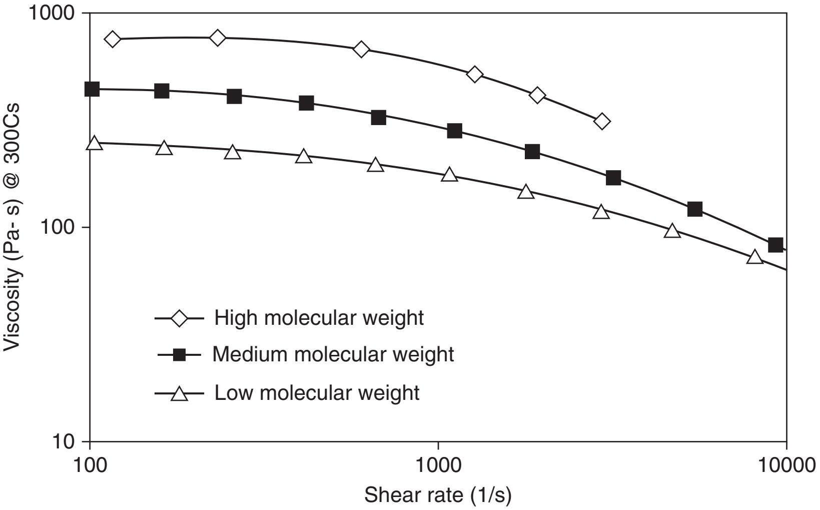

Figure 14.26 Polycarbonate resins are available in a broad range of melt viscosities, determined by the molecular weight of a given grade [207].

different molecular weights (with higher-molecular-weight grades having a higher viscosity). The portfolio ranges from ultralow-viscosity resins typically used for optical-quality storage discs [*compact discs/digital-video discs* (CDs/DVDs)], to very high-viscosity grades for multiple-wall extrusion and blow-molding applications. Although their rheology is still nonnewtonian, polycarbonates exhibit a very low degree of shear-thinning behavior compared with other thermoplastics.

Managing stress. Short- and long-term part performance in polycarbonate can be dependent on the amount of stress due to processing in addition to the stress predesigned into the application. Higher levels of stress can reduce part ductility and chemical resistance and therefore can greatly affect part life. Stress analyses on high-stress areas of a part are often done during the initial stages of the part's design. However, standard engineering equations give average stresses over an area and do not always indicate maximum stresses that may be caused by stress concentrators.

One common stress concentrator is a notch, since polycarbonate is very notch-sensitive. For example, a polycarbonate resin bar that has a notch with a 0.254-mm (0.010-in) radius will break with yield under lower forces when bent in the center compared to an unnotched bar. The material is not brittle; however, the notch concentrates stress to a value above the typical 66.2-MPa (9600-psi) flexural strength of polycarbonate, and it breaks more easily. The sharper radius concentrates the deformation across a smaller effective gauge section, for practical purposes reducing the apparent strength of the material. Another bar that has a 0.762-mm (0.030-in) radius tears in a more ductile mode, requiring a much greater force, because the deformation is spread across a large effective gauge section. In this case, the stress is distributed over a much larger area, and the maximum stress in the notch is between the 62.1-MPa (9000-psi) yield and the 66.2-MPa (9600-psi) break point for polycarbonate.

Equipment and machinery designs

Predrying. Polycarbonate resin must be thoroughly dried before molding to ensure optimum part performance and appearance. The typical recommended drying temperature is approximately 120°C (248°F). The time required to achieve sufficient drying is dependent on the type of dryer used (desiccant-bed dehumidifying dryers are typical) and varies from 2 to 4 h. Target moisture content should be a maximum of 0.02%. Excessive drying times of more than 24 h will usually not affect the physical or mechanical properties of the polymer; however, this situation might decrease release performance during processing due to driving off of low-MW release agents at prolonged exposure to elevated temperatures. Grades that are impact-modified may be affected by changes in the impact modifier during drying. Hence the manufacturer's drying guidelines should be consulted.

Equipment. In processing polycarbonate, screws with a high compression ratio or a short compression zone should not be used, to adequately convey and pressurize the melt stream. It is recommended that a conventional three-zone screw with a *length-to-diameter* (*L*:*D*) ratio of between 20:1 and 25:1 and a compression ratio of between 2:1 to 2.5:1 be used. Conventional materials of construction for screws and barrels are acceptable. However, screws and cylinders of a bimetallic type with high abrasion and corrosion resistance are preferred, especially in processing glass-filled polycarbonate grades. Note that use of a vented barrel and screw is not a satisfactory alternative to proper predrying and is therefore not recommended. If a vented barrel is used, then the level of moisture present in the material and the injection unit's percentage of available shot capacity will both have considerable influence on whether degradation is encountered as a result of hydrolysis.

The most common processing issues in working with polycarbonate-based resins are appearance defects. The most common type of aesthetic defect is the appearance of contaminant inclusions within transparent parts, commonly known as black specks. These defects are usually found to be degraded resin—either within the polycarbonate stream or from other resin sources—and occur when charred material, which has formed over time on the surface of the processing equipment, breaks away and enters the melt stream. This defect is typically addressed by practicing adequate shutdown and start-up procedures as well as standardized purging methods for changing over the equipment from one resin to another.

Other processing issues that can arise with polycarbonates are those that are common to other thermoplastics as well, including splay from underdrying the resin, gate blush and witness lines from high localized shear stresses, and dimensional issues such as part sink marks and voids, which must be addressed via part design if they cannot be corrected by changing processing conditions.

Polycarbonate resins are available in formulations with a wide variety of additive options, such as UV stabilizers and mold-release agents. More recently, manufacturers have expanded their portfolios to include materials that are compliant with the major international environmental standards.

Summary

With unmatched impact resistance, outstanding dimensional stability, and crystal clarity, polycarbonate resin continues to be a major volume and sales leader in the world of engineering thermoplastics. Polycarbonate resin provides designers with new opportunities for innovative, cost-effective products such as eyewear, compact discs, kitchen containers, and business equipment. Through ongoing resin development and further enhancements via blending technology, the performance portfolio offered by this versatile family of materials should continue to expand. This, in turn, will open up still greater opportunities for new applications and greater market growth for polycarbonate-based resins. Perhaps over the next 50 years, growth of these versatile materials will outpace that seen in their first half-century.

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Chapter 15

Reinforced Poly(Phenylene Sulfide)

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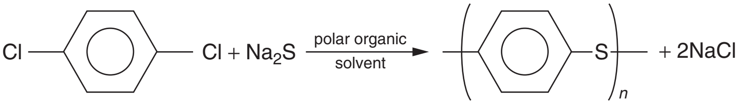
Poly(p-phenylene sulfide) (PPS) has a repeating structure composed of alternating sulfur atoms and 1,4-phenylene groups. PPS has a useful combination of thermal, chemical, mechanical, and electrical properties that has been reviewed elsewhere [1–5]. Combined with good processability [6], PPS has developed significant markets as an engineering plastic since its commercial introduction in 1973. PPS was originally manufactured under the registered trademark Ryton® by Phillips Petroleum Company and by Chevron Phillips Chemical Company LP since 2000. Although many synthetic routes to PPS have been discovered, the only commercially viable route is based on sodium sulfide and *p*-dichlorobenzene using *N*-methyl-2-pyrrolidone as the polymerization solvent.



(15.1)

The 1,4-disubstituted benzene structure in the polymer is determined by the *p*-dichlorobenzene and the direct replacement of the chlorines by sulfur during polymerization. While other isomers of PPS have been studied [7], they do not possess useful or marketable properties and have not been commercialized. Fortunately, the raw materials necessary to make *p*-PPS can be reacted under appropriate conditions to provide the desired polymer structure having sufficiently high molecular weight to be of commercial utility. Both raw materials are relatively inexpensive and available.

Edmonds and Hill Discovery

Edmonds and Hill discovered the first commercially viable process for the synthesis of PPS in 1967 in the laboratories of Phillips Petroleum Company. The patent [8] describing the Edmonds and Hill process was issued that year and effectively prevented others from entering the business until its expiration in 1984. The process involves the reaction of a "polymerizable" sulfur source derived from sodium sulfide and *p*-dichlorobenzene in a suitable polar organic compound at elevated temperature and pressure. *N-methyl-2-pyrrolidone* (NMP) is the preferred polar organic compound. The Edmonds and Hill process is still used commercially for some products manufactured by Chevron Phillips Chemical Company LP. The essential process steps in the Edmonds and Hill process are

- Synthesis of aqueous sodium sulfide from aqueous sodium hydrogen sulfide (or hydrogen sulfide) and aqueous sodium hydroxide
- Dehydration of the aqueous sodium sulfide in the presence of NMP to produce the "polymerizable" sulfur source
- Polymerization of the dehydrated sulfur source with *p*-dichlorobenzene, resulting in a reaction mixture comprising PPS, NMP, and by-products of sodium chloride and water
- Isolation of PPS from the reaction mixture
- Washing of the PPS to remove other reaction mixture components
- Polymer drying
- Optional oxidative heat treatment depending upon the end use of the PPS
- Optional compounding with various reinforcements, additives, etc., depending upon the end use
- Packaging as determined by market requirements

Surprisingly, the synthesis of PPS from sodium sulfide and *p*-dichlorobenzene was developed and optimized without the benefit of understanding the reaction mechanism. As such, the PPS polymerization became recognized for requiring unusual, but essential, features. Most striking was that high-molecular-weight PPS could only be obtained in a few media. NMP is the preferred reaction medium due to its unique combination of attractive price, commercial availability, relatively low toxicity, and effectiveness. The prereaction step in which aqueous sodium sulfide is dehydrated in the presence of NMP is preferred. This step provides a soluble, polymerizable sulfur source. Interestingly, during this dehydration step, some sodium sulfide is hydrolyzed and is liberated in the form of hydrogen sulfide and removed from the reaction mixture in the overhead condensate. The precise amount of hydrogen sulfide that is removed during the dehydration can vary, making precise understanding of the remaining sulfur species unclear. This leads to uncertainty in the stoichiometry of the next step, namely, the molar ratio of sulfur source to *p*-dichlorobenzene. Most unusual for a step-growth polymer, this uncertainty in the monomer stoichiometry has relatively little influence on the molecular weight of the PPS. Many recipes found in the patent literature actually call for a slight molar excess of *p*-dichlorobenzene relative to sulfur species. The resulting polymerization is then carried out at elevated temperature [typically 175 to 300°C (347 to 572°F)] under autogenous pressure for a prescribed period. At the conclusion of the polymerization, the reaction mixture may be cooled, causing the PPS to precipitate from solution. The PPS may then be recovered by filtration.

