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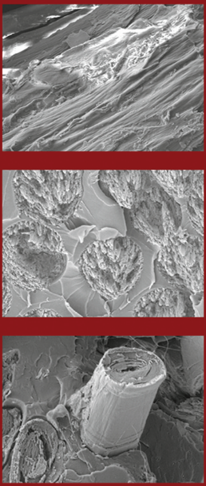
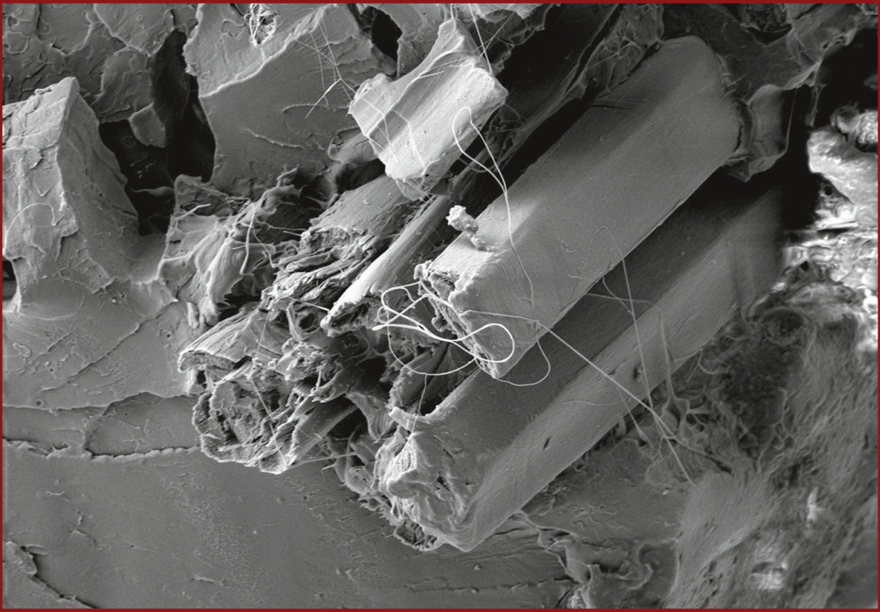


Biocomposites for High-Performance Applications

Current Barriers and Future Needs Towards Industrial Development

Edited by Dipa Ray



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Biocomposites for High-Performance Applications

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Edited by

Dipa Ray

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Preface

The development of high-performance polymer composites has revolutionized our society in many ways. These materials have excellent performance and have been immensely successful over the last few decades. But their adverse effects on the environment cannot be disregarded anymore. In recent times there has been an upsurge of awareness all over the world regarding the negative influence of such materials on global warming and the environment. Intensive search is ongoing for materials that will fit into this technology footprint without harming the environment. This has lead to a growing demand for materials derived from renewable resources that are environmentally friendly, nontoxic, sustainable, and lightweight with mechanical properties equivalent to the petroleum derived ones. Biocomposites fulfil many of such criteria and comprise a very important field of research in the current scenario. Biocomposite applications are slowly increasing in rigid packaging, automotives, consumer goods, and construction industries. However, significant efforts are required to make them more competitive and to take full benefit of their eco-friendliness. A number of investigative research have been carried out in the last decades in this field, but only few of them have moved to the higher level for commercial exploitation. This book aims to identify and highlight the barriers that currently exist in the field of biocomposites, particularly in their industrial-scale development and availability as a commercial product.