The PPS produced by the Edmonds and Hill polymerization is an off-white powder and possesses modest molecular weight. Molecular weight determinations by high-temperature GPC [5, 9, 10] suggest that the Edmonds and Hill PPS has approximately 150 to 200 repeating units. Dilute solution light-scattering experiments [11] showed that the weight-average molecular weight M_w is approximately 18,000. The inherent viscosity of PPS having this molecular weight, as measured in 1-chloronaphthalene at 206°C (403°F), is approximately 0.16 dL/g. Such low-molecular-weight PPS displays only modest mechanical properties. The polymer, however, has many useful properties, comprising exceptional chemical resistance, excellent thermal stability, and inherent fire and electrical resistance, which were attractive in the marketplace. The desire to extend these useful properties to higher-molecular-weight PPS having improved mechanical properties fueled the search for synthetic methods to achieve higher molecular weights. Despite its molecular weight limitation, the Edmonds and Hill PPS is useful in coatings and as a feedstock for a variety of "cured" (see curing discussion below) polymers used in reinforced injection-molding compounds.

Campbell Process for High-Molecular-Weight PPS

The Edmonds and Hill process provided modest-molecular-weight PPS that could be applied to a wide variety of applications. One logical application for a thermally resistant, chemically inert, and inherently flame-resistant polymer was fiber. The Edmonds and Hill polymer was, however, not well suited for fiber applications. In the uncured state, the polymer lacked sufficient molecular weight to have good fiber properties. In its cured state, the Edmonds and Hill polymer displayed poor "spinability." It was clear that higher-molecular-weight linear PPS was needed.

The discovery that polymerization additives could have a profound influence on the molecular weight of PPS was made by R. W. Campbell in the laboratories of Phillips Petroleum Company in 1975. The Campbell PPS process is a one-pot synthesis of high-molecular-weight linear PPS directly in the polymerization vessel [12]. PPS made by the Campbell process is "curable" but possesses sufficiently high molecular weight to have useful properties in the uncured state. Examples of applications where PPS made by the Campbell process is particularly preferred include fiber, film, extruded profiles such as pipe, and in reinforced injection-molding compounds and advanced composite materials. High-molecular-weight linear PPS was commercialized by Phillips Petroleum Company in 1979 and continues to be produced by Chevron Phillips Chemical Company LP.

The main distinguishing feature of the Campbell process as compared to the Edmonds and Hill process is the inclusion of a soluble salt such as an alkali metal carboxylate or a lithium halide along with the sodium hydroxide, sodium hydrogen sulfide, and NMP in the formation of the polymerizable sulfur source. The remaining process steps (dehydration, polymerization, polymer recovery, polymer washing, optional curing, optional compounding, and packaging) are nominally the same as those for the Edmonds and Hill PPS process. The polymers produced by the Campbell process are off-white polymers and have a linear structure. Various molecular weights have been reported [13–14] for PPS made by the Campbell process. More recent measurements have been reported [15] for a wide variety of Campbell process PPS. Table 15.1 summarizes the relationship between melt flow and weight average *molecular weight* (MW) for a typical Edmonds and Hill polymer and several polymers of varying molecular weight made by the Campbell process.

Another commercial process for the synthesis of high-molecular-weight PPS is currently being practiced by Ticona. The basic process as originally taught by Kureha Chemical Industry [16] has been reviewed elsewhere [1, 3, 5]. The essential difference of the Kureha process from the Campbell process is the use of a different polymerization modifier. The Kureha

TABLE 15.1 Molecular Weight and Melt Flow of PPS from the Campbell Process

Synthetic method	Polymerization modifier	Melt flow*	Weight average MW
Edmonds & Hill	None	3000	17,600
Campbell	Sodium acetate	385	44,000
Campbell	Lithium benzoate	158	46,040
Campbell	Lithium benzoate	39	69,000
Campbell	Lithium benzoate	15	76,620
Campbell	Lithium benzoate	3	100,800

*Melt flow was measured according to American Society for Testing and Materials (ASTM) test method D-1238, determined at 316°C (600°F) with a 5-kg driving weight, modified to use a 5-min preheat time.

process involves similar dehydration chemistry to that of the Edmonds and Hill process. A low-temperature polymerization is then carried out to produce a "prepolymer." Water is charged to the reaction mixture, and a second, higher-temperature polymerization step is carried out. The polymer is then recovered. The influence of the water in the Kureha process, as well as that of sodium acetate in the Campbell process, has been elucidated by Ash et al. [17].

A variety of noncommercial polymerization processes for PPS have been reported over the last few decades, and most have been reviewed elsewhere [5, 9]. Among these methods are the self-condensation of *p*-halobenzenethiolate salts [18–19], the use of *N*-methylcaprolactam, a higher-boiling homolog to NMP [20–21], as the polymerization medium; the use of a variety of polymerization modifiers [20, 22–25] designed to promote the synthesis of high-molecular-weight PPS; the use of a poly(ethylene glycol) [26] as a reaction medium; the use of a zero-valent palladium catalyst [27] to promote the polymerization of *p*-bromothiophenol in alcohol solvents under mild conditions; the reaction of elemental sulfur with diiodobenzene [28–36] to produce a poly(phenylene sulfide)-*co*-(phenylene disulfide); the thermolysis of bis(4-iodophenyl) disulfide [37] to produce PPS and elemental iodine; the oxidative polymerization of thiophenols and phenyl disulfides [38–44]; and the use of pentamethylcyclopentadienylruthenium(II) π complex to activate *p*-dichlorobenzene toward nucleophilic displacement reactions. Although all these synthetic methods are extremely interesting, none has apparently played a significant role in commercial manufacture of PPS.

PPS Polymerization Mechanism

The PPS polymerization is much more complex than might be suggested by the deceivingly simple overall equation. Detailed discussions of studies elucidating the mechanism for the PPS polymerization have been previously published [5, 45]. While the PPS polymerization can be described by a series of conventional [46–47] A-A + B-B step-growth condensation reactions, many experimental observations, however, deviate significantly from classical predictions. Among the most striking deviations is that the polymer yield and molecular weight are observed [48–53] to be significantly higher at early (i.e., incomplete) conversion of monomer than expected from classical step-growth theory. This deviation has been responsible for several mechanistic interpretations including the *single electron transfer* (SET) mechanism involving radical cations [48–49] as key intermediates, as well as more traditional nucleophilic aromatic substitution (S_NAr) having unequal reactivity of key intermediates [45]. In their detailed study, Fahey and Ash showed that the PPS polymerization is much more complex than expected with the solvent NMP participating in the dehydration step to provide a key intermediate. NMP reacts with Na_2S and H_2O

during the dehydration to produce *sodium N-methylaminobutanoate* (SMAB) and sodium hydrogen sulfide. SMAB functions in at least two important ways in the PPS polymerization. First, it functions to solubilize the sulfur source (anhydrous sodium sulfide and sodium hydrogen sulfide, which are virtually insoluble in NMP [45]), thereby promoting facile reaction with *p*-dichlorobenzene. Second, the amine moiety on SMAB functions to deprotonate thiophenol intermediates, converting them to vastly more nucleophilic thiophenoxide salts in subsequent reactions with aryl halide monomer or growing polymer end groups. In their study, Fahey and Ash provide a logical explanation for the unusual finding that the PPS polymerization proceeds in only a few selected media, with NMP being most preferred.

Another unusual characteristic of the PPS polymerization is that perfect 1:1 stoichiometry does not appear to be necessary for the synthesis of high-molecular-weight PPS. Examples in Campbell's patent for high-molecular-weight PPS [12] typically show 1 to 3 mol % excess *p*-dichlorobenzene relative to the sulfur source. In classical step-growth polymerization, this kind of stoichiometry imbalance would severely limit molecular weight. In the PPS process, however, Fahey and Ash showed that the S_NAr mechanism is the dominant mechanism in the PPS polymerization. It is well known [54] that the rate of reactions occurring by the S_NAr mechanism is responsive to changes in the aromatic ring substituents. Fahey and Ash showed that the rate of chloride displacement from growing PPS chlorophenyl end groups is significantly higher than the corresponding displacement from *p*-dichlorobenzene. The process implications of having greater reactivity for polymer end groups relative to monomer provide a basis for the insensitivity of the PPS polymerization toward monomer stoichiometry.