It is well known that natural fibres have emerged as an alternative to glass fibres in many applications, but they have been mostly known as low-performance materials. Significant technological advancements are required in terms of their supply, consistency, and large-scale manufacturability to ameliorate them to a higher level. Man-made cellulose fibres with uniform supply and consistent property can be explored for developing high-performance sustainable biocomposites. The inherent structures of the plant fibres, which are different from that of the man-made fibres, play a significant role in the energy absorption and failure behaviour of the biocomposites. Forensic identification techniques can be utilized to generate new information on biofibres to understand their behaviour under various loading conditions. Biopolymers of various grades, derived from natural or petroleum resources, currently exist in market and are highly favoured for applications in biomedical and packaging. But most of them cannot compete with the conventional plastics in price or performance. New bioresins with renewable contents are recently appearing in market, but further research and developments are required to enhance their performance and suitability for large-scale manufacturing. Fibre-matrix bonding, which plays the key role in a composite, is generally not optimized in biocomposites to attain the highest stress transfer at the interface. For glass fibre reinforcements, standard silane coupling agents are successfully employed by the fibre manufacturers to enhance their interfacial compatibility with different polymer matrices. But no standard coupling agents or surface modification techniques have yet been identified for biofibres which can be used in industrial level to enhance their performance. There remains a huge scope of future research in this area. Environmental degradation weakens the performance of biocomposites and refrain them from high-end applications. Significant research input is required to predict their durability and identify ways to enhance their environmental resistance property. Efficient processing is another important aspect which controls the success of biocomposite products. The importance of reactive extrusion and in situ compatibilization is likely to grow in coming years to produce high-performance recyclable products. Rapid composite manufacturing techniques such as microwave processing, UV curing, or e-beam curing are now becoming popular and research in these areas can open up novel manufacturing routes for biocomposites. A study on recent innovations can give an insight on the current research trends in academia and product developments in the industries.

The present book provides a comprehensive overview of the various aspects of biocomposites as mentioned above and pinpoints the current challenges and drawbacks associated with them. Identification of the problem can only lead to a plausible solution. With that view, future research needs have been discussed in this book. I believe the information provided in this book will be interesting for both the academia and industry.

The main credit of this book goes to the authors of the chapters for putting together all the valuable information, finding the current challenges, and applying their experience and knowledge to identify the future research needs. Finally I would like to thank all the authors who contributed in this book as well as the Elsevier Publishing staff who helped enormously in making this book possible.

D. Ray

Plant fibre reinforcements

1

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1.1 Introduction

Biocomposites have received considerable interest in recent years due to increased environmental awareness, concerns regarding the depletion of fossil fuels, increased drive towards sustainable technologies, and European reindustrialization based on the development of Bio-economy. The consumption of fibre-reinforced plastics (FRPs) in our daily lives is enormous and this lead to the global production of these materials up to 5.9 million ton in 1999, whereas in 2011, it reached up to 8.7 million ton [1]. Excellent mechanical properties make them suitable for high-performance applications such as automotives and aircrafts. But with the increasing use of FRPs, environmental issues like nonrecyclability and land fillings are also increasing day by day. To reduce these problems, interests are growing for the use of bioresources in FRPs instead of synthetic ones. Use of plant fibres in FRPs is a major effort towards the development of sustainable future. Different types of plant fibres are cultivated all over the world [2,3]. Jute is mainly produced in India and Bangladesh; tropical countries cultivate coir and sisal. United States is famous for commercial production of kenaf, whereas Europe produces flax and hemp. Some characteristics of these plant fibres like renewability, recyclability, biodegradability, low price, low density, and attractive mechanical properties make them a potential alternative to synthetic fibres. Plant fibre-reinforced composites are environmentally friendly and their use is slowly increasing in various areas, like transportation, building and construction industries, packaging, consumer products, etc. [4]. Plant fibres mainly comprise of cellulose, hemicellulose, lignin, waxes, ash, and water-soluble compounds. The chemistry and structure of the fibres determine their characteristics, functionalities, and processing efficiencies.

1.2 Plant fibres

Fibres are divided into two main categories, (1) natural fibres and (2) synthetic fibres. Natural fibres are subdivided based on their origins, like plant, animal, and mineral fibres. Plant fibres are often used as reinforcement in biocomposites. From biological science perspective plant fibres are mainly lignified secondary cell walls, called sclerenchyma cells, which give mechanical stability to the plant body. Some examples of these plant fibres include, cotton, jute, ramie, sisal, flax, hemp, etc. The classification of plant fibres is shown in Fig. 1.1.

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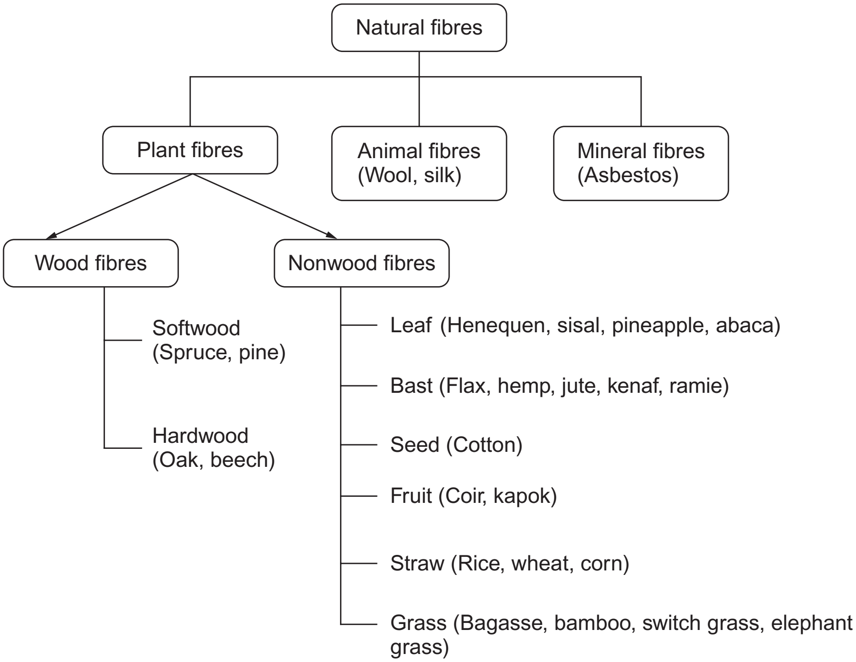


Fig. 1.1 Schematic representation of classification of natural fibres [2,3,5].

1.2.1 Sources of plant fibres

Plant fibres are classified based on their origin, i.e., the part of the plant from which they are derived (Fig. 1.1). Wood fibres are the main structural elements of wood, and are basically spindle-shaped cells of wood [6]. Wood fibres are extracted from wood by various mechanical and chemical pulping methods and are used as reinforcements in polymer composites. For composite applications wood flour is more attractive than individual wood fibres because of its low price and processing ease with conventional plastic processing methods. Wood fibres are of two types, softwood and hardwood. Bast fibres include flax, hemp, jute, kenaf, ramie, etc. These fibres are collected from inner bark (called phloem or bast) of the stems of the dicotyledonous plants [7]. Leaf fibres, which include, sisal, henequen, pineapple, abaca, etc., are obtained from leaves of monocotyledonous plants. Seed and fruit fibres are obtained from seeds and fruits of the plants, respectively. Straw fibres are actually stalks of the plants. Among all these plant fibres, flax, jute, ramie, kenaf, and cotton are commonly used as reinforcing materials in composites. According to 1997 report, 20 million metric ton of plant fibres were produced worldwide and cost of these fibres depend on the economy of the countries where they are produced [2,3]. Table 1.1 summarizes the production of some plant fibres and the places where these fibres are cultivated.

Table 1.1 **Production of some plant fibres and the largest producer countries [4]**

Plant fibres	Type	Worldwide production amount (10^3 ton)	Countries
Abaca	Leaf	70	Philippines, Ecuador, Costa Rica
Pineapple	Leaf	74	Philippines, Thailand, Indonesia
Sisal	Leaf	378	Tanzania, Brazil
Coir	Fruit	100	India, Sri Lanka
Cotton	Seed	25,000	China, India, USA
Oil palm	Fruit	40	Malaysia, Indonesia
Flax	Bast	830	Canada, France, Belgium
Hemp	Bast	214	China, France, Philippines
Jute	Bast	2300	India, China, Bangladesh
Kenaf	Bast	970	India, Bangladesh, USA
Ramie	Bast	100	China, Brazil, Philippines, India
Bagasse	Grass	75,000	Brazil, India, China
Bamboo	Grass	30,000	India, China, Indonesia

1.2.2 Chemistry of plant fibres

A single plant fibre is 1–50 mm in length and the diameter is around 10–50 μm. Fig. 1.2 shows the structure of a single fibre where the central lumen is surrounded by cell walls. The cell wall of a fibre is composed of a primary wall and a secondary wall. Primary cell wall controls the growth rate and direction, cell–cell interactions, and provide structural support as well as mechanical strength. The secondary cell wall is built up of three layers, S1, S2, and S3, and provides mechanical strength to the fibre.