Postpolymerization Treatments

After recovery from the polymerization reaction mixture, PPS can be further treated in ways that modify the suitability of the polymer for specific applications. These treatments include an oxidative heat treatment (commonly referred to as *curing*), techniques to modify the molecular weight distribution of PPS (typically narrowing the molecular weight distribution by fractionation), and performing cation exchange reactions on PPS to alter the ion-exchangeable species present in the polymer.

Curing of PPS

The first PPS produced commercially was the Edmonds and Hill polymer that possessed only modest molecular weight. Fortuitously, the polymer possessed an inherent trait that allowed it to be converted to a tougher, more useful material simply by administering an oxidative heat treatment. This property of the PPS to undergo “change” during thermal treatments was recognized early in the development of PPS. Prior to PPS becoming a commercial material, Smith and Handlovits [55] recognized that such thermal treatments could favorably alter the properties of PPS while still retaining a thermoplastic nature. Such oxidative heat treatments were referred to as curing of PPS. This, of course, should not be confused with curing of thermosetting polymers that do not have the ability for reprocessing. Cured PPS can be repeatedly melt-processed with minimal changes in properties or processability. Curing is an intentional process step in which the polymer is heated, usually with air exposure, for an extended time. Curing causes several changes in the polymer: Melt viscosity increases, toughness increases, kinetics and extent of crystallinity decrease, and the color gradually darkens (from white to tan, brown, or black depending on the degree of cure. Curing can be carried out either above (i.e., in the melt [56]) or below (i.e., in the solid state [57]) the crystalline melting point of PPS. Curing above the crystalline melting point is typically carried out for applications such as coatings. Melt curing is not used commercially to produce cured feedstocks for reinforced compounds. Solid-state curing, however, is a convenient process for curing large batches of PPS, generally in the range of 170 to 280°C (338 to 536°F). The extent of cure can be followed easily by measuring changes in the melt flow rate of the polymer in a modified version of ASTM D-1238. The rate of solid-state curing is a strong function of temperature. Rapid decreases in flow rate are observed when PPS is cured at higher temperatures. Curing PPS is an exothermic process requiring care to maintain good temperature control. If temperature control is lacking, localized hot spots may develop, resulting in isolated melting of polymer and the production of aggregates. An agitated bed helps alleviate these problems. Table 15.2 shows typical melt flow values for PPS suitable for a variety of applications.

The reactions that occur when PPS is cured remain incompletely characterized, in large part due to the difficulty of analyzing a polymer that doesn’t dissolve [58] in any solvent below 200°C (392°F). It is generally acknowledged that curing PPS results in a complex mixture of reactions

TABLE 15.2 Typical Melt Flow Values for Cured PPS for Various Applications

PPS polymer	Melt flow, g/10 min
Uncured Edmonds & Hill PPS	~3000
PPS for powder coating	1000
PPS for glass- and mineral-filled compounds	600
PPS for glass-filled compounds	60–150
PPS for compression molding compounds	0

that cause loss of low-molecular-weight fragments [59, 60] that may volatilize during the process; thermally induced homolysis of carbon-sulfur bonds, resulting in aryl and thiyl radicals that can react to form biphenyl branching structures; arylthio metathesis [61] (sulfide interchange reactions) that can shift the molecular weight distribution; and oxygen uptake and production of oxidized sulfur moieties [61].

One of the conveniences afforded by curing PPS is that a single uncured polymer can give rise to an entire family of cured polymers having various extents of cure. The various cured PPS polymers can be optimized for specific applications.

Fractionation of PPS molecular weight distributions

Fractionation involves the orderly separation of polymer molecules on the basis of molecular weight, resulting in fractions that have different molecular weights [62]. Fractionation that removes a specific portion of a parent polymer's molecular weight distribution results in the production of an offspring polymer that has a narrowed molecular weight distribution. Alteration of the molecular weight distribution can influence the properties of the polymer, thereby providing a method to customize the properties of a polymer for a specific application.

The polymer recovery technology used to isolate a polymer from its reaction mixture can influence whether or not fractionation occurs. At least two major classes of polymer recovery technology have been disclosed in the patent literature that describes commercial processes. The first commercial recovery process for PPS is a flash evaporation [63–67] process having as a key step the adiabatic removal of a large portion of the solvent. The resultant reaction mixture contains essentially those components that have no or very low volatility. Thus, by virtue of their high boiling points, oligomeric PPS species remain essentially in the product. As such, the flash recovery is essentially a nonfractionating type of recovery. The flash recovery continues to be a viable recovery technique for both Edmonds and Hill PPS as well as higher-molecular-weight Campbell PPS.

The second commercial recovery technique is substantially different from the flash recovery process because the key process steps involve generating a two-liquid phase reaction mixture and subsequently cooling the reaction mixture to produce a polymer slurry comprising relatively large granular particles and very fine particle size solids. The granular polymer is recovered from the reaction mixture by a filtration step, typically carried out by using a sieve to retain the polymer granules. An important distinction from the flash recovery is that this precipitation-filtration process is applied exclusively to high-molecular-weight Campbell PPS. The first publication [68] of this recovery technique disclosed the process of adding water to cause or enhance the formation of a two-liquid phase reaction mixture and subsequently cooling this reaction mixture to form a polymer slurry. Subsequent patents [69–70] have disclosed process variations but retain the common theme of having a compound present in the reaction mixture to promote the formation of two liquid phases. Promoter compounds have been found throughout the PPS patent literature [12, 16], but the composition of the two liquid phases was only determined somewhat later [17]. One liquid phase is polymer-rich and contains all the high-molecular-weight PPS as well as a portion of the low-molecular-weight PPS. The second liquid phase comprises the remainder of the low-molecular-weight PPS. Upon cooling, the phase that contains the high-molecular-weight PPS solidifies into relatively large particles or granules, while the phase that contains only low-molecular-weight PPS solidifies into very fine powdery particles. A simple particle size separation (such as with a sieve) separates the two products. Since a portion of the low-molecular-weight-species is removed by such a separation, this particle formation-filtration recovery is inherently a fractionating type of recovery. The granular PPS product has a reduced oligomer content compared to comparable flash-recovered PPS. Fractionation of the molecular weight distribution for a polymer is well characterized by *size exclusion chromatography* (SEC). SEC of the separated components from a precipitation-filtration PPS recovery process has been published and discussed elsewhere [5, 9]. PPS that is recovered by a precipitation-filtration process has a higher weight average molecular weight compared to comparable PPS recovered by a flash process. Generally, fractionation of PPS polymers by this technique results in products having lower levels of offgassing during melt processing, higher melt viscosity, greater impact strength, and improved tensile strength and elongation.

Ion-exchange treatments of PPS

The properties of PPS can be influenced by ion-exchange treatments. The chemical nature of end-groups on PPS comprises expected end groups (i.e., unreacted end groups expected from the step-growth condensation reactions) as well as unexpected end groups. Expected end groups consist of —C_6H_4Cl and —$C_6H_4S^-Na^+$ (or —C_6H_4SH end groups if the reaction mixture has been acidified). The unexpected end groups arise from side reactions that occur during the course of the polymerization. Table 15.3 summarizes end groups that have been identified on PPS. The relative concentrations of these end groups are not given, as the detection methodology was only qualitative.

The detection of phenolic end groups was accomplished by derivatizing PPS with isotopically labeled acylating agents, followed by high-temperature

TABLE 15.3 End Groups Detected on PPS

End group	Expected?	Found?	How?
—C_6H_4Cl	Yes	Yes	In oligomers
—C_6H_4SH	Yes	No	—
—C_6H_5	No	Yes	In oligomers
—C_6H_4OH	No	Yes	Derivatization
—$C_6H_4NR'R''$	No	Yes	In oligomers

solution NMR [71]. The —C_6H_5 end group is most likely due to competing radical reactions similar to those $S_{RN}1$ side reactions documented in arylene ether step-growth polymerizations [72–73]. The origin of —C_6H_4OH and —$C_6H_4NR'R''$ end groups has been hypothesized [5] to be the result of competing S_NAr reactions of —C_6H_4Cl with OH^- and nitrogen nucleophile of SMAB.

Several of the end groups listed in Table 15.3 are capable of participating in ion-exchange reactions. Among these end groups are thiophenol, phenol, and carboxylic acid resulting from the displacement of chloride ion from chlorophenyl end groups by the nitrogen nucleophile on SMAB. The PPS polymerization is conducted under highly basic conditions, making the conjugate salt the usual form of these acidic end groups. The first recognition that the nature of these ion-exchangeable end groups has a profound influence on the crystallization kinetics of PPS was made by Lopez et al. [74, 75]. Lopez and coworkers were able to show that the bulk kinetics of crystallization were dramatically faster when PPS had a hydrogen ion end group (i.e., the conjugate acid of the naturally occurring salt end groups). The bulk kinetics of crystallization are influenced by two factors: nucleation density and linear growth rate. The linear growth rate was shown to be relatively insensitive to the nature of the end group counter ion. Nucleation density, however, was highly responsive to the nature of the end group counter ion. The conjugate acid form of PPS was found to promote much higher nucleation density. The same trends were also found by Risch [76] and Srinivas et al. [77–78] in studies involving ion-exchange reactions on fractionated PPS. Fractionated PPS containing fewer end groups was found to have an attenuated response toward ion-exchange reactions. The influence of ion-exchange reactions on highly fractionated PPS was essentially negligible.