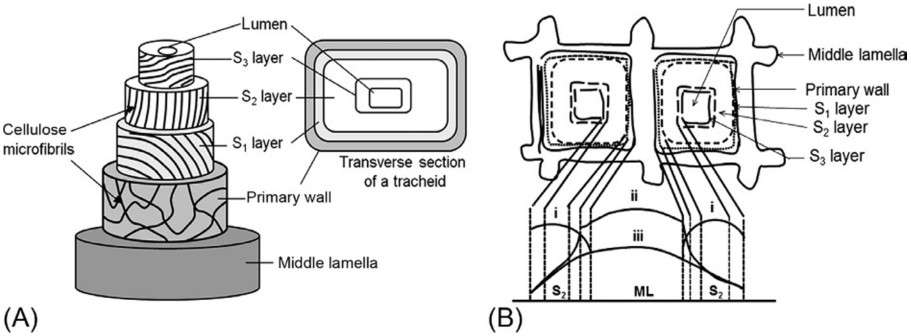


Fig. 1.2 (A) Three-dimensional structure of the secondary wall of a xylem cell and (B) the relative amounts of cellulose, hemicellulose, and lignin across a cross-section of two wood cells [8].

Most of the plant fibres (except cotton), irrespective of wood or nonwood, are lignocellulosic in nature, and cell walls of these fibres comprise of lignin, cellulose, and hemicellulose as the main constituents. The amount of these constituents varies from plant to plant depending on age, species, and could vary in different parts of the plants as well [4]. The chemical composition of different plant fibres are given in Table 1.2.

Cellulose microfibrils, having diameter of 10–30 nm, remain embedded in the hemicellulose/lignin matrix, and act as the reinforcement, which are responsible for providing mechanical strength to the fibres. These microfibrils are linked together to form the cellulose fibres. Cellulose (mainly α-cellulose) is the main constituent of most of the plant fibres. It is a linear macromolecule with degree of polymerization from several 100s to over 10,000. The chains consist of D-anhydroglucose ($C_6H_{11}O_5$) repeat units and are linked together by β-1,4-glycosidic linkages. There are three hydroxyl groups present in each repeat unit. These hydroxyl groups and their hydrogen bonding ability control the crystalline packing in cellulose and also govern their physical properties [2,3,5,9].

Hemicellulose is the second most abundant biopolymer constituent available in plant cell walls [10]. A group of heterogeneous polysaccharides, such as, glucans, mannans, galactans, arabinans, and xylans are collectively termed as hemicellulose. Sometimes nonlinear hemicellulose molecules are hydrogen bonded to cellulose, pectin, lignin, and other constituents in the plant cell wall, and act as a matrix forming the cellulose/hemicellulose network, which is thought to be the main structural component of the fibre cell.

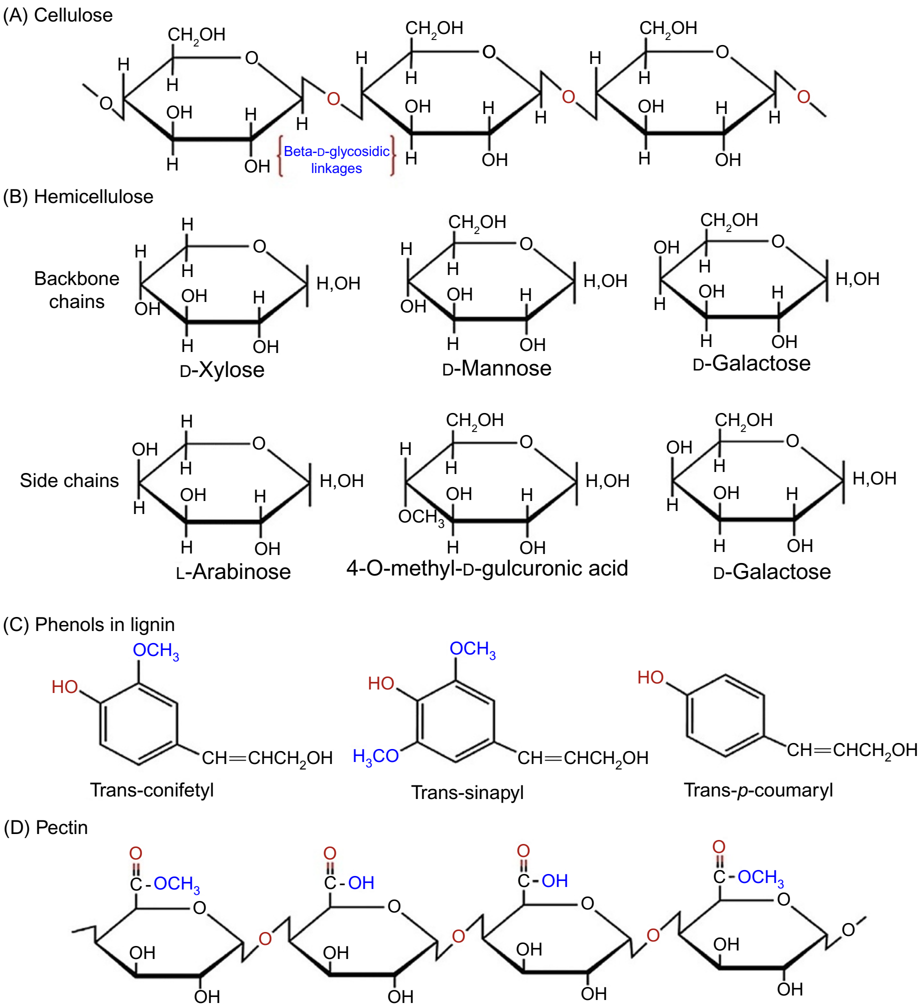
Lignin is another major component of plant cell wall which provides strength, rigidity, and protection against microbial pathogens of cell walls of the plant fibres. It is polyphenylpropanoid complex, which comes from alcohols, like, *p*-coumaryl, coniferyl, and sinapyl [11]. Pectin is the other component associated with plant cell walls. Galacturonic acids are the major constituents in many pectins. The amount of pectin in plant fibres is generally low, but pectin plays a major role in fibre processing [5]. Fats, waxes, and lipids are the other constituents of plant fibres with diversified functions [12]. In many organisms, fats and oils are the principal storage forms of energy. Lipids act as enzyme cofactors, electron carriers, and light-absorbing pigments, whereas, phospholipids and sterols are the structural compounds of membranes. Waxes are esters of long-chain alcohols (carbon 14 and up to carbon greater than 50). The accumulation of wax on the cuticle provides a protective layer against drying and microbial attack on the plants [5]. These compounds are present in relatively low amount in most of the plant fibres except in rice straw and rice husk [5]. The wax content in the fibre plays an important role in composite processing by influencing the wettability and interfacial fibre/matrix adhesion. The chemical structures of the plant fibre constituents are shown in Fig. 1.3.

1.2.3 Properties of plant fibres

Properties of plant fibres depend on several factors, such as structure, microfibrillar angle, cell dimensions and defects, chemical composition, geographical location of the plants, and part of the plant from where the fibres are extracted. The properties are generally varied in different stages of the fibre production because of different influencing factors at each stage [4]. Density of the fibres plays an important role in alteration of mechanical properties, for example, fibres with higher density are much stiffer and stronger than fibres with lower density [5]. Strength of the plant fibres also varies with

Table 1.2 Chemical composition of plant fibres [2–4]

Fibres	Chemical constituents				
	Cellulose (wt%)	**Hemicellulose (wt%)**	**Lignin (wt%)**	**Pectin (wt%)**	**Wax (wt%)**
Abaca	56–63	20–25	7–9	1	3
Pineapple	70–82	–	5–12	1.1	–
Sisal	67–78	10–14.2	8–11	10	2
Coir	36–43	0.15–0.25	41–45	3–4	–
Cotton	82.7	5.7	–	0–1	0.6
Oil palm	65	29	–	–	–
Flax	71	18.6–20.6	2.2	2.3	1.7
Hemp	70.2–74.4	17.9–22.4	3.7–5.7	0.9	0.8
Jute	61–71.5	13.6–20.4	12–13	0.2	0.5
Kenaf	31–39	21.5	15–19	3–5	–
Ramie	68.6–76.2	13.1–16.7	0.6–0.7	1.9	0.3
Bagasse	55.2	16.8	25.3	–	–
Bamboo	26–43	30	21–31	–	–


(A) Cellulose

(B) Hemicellulose

(C) Phenols in lignin

(D) Pectin

Fig. 1.3 Structural organization of the major constituents in the fibre cell wall: (A) cellulose, (B) hemicellulose, (C) phenolic compounds in lignin, and (D) pectin.
Reproduced with permission from Gurunathan T, Mohanty S, Nayak SK. A review of the recent developments in biocomposites based on natural fibres and their application. Compos Part A 2015;77:1–25, Elsevier.