Ion-exchange reactions on PPS as carried out by buffer washing [79] and acid washing [80] also influence the rate at which PPS cures. Treating PPS with solutions having a pH of 9.25 or less converts PPS to a more rapid-curing form. Such rapid-curing PPS can be converted back to a slower-curing form by treatment with a basic solution having pH greater than 11.6. The reversible nature of this transformation is consistent with a protonation-deprotonation having a pK_a between 9.25 and 11.6.

Applications of Reinforced PPS Compounds

Commercial applications for reinforced PPS compounds generally exploit the plastic material's exceptional combination of resistance to thermal degradation, dimensional integrity at elevated temperatures, resistance to chemical attack, and inherent flame-retardant behavior. It is one of these performance features, or a combination thereof, that leads designers to select PPS. Without the need for such enhanced performance benefits, less expensive engineering plastics will often suffice.

With exceptional resistance to thermal degradation and chemical attack, reinforced PPS compounds will maintain a greater degree of mechanical strength and dimensional integrity with extensive exposure to elevated temperatures and/or corrosive chemical environments. Therefore it is often possible to save material cost by using thinner wall sections than could be used with other engineering plastics. Compared to using thermoset materials, reinforced PPS compounds offer material savings through the ability to recycle scrap and more precise molding tolerances that allow designers to avoid secondary machining operations. Because of their inherent nonflammability, reinforced PPS compounds have UL-94 V-0 ratings without the need for flame-retardant additives. For these reasons, reinforced PPS is often chosen as the insulating material in electrical components exposed to high temperatures in appliances such as toasters, ovens, electric fry pans, steam irons, and hair dryers. Reinforced PPS compounds have also been used for sockets and reflector housings in lighting fixtures. The versatile molding capabilities of using reinforced PPS, along with the ability to do insert molding, often allow designers to incorporate cost savings through multiple-component integration and part consolidation. This has led to many innovative and cost-saving designs for end bell and brush holder assemblies in electric motor applications and for electrical switch and control components.

As an alternative to using metals, reinforced PPS compounds offer the capability to mold complex shapes to tight tolerances, reducing production costs compared to extensive machining operations, while incorporating a reduction in part weight. Since PPS is resistant to chemical attack by common solvents, salts, caustic solutions, and acids, reinforced PPS parts are generally just as corrosion-resistant as metal parts and are often even more corrosion-resistant. This has led to utilizing reinforced PPS, instead of stainless steel and aluminum, in furnace and air conditioning components, such as flue collectors, induced-draft blower housings, secondary heat exchanger headers, and compressor mufflers and reservoirs. Reinforced PPS compounds are also a cost-effective alternative to steel and brass in a wide variety of pump and valve components, such as housings, impellers, shafts, vanes, valve bodies, diverters, seats, and seals. Reinforced PPS compounds are even used in long-life downhole oil field equipment such as centrifugal lift components, rod guides, and rod scrapers.

Automotive components continue to be a growing market for reinforced PPS compounds, which are capable of withstanding mechanical stress and maintaining dimensional integrity even when exposed to common automotive fluids at elevated temperatures. Because of the ability to mold complex parts to tight tolerances, thus eliminating expensive machining costs, reinforced PPS is often chosen as an alternative to metals that also provides weight savings and is resistant to salt corrosion. These features, along with resistance to fuels, oils, and hydraulic fluids, have allowed reinforced PPS parts to replace metal components in fuel pump end caps and impellers, as well as power train and transmission components such as lock-up collars and servo pistons. Having excellent resistance to coolants, even at elevated temperatures, reinforced PPS compounds also often replace metals in coolant system components such as water pump impellers, thermostat housings, and heater core end tanks. The introduction of more chemically aggressive "long-life" coolants has made PPS even more attractive for such applications, compared to the less chemically resistant polyamides and polyesters [81]. Cost savings are often achieved through insert molding capability to facilitate multiple-component integration. Such advantages have allowed replacement of aluminum in a complex motor end cap for an antilock braking system, and replacement of thermoset materials in automotive headlamp sockets, switch components, sensors, and alternator components. As under-the-hood temperatures continue to increase, connectors and other components typically molded from nylons and polyesters may need to be converted to higher-temperature materials. Reinforced PPS may be one the few engineering plastics capable of meeting the new SAE/USCAR-2 Class V standards for electrical connectors capable of 175°C (347°F) service temperatures [82].

Precision molded electrical and electronic components have been a primary application area for reinforced PPS compounds over the past 30 years. Because of their excellent flow and low shrinkage, reinforced PPS compounds are selected for precision molding of thin-walled connectors and sockets, being surpassed only by liquid-crystal polymers in this regard. Trends toward miniaturization in recent years have driven more of these applications to liquid-crystal polymers; however, reinforced PPS compounds still generally offer advantages over liquid-crystal polymers in weld line strength and cost. Compared to polyamides and polyesters, reinforced PPS compounds offer advantages of superior stiffness and mechanical integrity for reliable assembly, high-temperature dimensional stability for *surface mount technology* (SMT) soldering operations, and UL-94 V-0 flammability ratings without the use of flame-retardant additives. Special reinforced PPS compounds have been developed to provide enhanced flow in thin walls and less tendency to flash in holes and slots in high-precision molding applications. For these reasons, reinforced PPS compounds continue to be used for a variety of electronic connectors and sockets, as well as internal hard disk drive components such as bottom entry connectors and actuator arms. The introduction of lead-free solders, which require board temperatures up to 260°C (500°F) in SMT soldering operations, requires that the SMT oven air temperatures be as high as 280°C (536°F). Some liquid-crystal polymers can withstand such conditions, but polyamides that have high enough melting temperatures still tend to absorb moisture and blister under such conditions [83]. Although these conditions could prove challenging even for reinforced PPS compounds, newer SMT equipment having more precise and reliable temperature control should allow for lower oven air temperatures and mitigate this problem for PPS. The electrical insulating properties and high-temperature dimensional stability of reinforced PPS compounds also make them useful for coil bobbins, for housings and mounting bases of switches and relays, and for potting cups or direct encapsulation of electronic components. Higher strength, faster cycle times, and less waste provide advantages over thermoset materials in such applications.

Design Considerations

Successful applications of reinforced PPS compounds rely on part designs that take advantage of the high modulus, hardness, and dimensional stability of PPS while avoiding the need for ductility or flexibility. Problems are seldom encountered when good plastics design practices [84] are employed. The minimum wall thickness for injection-molded parts is typically about 0.5 mm (0.02 in), since flow length will be restricted to no more than about 5 cm (2 in) and will be quickly arrested in thinner wall sections. To avoid formation of sinks, internal voids, and internal stress cracking, the maximum wall thickness should not be more than about 10 mm (0.39 in). The design issues that most often arise with reinforced PPS parts are lack of uniform wall thickness, failure to compensate for the reduced strength of weld lines, failure to radius corners, and failure to account for anisotropy.

Uniform wall thickness throughout the entire part will ensure more uniform shrinkage behavior during molding, which decreases warpage and residual stress. Whenever possible, thicker part sections should be cored, the thinnest wall sections should be no less than 40% of the thickest wall sections in the part, and parts should be gated to fill from thicker sections into thinner sections.

Gate location and fill patterns should be planned so that weld lines will be eliminated or located in areas of minimal stress whenever possible. There is typically no fiber reinforcement across weld lines, so under the best conditions weld line strength is limited to the no more than the strength of unreinforced PPS polymer, about 85 MPa (12.3 kpsi) tensile strength. If weld lines must bear stress, the part design must compensate for the reduced strength. To attain the best possible weld line strength, part and mold design should allow for rapid injection, a hot flow front, thorough packing, adequate venting, and should avoid backfilling wherever weld lines are formed.

All corners in reinforced PPS parts should have a radius of 60% of the wall thickness. This will eliminate stress concentration points and potential sites for crack initiation, and it will also help to create smoother flow patterns during filling to reduce the potential for molded-in stresses and void formation. Reinforced PPS is a particularly notch-sensitive semicrystalline thermoplastic, so sharp inside corners create crack initiation points and must be avoided in part designs.

As with all fiber-reinforced injection-molding compounds, reinforced PPS compounds will tend to develop more alignment of reinforcing fibers parallel to the direction of flow during mold filling, resulting in anisotropic material properties. The mechanical strength of reinforced PPS compounds can be up to 60% greater in the flow direction compared to the transverse direction. Part and mold design should exploit the enhanced strength from fiber orientation where parts will experience more stress in service, while minimizing potential stress transverse to fiber alignment. Also, there will typically be twice as much shrinkage and thermal expansion along axes transverse to fiber alignment compared to along axes parallel to fiber alignment.

Reinforced PPS Injection-Molding Compounds

By far, the largest number and widest variety of commercial applications for reinforced PPS are fabricated by injection molding. The most common reinforced PPS injection-molding compounds may be divided into two general groups. One group is reinforced with glass fiber, most typically about 40% by weight. The other group utilizes a combination of glass fiber reinforcement and mineral fillers, typically in a total amount of 50 to 70% by weight, with roughly equal-weight parts of glass fiber and other fillers. These compounds utilize chopped strand K-filament or G-filament glass fibers and common mineral fillers such as calcium carbonate, calcium sulfate, talc, or mica. Coupling agents are often employed to enhance adhesion of the PPS polymer matrix to the reinforcement. Such materials fulfill the requirements of most reinforced PPS injection-molding applications. More specialized grades have also been developed utilizing long glass fiber, graphite fiber, lubricating fillers such as graphite or perfluoropolymers, as well as electrically or thermally conductive fillers. Compounds of these types are typically targeted for specific applications having relatively limited market size.