chemical compositions and thus the high strength of kenaf fibre and low strength of coir fibre could be explained in terms of cellulose contents [4]. Similarly higher mechanical properties can also be attributed to small fibrillar angles, fibre diameters, and high aspect ratios of the fibres. Another factor affecting the mechanical properties is moisture content which is related to the pore volumes, chemical composition, relative humidity, and crystallinity of the plant fibres. The physical and mechanical properties of different plant fibres are reported in Table 1.3. The values for synthetic fibres are also included in the table for comparison purpose.

Table 1.3 **Physical and mechanical properties of different plant and synthetic fibres [2–5]**

	Physical properties				Mechanical properties		
	Diameter (μm)	**Density (g/cm^3)**	**Moisture content (%)**	**Microfibrillar angle (degree)**	**Tensile strength (MPa)**	**E-modulus (GPa)**	**Elongation at break (%)**
Plant fibres							
Abaca	–	1.5	5–10	–	400	12	3–10
Pineapple	20–80	–	11.8	14	413–1627	34.5–82.5	1.6
Sisal	50–200	1.4	10–22	10–22	468–640	9.4–22	3–7
Coir	100–460	1.1	8	30–49	131–175	4–6	15–40
Cotton	12–38	1.5–1.6	7.85–8.5	46	287–800	5.5–12.6	7–8
Oil palm	150–500	0.7–1.55	–	42	248	3.2	25
Flax	40–600	1.5	8–12	5–10	345–1100	27.6	2.7–3.2
Hemp	25–500	–	6.2–12	2–6.2	690	30–60	1.6
Jute	25–200	1.3–1.4	12.5–13.7	8	393–773	13.0–26.5	1.2–1.5
Kenaf	–	–	–	–	930	53	1.6
Ramie	–	1.5	7.5–17	7.5	400–938	61.4–128.0	1.2–3.8
Bagasse	–	1.25	8.8	–	290	17	–
Bamboo	–	0.6–1.1	8.9	8–11	140–230	11–17	–
Synthetic reinforcement fibres							
E-glass	–	2.50–2.55	–	–	2000–3500	73	29
Aramid	–	1.40–1.45	–	–	3000–3150	63–67	45–48
Carbon	–	1.40–1.75	–	–	4000	230–500	164–171

Plant fibres generally have lower densities than the synthetic fibres which lead to lighter weight products. But mechanically they are much weaker than the man-made synthetic fibres like glass or carbon. And inconsistency in fibre properties from one batch to another makes their mechanical performance even more uncertain. Hence, hybridization of plant fibres with stronger fibres like glass and carbon is often done to enhance the overall mechanical properties of the product while maintaining the lighter weight and partly the green credentials.

1.3 Major issues related with plant fibre reinforcements

1.3.1 Variability in fibre properties

Various types of natural fibres grow all over the world depending on different geographical locations. Flax and hemp are more predominant in Europe, whereas jute, ramie, kenaf, and sisal have been of greater interest in Asia. Generally, higher cellulose content and microfibrillar angle impart higher strength property. The properties of plant fibres are dependent on their chemical composition, growing conditions like temperature, humidity, and quality of soil, age of plant and species, harvesting time and technique, etc. The fibres show variation in properties even with seasonal change in climate. Fibres extracted manually and extracted mechanically show a significant difference in their strength properties [13]. This variability in the fibre properties increases uncertainty in their consistent performance and induce a negative impact. The constraint in controlling the plant-related parameters needs to be addressed by the scientific community to increase the reliability of such products [14]. In future new pathways may be discovered by the plant scientists using the route of biotechnology to synthesize or grow genetically modified plant fibres with optimum balance of surface properties and mechanical strength. Biofibres with consistent mechanical properties and tailored surface characteristics can be an important reinforcement candidate for high-performance composite application. Future research is welcome in this direction.