A comparison of the engineering properties of typical unfilled, glass-fiber-reinforced, and glass-fiber- and mineral-filled PPS compounds suitable

TABLE 15.4 Typical Engineering Properties of Reinforced Poly(Phenylene Sulfide) Compounds

Property	Test method	Unfilled	40% Glass fiber	65% Glass fiber and mineral
Tensile strength, MPa (kpsi)	ASTM D-638	90 (13)	195 (28)	130 (19)
Elongation at break, %	ASTM D-638	10	1.7	1.0
Flexural strength, MPa (kpsi)	ASTM D-790	145 (21)	270 (39)	215 (31)
Flexural modulus, GPa (Mpsi)	ASTM D-790	3.5 (0.5)	14.5 (2.1)	19.5 (2.8)
Notched Izod impact, J/m (ft·lb/in)	ASTM D-256	50 (1.0)	85 (1.6)	55 (1.0)
Unnotched Izod impact, J/m (ft·lb/in)	ASTM D-256	800 (15.0)	640 (12.0)	215 (4.0)
Compressive strength, MPa (kpsi)	ASTM D-695	110 (16)	275 (40)	240 (35)
Dielectric strength, kV/mm (V/mil)	ASTM D-149	24 (600)	22 (550)	18 (450)
Arc resistance, sec	ASTM D-495	50	125	180
Comparative tracking index, V	UL-746A	150	150	250
Dielectric constant at 1 MHz, 25°C	ASTM D-150	3.1	3.7	4.7
Dissipation factor at 1 MHz, 25°C	ASTM D-150	0.002	0.002	0.002
Volume resistivity, Ω·cm	ASTM D-257	1×10^{16}	1×10^{16}	1×10^{15}
HDT at 1.8 MPa (264 psi), °C (°F)	ASTM D-648	120 (248)	265 (509)	265 (509)
Water absorption, %	ASTM D-570	0.02	0.02	0.02
Flammability rating	UL-94	V-0	V-0 / 5VA	V-0 / 5VA
Density, g/cm^3	ASTM D-792	1.35	1.65	1.95

for injection molding is tabulated in Table 15.4. Commercial suppliers of reinforced PPS injection-molding compounds all offer grades exhibiting such properties. The *heat deflection temperature* (HDT) data show how glass fiber reinforcement is generally required to achieve the degree of elevated-temperature dimensional integrity that sets PPS compounds apart from less expensive engineering thermoplastics. Unfilled PPS typically provides only the benefits of chemical resistance and nonflammability compared to less expensive engineering plastics. The 40% glass-fiber-reinforced PPS grades generally provide better mechanical strength, toughness, impact resistance, and plastic flow in thin-wall sections than do the more highly filled grades. The more highly glass-fiber- and mineral-filled PPS grades provide advantages of higher modulus (stiffness), better high-voltage arc track resistance, and lower cost.

A variety of grades are available within these two groups that provide slightly differing balances of plastic flow and mechanical properties. Special 40% glass-fiber-reinforced grades are available that have about 30% lower melt viscosity and less tendency to flash in tiny holes and slots, making them especially useful for molding small, thin-walled electrical and electronic connectors. However, this is achieved at the expense of about a 10% lower tensile strength and flexural strength and about 25% lower elongation and unnotched Izod impact strength than shown in Table 15.4. Some grades containing both glass fiber and mineral filler have been developed to provide about 15% higher tensile strength and flexural strength along with about 50% higher unnotched Izod impact strength than shown in Table 15.4 but have about 30% higher melt viscosity. These are used in applications where the mechanical strength of typical glass-fiber- and mineral-filled PPS compounds is insufficient, but the cost of 40% glass-fiber-reinforced PPS compounds is prohibitive.

Reinforced Blends of PPS with Other Polymers

A substantial amount of work has been reported on blending of PPS with a variety of other polymers, and some glass-fiber-reinforced blends are now emerging in the market. Blends of PPS with a variety of rubber impact modifiers [85–92], various polyamides [93–97], poly(phenylene oxide) [98–101], polycarbonates [98, 102–103], poly(aryl sulfone)s [98,104–105], polyetherimide [106], poly(amide imide) [104, 107], poly(ethylene terephthalate) [108], poly(butylene terephthalate) [109], polystyrene [110], and liquid-crystal polymers [111–113] have all been described in the literature. In most cases, a block copolymer or grafting agent is necessary to improve compatibility of the blend phases and achieve a sufficiently high degree of dispersion to provide desirable performance enhancements. The most useful results are generally achieved when PPS comprises the continuous phase of the blend, although small amounts of PPS have been shown to provide processing [106, 114] and flame resistance [115–116] benefits in some cases. There are no known miscible blends of PPS with other polymers. The primary objectives of blending PPS with other polymers are generally to improve the impact resistance, ductility (elongation), or HDT compared to reinforced PPS compounds. The primary disadvantage of such blends is that they tend to sacrifice the resistance to thermal degradation, resistance to chemical attack, and inherent nonflammability for which PPS is so well known. *Polytetrafluoroethylene* (PTFE) is often blended with PPS to provide improved surface lubricity and wear behavior, although in these blends the PTFE does not really melt during processing and behaves more as a filler dispersed in the PPS polymer matrix, rather than as a polymer blend.

Of the various reported blends of PPS with other polymers, only blends of PPS with ethylene copolymer impact modifiers, polyamides, and PTFE are beginning to show wide utility in applications for reinforced plastics.

TABLE 15.5 Typical Engineering Properties of Reinforced Poly(Phenylene Sulfide) Blends

Property	Test method	40% Glass fiber PTFE	40% Glass fiber nylon 6,6	30% Glass fiber ethylene coploymer
Tensile strength, MPa (kpsi)	ASTM D-638	195 (28)	205 (30)	145 (21)
Elongation at break, %	ASTM D-638	1.7	2.0	2.0
Flexural strength, MPa (kpsi)	ASTM D-790	275 (40)	270 (39)	195 (28)
Flexural modulus, GPa (Mpsi)	ASTM D-790	14.5 (2.1)	12.5 (1.8)	8.5 (1.2)
Notched Izod impact, J/m (ft·lb/in)	ASTM D-256	85 (1.6)	100 (1.9)	100 (1.9)
Unnotched Izod impact, J/m (ft·lb/in)	ASTM D-256	695 (13.0)	745 (14.0)	745 (14.0)
Compressive strength, MPa (kpsi)	ASTM D-695	240 (35)	205 (30)	205 (30)
Dielectric strength, kV/mm (V/mil)	ASTM D-149	550 (22)	600 (24)	600 (24)
Arc resistance, sec	ASTM D-495	125	100	120
Comparative tracking index, V	UL-746A	150	250	150
Dielectric constant at 1 MHz, 25°C	ASTM D-150	3.6	3.8	3.5
Dissipation factor at 1 MHz, 25°C	ASTM D-150	0.003	0.015	0.010
Volume resistivity, Ω·cm	ASTM D-257	1×10^{16}	1×10^{13}	1×10^{13}
HDT at 1.8 MPa (264 psi), °C (°F)	ASTM D-648	265 (509)	245 (473)	250 (490)
Water absorption, %	ASTM D-570	0.02	0.30	0.05
Flammability rating	UL-94	V-0	—	V-0
Density, g/cm^3	ASTM D-792	1.75	1.55	1.50

The properties of some examples of such glass-fiber-reinforced blends are tabulated in Table 15.5. These blends typically exhibit higher impact resistance, greater ductility (elongation), and lower modulus (stiffness) compared to reinforced PPS compounds. The blends of PPS with polyamides have also shown some advantages in injection-molding processes, such as greatly enhanced flow in thin-wall sections, less tendency to flash in tiny holes and slots, and faster cycle times compared to reinforced PPS compounds. The addition of PTFE lowers the dynamic coefficient of friction and reduces the wear rate of reinforced PPS compounds. For 40% glass-fiber-reinforced PPS compared to 40% glass-fiber-reinforced PPS/PTFE blend, the dynamic coefficient of friction is about 0.5 compared to about 0.3, respectively, and the wear rate is about 0.05 mm/h (0.002 in/h) compared to about 0.0013 mm/h (0.00005 in/h), respectively.

TABLE 15.6 Thermal Aging of Reinforced Poly(Phenylene Sulfide)-Based Compounds

Compound	Temperature and duration	Tensile strength retained, %	Elongation retained, %	Impact strength retained, %
PPS	145°C 1000 h	98	94	99[*]
40% Glass fiber	165°C 500 h	100	95	94[‡]
	165°C 1000 h	96	92	77[‡]
	165°C 2000 h	97	91	82[‡]
	175°C 1000 h	94	88	102[*]
PPS/polyamide 6,6	145°C 1000 h	86	68	108[*]
40% Glass fiber	165°C 500 h	84	70	52[‡]
	165°C 1000 h	82	68	49[‡]
	165°C 2000 h	76	60	43[‡]
	175°C 1000 h	83	62	101[*]
PPS/ethylene copolymer	150°C 1000 h	109	78	96[†]
35% Glass fiber	165°C 500 h	110	87	91[*]/92[†]
	165°C 1000 h	110	83	82[*]/81[†]
	165°C 2000 h	91	40	42[†]
	180°C 1000 h	88	41	76[*]/36[†]

[*] Notched Izod.
[†] Unnotched Izod.
[‡] Unnotched Charpy.