1.3.2 Raw material supply

A major barrier for industrial-scale development of biocomposites is the limited supply of proper reinforcement form of natural fibre fabrics [15]. Suitable reinforcement forms are absolutely essential for manufacturing composites with desired properties in an appreciably large scale. Various research works have been reported in academia over the years using different types of biofibres such as jute, flax, hemp, sisal, kenaf, bamboo, pineapple leaf fibre, etc. But the supply of most of these fibres was limited to a small scale which suits only laboratory research. The reinforcement textiles available in large scale were limited only to nonwoven mats, or woven textiles produced mainly for apparel applications. Neither was particularly produced for high-performance composite application. Only in last few years new manufacturers are coming up with various forms of biofibre reinforcements in industrial scale. New varieties of unidirectional (UD), woven and nonwoven biofibre reinforcement forms are appearing in market on its own or in hybrid combination with carbon or glass or aramid fibres. This is a significant step forward for biocomposite industries who are willing to bring such products in market.

1.3.3 Moisture absorption

As mentioned before, natural fibres are rich in cellulose, hemicellulose, lignin, and pectins which contain hydroxyl groups making them hydrophilic (Fig. 1.3). The main constituent cellulose is semicrystalline in nature and contains large number of −OH groups. The −OH groups present in the amorphous part of the cellulose are more accessible by the external moisture, while the −OH groups in the crystalline regions are less. But hemicellulose being mostly amorphous, its −OH groups are more accessible by the water molecules and moisture absorption takes place through them. Lignin, being more hydrophobic, plays a less significant role in moisture absorption. The plant fibres are thus highly susceptible to moisture absorption and undergo swelling in moist environment [16–21]. The absorbed moisture causes debonding at the fibre/matrix interface and there is deterioration in properties. A fibre/matrix debonding initiated by absorbed water was shown by Dhakal et al. [22] in a hemp fibre-reinforced composite (Fig. 1.4).

Several attempts have been made by the researchers to reduce hydrophilicity of the plant fibres by chemical treatment or grafting route [13,23,24]. Chemical modification of the surface helps in reduction of moisture uptake as well as in increasing the compatibility with more hydrophobic polymers. However, this has mostly been limited to lab-scale research and there has not been any viable solution in industrial level. This therefore comprises another very important area of future research.

1.3.4 Compatibility with polymer matrices

Plant fibres have highly hydrophilic surface characteristics due to the presence of large number of hydroxyl groups and can have good chemical interaction only with hydrophilic resins like phenolic or polyurethane through the formation of hydrogen

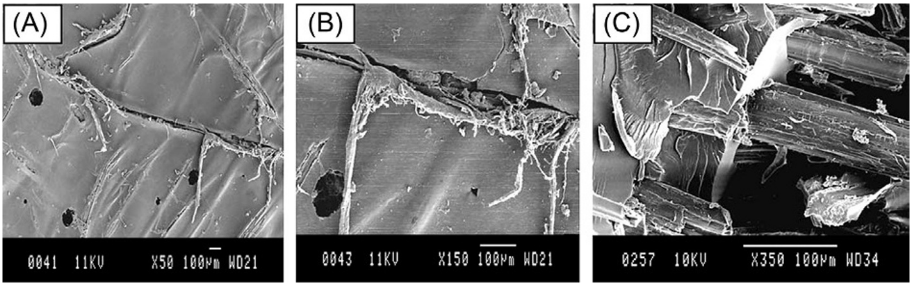


Fig. 1.4 Failure showing (A) matrix cracking (B) fracture running along the interface (C) fibre/matrix debonding due to attack by water molecules.
Reproduced with permission from Dhakal HN, Zhang ZY, Richardson MOW. Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites. Compos Sci Technol 2007;67:1674–1683, Elsevier.

bonds. But with hydrophobic resins, fibre/matrix compatibility at the interface is a major problem and fibre wettability is poor which gives rise to interfacial defects which finally act as stress concentrators and failure points in the composites.

Hence methods of promoting fibre wettability and interfacial bonding are absolutely essential to improve the performance of biocomposites. For glass fibres, standard silane coupling agents are applied by the fibre manufacturers which impart interfacial compatibility with different polymer matrices. But for plant fibres, no such coupling agents or surface treatment methods have yet been identified which can be employed in industrial scale. Several research papers have been published on enhancing the fibre/matrix interfacial bonding in biocomposites using various physical and chemical routes (shown in Fig. 1.5) [25–48].