One of the primary reasons that these blends are showing greater commercial applicability than blends with other polymers is that the proper blend composition with these polymers minimizes sacrifice of the inherent benefits of PPS. These reinforced blends maintain high HDTs and exhibit good thermal-aging performance, making them useful in applications requiring extensive exposure to temperatures up to at least 150°C (302°F). The thermal-aging performance of the ethylene copolymer and polyamide blends compared to a PPS compound is shown in Table 15.6. Although the chemical resistance behavior of the ethylene copolymer and polyamide blends is not as good as that of PPS, such compounds have shown excellent resistance to automotive fluids at elevated temperatures, as shown in Table 15.7. The polyamide blends are somewhat susceptible to attack by engine coolant, but no more susceptible than polyamides that have been used in automotive coolant system applications. Since PTFE also has excellent thermal stability and a broad range of chemical resistance, blending with PTFE does not sacrifice thermal-aging performance or chemical resistance behavior. The ethylene copolymer and polyamide blends require flame-retardant additives to attain the same degree of flammability resistance as PPS compounds, but the addition of PTFE does not adversely affect flammability resistance. Although these reinforced blends of PPS with other polymers have not appeared to open new markets for PPS, they have expanded the utility of PPS in existing markets by bridging cost/performance gaps between reinforced PPS and other reinforced thermoplastics.

TABLE 15.7 Resistance of Poly(Phenylene Sulfide)-Based Compounds to Automotive Fluids

Compound and duration	Fluid and temperature	Tensile strength retained, %	Flexural modulus retained, %
PPS	Gasoline, 93°C (200°F)	101	99
40% Glass fiber	M85 fuel, 93°C (200°F)	99	99
2160 h	Motor oil, 149°C (300°F)	97	101
	Engine coolant, 121°C (250°F)	94	101
PPS/polyamide 6,6	Gasoline, 93°C (200°F)	89	98
40% Glass fiber	M85 fuel, 93°C (200°F)	66	85
2160 h	Motor oil, 149°C (300°F)	90	107
	Engine coolant, 121°C (250°F)	68	84
PPS/ethylene copolymer	Gasoline, 100°C (212°F)	68	82
35% Glass fiber	M85 fuel, 100°C (212°F)	84	89
1000 h	Motor oil, 150°C (302°F)	93	89
	Engine coolant, 150°C (302°F)	69	98

Thermal Stability

Compared to other engineering plastics, PPS compounds exhibit a superior combination of both elevated-temperature mechanical integrity and long-term resistance to thermal degradation. Table 15.8 compares the elevated-temperature performance of various reinforced engineering plastics as indicated by the heat deflection temperature and UL *relative thermal index* (RTI).

The heat deflection temperature test is a method of comparing the relative ability of plastic materials to maintain dimensional integrity at elevated temperatures. It indicates the temperature at which a plastic material will no longer maintain its shape under an applied load (in this

TABLE 15.8 Elevated-Temperature Resistance of Glass-Fiber-Reinforced Engineering Plastics

Polymer	Heat deflection temperature [117], ASTM D-648 at 1.8 MPa (264 psi), °C (°F)	UL relative thermal index [118], UL-746B, °C (°F)
Liquid-crystal polymers	250–345 (482–653)	200–260 (392–500)
Poly(phenylene sulfide)	250–270 (482–518)	200–240 (392–464)
Polyetherimide	210–215 (410–419)	170–180 (338–356)
Polyphthalamide	265–290 (509–554)	110–160 (230–320)
Polyamide 4,6	270–285 (518–545)	110–150 (230–302)
Phenolic thermoset	190–240 (374–464)	150–180 (302–356)
Polybutylene terephthalate	195–235 (383–455)	120–150 (248–302)
Polyamide 6,6	220–255 (428–491)	105–130 (221–266)

case 1.82 MPa, or 264 psi) as the temperature is gradually increased at the rate of 2°C (3.6°F) per minute. PPS is a semicrystalline polymer with a crystalline melting point of 285°C (545°F), and reinforcing fillers enhance the dimensional integrity at temperatures above the glass transition temperature of 85°C (185°F). As a consequence, reinforced PPS compounds typically exhibit HDTs in excess of 260°C (>500°F), placing them among the best of engineering plastics capable of withstanding brief high-temperature exposures such as the surface mount technology PC board soldering processes.

The Underwriters Laboratories relative thermal index (UL RTI) is a method of comparing the relative long-term thermal stability of plastic materials in terms of resistance of the polymer to thermal degradation. It indicates the temperature at which a plastic material is expected to retain at least 50% of its original mechanical strength after 100,000 h, and is typically considered to be the maximum continuous-use temperature of the material. The highly stable chemical structure of the PPS molecule makes reinforced PPS compounds highly resistant to thermal degradation, as evidenced by their exceptionally high UL RTIs of 200 to 240°C (392 to 464°F). Over the long term, PPS compounds will retain their original performance characteristics better than other engineering plastics in applications requiring extensive exposure to high temperatures. Many of the engineering plastics that can meet or exceed the HDT of reinforced PPS compounds cannot also match the resistance of PPS to thermal degradation. Only more highly priced engineering plastics, such as liquid-crystal polymers, share this distinction.

Dimensional Stability

Compared to other engineering plastics, reinforced PPS compounds have exceptional dimensional stability, in terms of both precision moldability and the long-term ability to maintain dimensional integrity at elevated temperatures and in hostile chemical environments. The low melt viscosity and low mold shrinkage (typically 0.2 to 0.5%) of reinforced PPS injection-molding compounds make it possible to reproducibly mold thin-walled and complex parts to tight tolerances while incurring minimal difficulties with warpage. Typical molding tolerances are ±0.001 mm/mm, and even tighter tolerances can be achieved in small, optimally gated parts. Furthermore, the high modulus, high HDT, low thermal expansion, extremely low creep behavior, and wide-ranging chemical resistance of reinforced PPS compounds ensure that parts will retain their dimensional integrity over an extended time, even at elevated temperatures and in hostile chemical environments. The chart shown in Fig. 15.1 illustrates the excellent elevated-temperature creep behavior of reinforced PPS compounds. The data shown in Table 15.9 compare the coefficient of linear

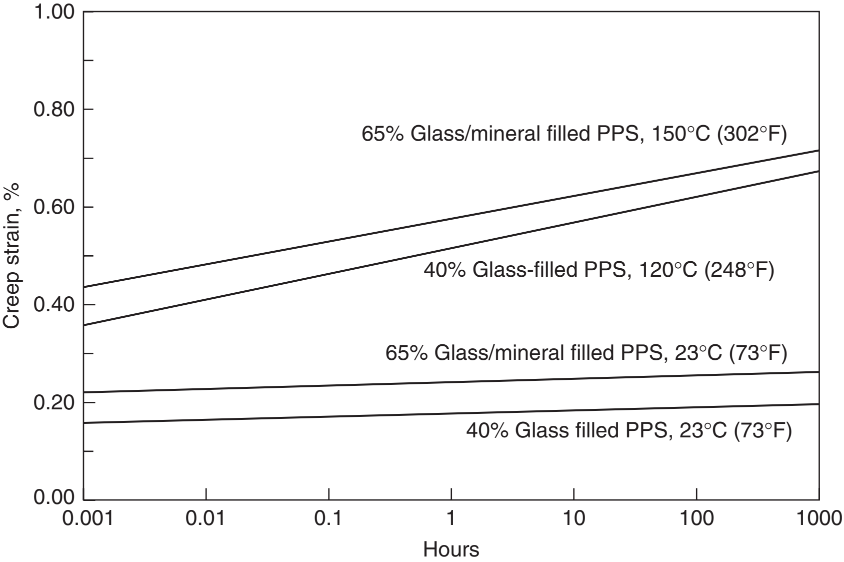


Figure 15.1 Tensile creep of reinforced poly(phenylene sulfide) compounds at 35 mpa (5000 psi) stress.

thermal expansion and water absorption of various reinforced engineering thermoplastics. Many of the engineering plastics that can meet or exceed the HDT of reinforced PPS compounds exhibit higher thermal expansion and/or water absorption behavior. So despite having high HDTs, those materials may show greater tendency to deform or blister when exposed to elevated temperatures.

TABLE 15.9 Thermal Expansion and Water Absorption of Glass-Fiber-Reinforced Engineering Plastics

Polymer	Coefficient of linear thermal expansion [117, 119], ASTM D-696, flow direction $\times 10^{-6}$ m/(m·°C) [$\times 10^{-6}$ in/(in·°F)]	Water absorption [117, 119], ASTM D-570, 24 h, 23°C (73°F), %
Liquid-crystal polymers	5–75 (9–135)	0.01–0.10
Poly(phenylene sulfide)	10–25 (18–45)	0.02–0.08
Polyetherimide	15–20 (27–36)	0.10–0.20
Polyphthalamide	5–15 (9–27)	0.10–0.30
Polyamide 4,6	20–40 (36–72)	0.9–1.5
Phenolic thermoset	5–30 (9–54)	0.03–1.2
Polybutylene terephthalate	15–40 (27–72)	0.05–0.10
Polyamide 6,6	15–55 (27–99)	0.4–1.1

Chemical Resistance

PPS is well known to be one of the most chemically resistant engineering thermoplastics, surpassed only by perfluoropolymers. There is no organic solvent known to dissolve PPS at temperatures below 200°C (392°F), and the PPS polymer backbone may only be attacked and degraded by powerful oxidizing agents under extreme conditions of temperature and/or concentration. PPS is resistant to all fuels, including “flex fuels” that contain alcohols, as well as other automotive fluids such as motor oils, lubricants, hydraulic fluids, and engine coolants, including the newer “long-life” *organic acid technology* (OAT) type of coolants [81, 120]. Although hydrochloric acid and nitric acid tend to attack PPS, the polymer is highly resistant to sulfuric acid and phosphoric acid, even at high concentrations and elevated temperatures [121]. In a study comparing the chemical resistance of several engineering plastics when tested for compatibility with 127 different chemical reagents, PPS exhibited the widest range of chemical compatibility [122]. PPS retained at least 75% of its original tensile strength after 24 h at 93°C (200°F) in 120 of the 127 reagents tested, compared to 109 reagents for phenolic thermoset; 70 reagents for nylon 6,6; 65 reagents for modified poly(phenylene oxide); and 50 reagents for polycarbonate. This inherent chemical stability of PPS makes reinforced PPS compounds more suitable than most other engineering plastics for service in a wide variety of hostile chemical environments, even at elevated temperatures. Unlike polyamides and polyesters, the PPS polymer is not hydrolyzed and degraded by hot water. However, under superheated conditions [above 100°C (212°F)], water may hydrolyze the bonds created by coupling agents, thus compromising the adhesion between the PPS polymer matrix and the glass fiber reinforcement and weakening the plastic compound. Special grades utilizing unique coupling agents have been developed to resist this mode of attack [123].

Nonflammability

PPS is inherently flame-retardant due to the chemical structure of the polymer backbone, a chain of aromatic rings linked by sulfur atoms, which causes the material to tend to char during combustion, making it self-extinguishing. The addition of common glass and mineral fillers only serves to enhance this effect. As a result, reinforced PPS compounds attain the highest Underwriters Laboratories nonflammability ratings, UL-94 V-0 and UL-94 5VA, without using flame-retardant additives. The limiting oxygen index, another good method of comparing the flammability of various materials, is the minimum percentage of oxygen in a test atmosphere that allows the plastic to support continued combustion. The limiting oxygen indices of reinforced PPS compounds are typically about 50%, well over twice the oxygen content of ambient air. The minimum combustion temperature reported for 40% glass-filled PPS is 540°C (1004°F), and the ASTM D-1929 flash point reported for 40% glass-filled PPS is > 499°C (> 930°F). Unlike many other organic compounds that contain aromatic rings, PPS does not tend to generate an excessive amount of smoke during combustion. The NIST smoke density test obscuration time (time required for the specific optical density to reach 16) for 40% glass-filled PPS was determined to be 15.5 min smoldering and 3.2 min flaming. All these results show PPS to be among the best engineering plastics for fire safety.

Many other engineering plastics require flame-retardant additives to achieve self-extinguishing behavior, but flame-retardant additives tend to be detrimental to the mechanical and electrical properties of a plastic compound. Most common flame-retardant additives break down under the melt-processing conditions of engineering thermoplastics, so parts molded using regrind will not be as flame-resistant as parts molded from virgin material, and the thermal degradation of flame-retardant additives can produce toxic and/or corrosive offgases. Since reinforced PPS compounds require no flame-retardant additives, regrind is as flame-resistant as virgin material, and the other undesirable effects of using flame-retardant additives are also avoided.

Injection Molding

Reinforced PPS injection-molding compounds are readily processed on conventional reciprocating screw injection equipment at melt temperatures of 315 to 345°C (599 to 653°F). Barrel temperature set points should be about 310 to 340°C (590 to 644°F), since actual plastic melt temperatures will tend to be a little higher than the barrel temperature set points. PPS/polyamide blends may need to be processed at slightly lower melt temperatures, 285 to 300°C (545 to 572°F), to avoid degrading the polyamide component of the blend, so barrel temperature set points should be 265 to 295°C (509 to 563°F). Shot sizes should be between 25 and 75% of the barrel capacity, and clamping force should be sufficient to supply up to 55 MPa (4.0 ton/in^2) of projected part surface area. It is generally best to utilize a constant, high-velocity injection rate until the part is almost completely (95 to 99%) filled, and then switch over to a pack-and-hold stage, applying the maximum possible pressure without generating excessive flash. The injection rate should be as fast as possible without causing mold flash or warpage, and the injection pressure setting should be high enough to prevent the molding machine from automatically reducing injection speed due to the peak injection pressure exceeding the set point. Optimum part packing can typically be determined by the method of increasing pack pressure until maximum possible part weights are achieved. During injection molding, there may be offgases that can be irritating to mucous membranes, so molding processes should be conducted only in areas having adequate ventilation.

The crystallization behavior of PPS becomes a critical issue with production of injection-molded parts. The mold surface temperature should typically be maintained at 135 to 150°C (275 to 302°F) to attain the maximum possible degree of polymer crystallinity and ensure the best possible long-term elevated-temperature dimensional integrity of the part. This is best achieved by use of circulating hot oil; however, electric cartridge heaters have also been used. When lower mold surface temperatures are used, the parts will cool more quickly and not develop a sufficient degree of crystallinity. If such parts are ever subjected to service conditions at temperatures above the glass transition temperature of PPS [about 85°C (185°F)], part deformation may occur due to differential shrinkage resulting from thermally induced crystallization. If lower mold surface temperatures must be used, the mold surface temperature should be maintained below 85°C (185°F) to ensure a consistently low level of part crystallinity and achieve the best possible part-to-part reproducibility. Service at elevated temperatures should be avoided for such parts, unless a postmold annealing process is conducted (see below). At low mold surface temperatures, thicker-walled parts may tend to develop amorphous outer surfaces with greater crystallinity in internal wall sections, as the internal regions will tend to cool more slowly. This can be a source of part-to-part dimensional variations. Mold surface temperatures between 85 and 135°C (185 and 275°F) should never be used in injection-molding PPS compounds. In that temperature range, the degree of crystallinity will vary from part to part, and resultant variations in shrinkage behavior will cause inconsistent part-to-part dimensional tolerances. Reinforced PPS/polyamide alloys may attain a sufficient degree of crystallinity with mold surface temperatures as low as 95°C (203°F), but to ensure the optimum degree of crystallinity, mold surface temperatures above 120°C (248°F) are still preferred.

If service conditions should require repeated or extensive exposure to temperatures above 200°C (392°F), postmold "annealing" of reinforced PPS parts may be desirable. This is accomplished by heating the parts for 2 h at a temperature above the maximum expected service temperature of the part, driving the PPS polymer to a slightly higher degree of crystallinity by thermally induced crystallization processes before the parts are ever put into service. Parts molded using a mold surface temperature below 85°C (185°F) may also be converted from a primarily amorphous state to a semicrystalline state by such annealing processes. It may be necessary to fixture parts during the annealing process to ensure that critical dimensional tolerances are not compromised by the differential shrinkage that results from thermally induced crystallization.

Aside from part crystallinity, mold surface temperature also significantly affects the surface finish and appearance of parts injection-molded from reinforced PPS compounds. Mold surface temperatures above 135°C (275°F) will produce a "resin-rich" part surface, which provides a smooth and glossy part surface finish. Lower mold surface temperatures will tend to produce a more dull and mottled part surface finish, due to fillers and reinforcements being more exposed at the part surface. Postmold annealing will not alter the surface finish, although there may be a discernible shift in color due to the polymer transitioning from the more translucent amber color of its amorphous state to the opaque off-white to tan color of its crystalline state. Even pigmented PPS compounds may exhibit a discernible change in appearance due to thermally induced crystallization.

PPS does not tend to absorb a lot of moisture; however, drying is recommended prior to processing to drive off any surface moisture or moisture that may have been absorbed by hygroscopic fillers. Generally 2 to 4 h at 150 to 175°C (302 to 347°F) is sufficient to remove any moisture that could cause excessive outgassing or drool during processing. Unlike with polyamides or polyesters, the presence of moisture during processing will not cause PPS polymer degradation. Tests have shown that exposure of reinforced PPS compounds to such temperatures for up to 24 h will cause no detrimental effects to the material. Reinforced PPS/polyamide blends should be dried at somewhat lower temperatures, 4 to 6 h at about 80°C (176°F), to avoid any possible detrimental effects to the polyamide component.

Because of the glass and mineral fillers used in reinforced PPS compounds, abrasion-resistant screws, barrels, and molds are generally required. Barrels constructed of Xaloy 801 and Stellite or Colmonoy 6 flighted screws having 16:1 to 20:1 *L/D* and about 2.5:1 compression ratio are good choices. Ring-type check valves and reverse-taper (nylon tip) or automatic positive shutoff type of nozzles, constructed of similar abrasion-resistant materials, provide more trouble-free processing. For the longest possible mold life, A-2, D-2, or D-7 tool steels hardened to Rockwell C-60 or higher are best; however, softer steels such as S7 or H13 may sometimes be used for short runs. Various surface treatments, such as chrome plating, electroless nickel plating, or nitriding can also prolong mold life. Standard sprue designs with nominal 2° draft and reverse taper or Z-cut sprue puller systems are typically used. Full round or trapezoidal runners are preferred, runner length should be kept to a minimum, and multicavity molds should have balanced runner systems. Proper mold venting is essential to ensure adequate part filling, as well as to prevent burning and accelerated mold wear due to gas entrapment. Adequate venting can be achieved by properly positioned 0.0075- to 0.0125-mm (0.0003- to 0.0005-in) deep by 6.35-mm (0.25-in) wide channels cut on the parting line, or by flattening ejector pins 0.02 mm (0.0008 in) on one to four sides.

Compression Molding

Compression molding of PPS compounds is an alternative method to injection molding for producing thicker-walled parts or avoiding tooling costs for smaller production quantities. PPS blended with various fillers and reinforcements can be compression-molded into sheets, solid rods, or hollow rod forms, which may subsequently be machined to produce the desired final shapes. The engineering properties of compression-molded PPS compounds may be fairly similar to those of commercially available injection-molding compounds having similar formulations, except that the mechanical strength is typically somewhat lower due to the more extensive curing history of the PPS polymer. Furthermore, surface defects from machining operations may act as crack propagators and compromise the mechanical strength of a part. Mechanical properties of compression-molded parts are generally more isotropic than those of injection-molded parts due to more random alignment of reinforcing fibers. This method has been used to produce parts such as pump impellers, pump packing, housings, bushings, bearings, gas and air compressor pistons, piston rings, seals, and balls for ball valves. Polytetrafluoroethylene is often blended with the PPS and other fillers to provide enhanced surface lubricity and wear resistance for many of these applications.

The commercially available PPS injection-molding compounds have much too low a melt viscosity to be suitable for compression molding. Blends of PPS powder and fillers must be subjected to an extensive curing process, to increase the melt viscosity of the polymer to a sufficient degree for compression molding and to partially degas the polymer to prevent voids from forming during the compression-molding process. A typical curing process will require anywhere from 12 to 24 h at about 270°C (518°F). In some extreme cases, it may even be necessary to further cure the mixture at temperatures above the melting point of PPS, as high as 370°C (698°F), to further increase the melt viscosity of the polymer and more thoroughly degas the mixture. Once cured and degassed, the blends may be compression-molded at temperatures of 315 to 400°C (599 to 752°F) while applying 135 to 690 bar (1958 to 10,005 psi) pressure, depending on the part length and diameter. The rate of heating may be as rapid as desired, and the heating time need only be sufficient to thoroughly melt the polymer within the mold. But to prevent stress cracking, the cooling rate must be controlled to no more than 2°C (4°F) per minute until the part temperature drops below 150°C (302°F).

Composites

High-molecular-weight PPS may be used as the binder matrix to produce thermoplastic composite materials capable of withstanding high temperatures and chemically corrosive environments. PPS composite materials have been produced from unidirectional reinforcements, mats, and woven fabrics of glass, carbon, and aramid fibers. Tough and strong, stampable sheets, produced from 20 to 40 wt % loading of chopped fiber or continuous fiber mat, may be rapidly compression-molded into desired shapes. Much stronger and tougher laminate composites may be produced from PPS prepreg materials having 40 to 70 wt % loading of unidirectional fiber or woven fabric [124–127]. PPS fibers may also be intermingled with reinforcing fibers and woven together into a fabric that may be thermoformed [128]. Unlike thermoset prepreg materials, PPS prepreg materials may be stored at room temperature for months or years before being used. The PPS prepreg materials are typically converted to laminated structures by heating above the crystalline melting point of PPS [285°C (545°F)] while applying 345 to 1380 kPa (50 to 200 psi) pressure. Any of a wide variety of final shapes may be produced by conventional thermoforming techniques [124, 129], heated filament winding [130], or pultrusion [131–132].

Typical PPS stampable sheet composites exhibit tensile strength of 100 to 200 MPa (14.5 to 29 kpsi) and tensile modulus of 6 to 14 GPa (870 to 2000 kpsi). Laminate composites produced from unidirectional fiber or woven fabric prepreg can have up to 10 times higher tensile strength and modulus, and the degree of strength and modulus may be geometrically oriented by directing the fiber orientation in lay-up and winding processes. Izod impact strength may be on the order of 500 to 1500 J/m (9.4 to 28 ft·lb/in). PPS composite materials have found application in a variety of areas, including recreational products such as golf club shafts, as well as specialized automotive, aircraft, aerospace, and undersea applications. Their greatest utilization has come in some heavy industrial applications such as fan blades for air handling systems and doctor blades for film and sheet processing equipment.

Other Fabrication Processes

Reinforced PPS compounds may be extruded into profile shapes or sheets under carefully controlled processing conditions using a 24:1 to 28:1 *L/D* standard metering screw with 3:1 compression ratio and a heated die clamp. Typical barrel temperature set points are about 285 to 310°C (545 to 590°F). Some extruded rods and sheets of reinforced PPS compounds are used as stock for machining small quantities of parts, as is compression-molded stock. Thermoforming of extruded sheet may be performed using conventional techniques at temperatures above the crystalline melting point of PPS of 285°C (545°F) [133].

There have been reports of some success at producing parts from reinforced PPS compounds by blow molding [134–135]. For blow-molding processes, high-molecular-weight PPS must be blended with lower amounts (no more than 20 wt %) of reinforcement and often blended with other polymers to achieve the necessary combination of melt strength and melt ductility. This sacrifices the strength and elevated-temperature dimensional integrity that PPS is generally chosen to provide. It has also proved difficult to obtain acceptable surface finishes by blow-molding reinforced PPS compounds. For these reasons, there are not yet wide commercial applications employing blow molding of reinforced PPS compounds; however, development efforts continue in this area.

Machining

It is generally best to form all necessary part features, to the greatest extent possible, during the molding process. Machined surfaces are more prone to abrasion, crack formation, and fluid penetration than resin-rich molded surfaces. But in instances where postmold machining operations are necessary, reinforced PPS compounds can be readily machined using conventional methods. Typical operations such as turning, milling, drilling, and tapping may be conducted by practicing standard techniques as with any other thermoplastic materials, and grinding and lapping can achieve optical finishes. Since glass and mineral fillers can cause severe wear of machining tools, using carbide- or diamond-tipped tools will prolong tool life. If a coolant is needed, ethylene glycol is quite effective and will not adversely affect the PPS polymer. The best results are generally obtained using moderate cutting speeds and fast feed rates because a slow feed rate results in excess abrasion by the tool and tends to give a poor surface appearance. Although fairly deep cuts of up to 3.2 mm (0.125 in) can be made initially, finish cuts should take off no more than 0.13 mm (0.005 in) of material to ensure the best possible surface finish.

Postmold Assembly Methods

Reinforced PPS compounds are amenable to a wide variety of postmold assembly processes including mechanical fastening methods, welding and staking methods, interference and snap fits, and adhesive bonding.

The high modulus and creep resistance of reinforced PPS compounds make them more suitable than many other plastic materials for fastening with bolts, screws, or rivets. For one-time bolted assemblies, tapped or molded-in threads with bolts screwed in three to four diameters may be used. However, with bolted assemblies where repeated assembly and disassembly of parts are expected, or if torque retention at elevated temperature is a concern, ultrasonic or molded-in metal inserts may be used. Molded-in metal inserts should be preheated to the mold temperature before being placed in the tool for molding. For assembly with self-tapping screws, BF-type or BT-type steel thread cutting screws work well, using hole sizes as recommended for phenolformaldehyde thermosets by the

Machinery's Handbook. For rivet assembly, semitubular rivets are best, and tubular rivets may also be used.

Parts molded from reinforced PPS compounds may be joined by ultrasonic welding, vibrational welding, or spin welding, and they may be joined to other components by ultrasonic staking or heat staking. Since welds are primarily composed of neat polymer with little or no fiber reinforcement, the strength of welds is generally no better than the strength of unreinforced PPS, about 85 MPa (12.3 kpsi) tensile strength. In any welding or staking process, the PPS resin is melted and rapidly cooled, so the PPS polymer in the weld or head will be in the amorphous state. Therefore, welded or staked assemblies may need to be annealed if the application requires a thoroughly crystalline part. Shear joints are preferred for ultrasonic welding, and best results have been obtained using high power with a high-amplitude booster, low pressure, and slow horn speed.

Despite the minimal ductility and capability for flexure, snap fits and interference fits are possible with reinforced PPS compounds, since their high modulus makes it possible to attain adequate holding strength with minimal interference. Snap-fit applications typically involve only one-time assembly, and press-fit components should not induce more than about 0.5% hoop strain. Considerable force is often required for assembly and must be applied with care to prevent part cracking. Molded-in inserts are preferred over press fitting for larger components such as hubs or bearings.

Despite the chemically nonreactive nature of PPS, there are adhesives that will bond PPS, providing the surface is properly prepared for good surface wetting by the adhesive. Acrylic, cyanoacrylate, and two-part epoxy adhesives have been found most effective for bonding PPS [136–137]. Various surface preparation methods can significantly improve bonding. At a minimum, the bonding surface should be cleaned and degreased, using any of a number of common solvents. Sanding or grit blasting will increase the bonding surface area and provide a mechanical aid for bonding. Surface oxidation by flame, corona, or plasma treatment will improve surface wetting and polarity. Chemical etching with chromic acid or nitric acid is especially effective because it provides a combination of surface oxidation and microscopic roughening. A paramount concern with adhesive bonding of reinforced PPS parts is that the adhesive compound and the bond interface must be able to withstand the service conditions of the parts.

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James M. Margolis has been extensively involved in engineering plastics for 40 years and he continues to provide companies with special studies and multiclient reports. He was SPE seminar leader for Automotive Plastics (1979–1980) and Engineering Thermoplastics (1982–1984). Mr. Margolis was also on the Editorial Steering Committee, Section Chairman, and author of *Engineering Resins* for the *ASM International Engineering Materials Handbook*, *Volume 2* (1988). He is editor/chapter author of several books and publications, including *Instrumentation for Thermoplastics Processing*, *Decorating Plastics*, *Advanced Thermoset Composites—Industrial and Commercial Applications*, and *Medical and Hospital Products*.