But none of these surface modification methods could be translated to industrial scale due to various constraints. The plant fibre reinforcements available in market generally do not contain any coupling agents on their surface. Serious planning and

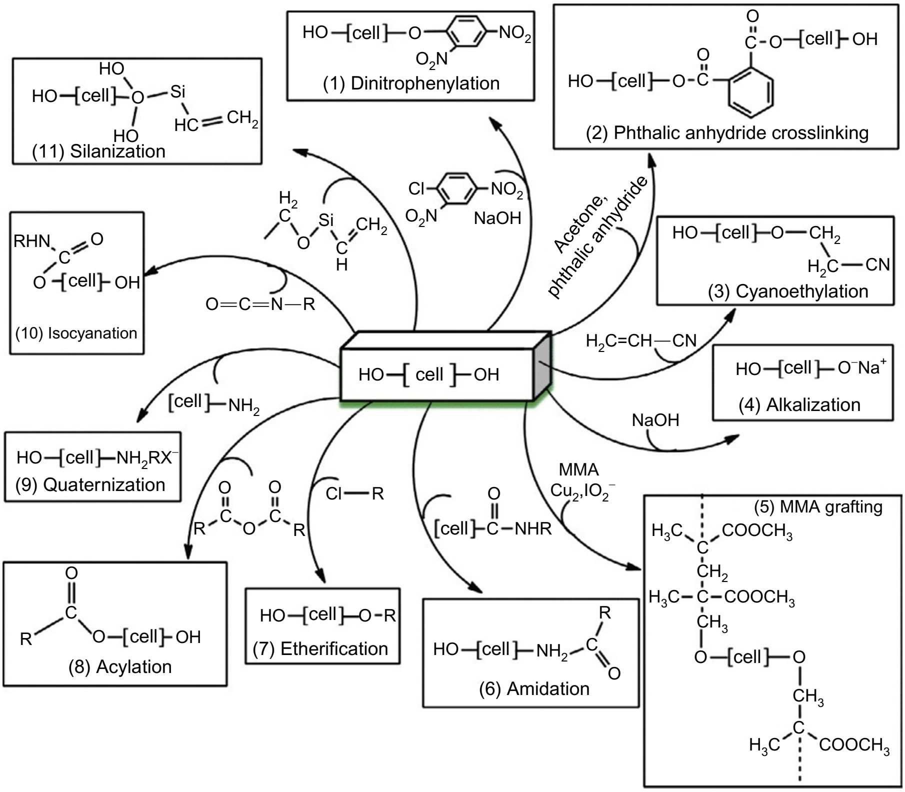


Fig. 1.5 Schematic representation of some of the surface modifications of natural fibre. Reproduced with permission from Gurunathan T, Mohanty S, Nayak SK. A review of the recent developments in biocomposites based on natural fibres and their application. Compos Part A 2015;77:1–25, Elsevier.

dedicated research are required in conjunction with the fibre manufacturers to advance this technology. This is a major requirement in order to develop high-performance biocomposites.

1.3.5 Flammability and thermal degradation

Plant fibres generally degrade before any glass transition or melting [49,50] and have poor flame resistance. For example, the limiting oxygen index (LOI), which is the minimum concentration of oxygen in a mixture of oxygen and nitrogen that is needed to support the flaming combustion of a material, is 18–20 for cotton, whereas wool has an LOI value of 25 [51]. When plant fibres are exposed to a fire, they undergo thermal degradation and combustion depending on the surrounding conditions like oxygen concentration, air circulation around the combustion area, etc. [52]. The thermal degradation of plant fibres leads to desorption of adsorbed water, cross-linking of cellulose chains with the evolution of water to form dehydrocellulose, decomposition of the dehydrocellulose to produce char and volatiles, formation of levoglucosan, and decomposition of the levoglucosan to yield inflammable and noninflammable volatiles and gases, tar, and char [50,53,54]. Manfredi et al. [55] reported that the thermogravimetric analysis of jute and sisal fibres is somewhat similar, while that of flax is different. Flax starts to degrade at a higher temperature than that of jute or sisal. Thermal degradation behaviour of the plant fibres depends on the proportion of various chemical constituents present in the fibres, of which some are inflammable and some are not. The thermal decomposition of cellulose, between 260°C and 350°C, leads to the formation of inflammable gases, noncombustible gases, tars, and char [56–58]. Thermal degradation of hemicellulose occurs between 200°C and 260°C, but produces less combustible gases. The thermal degradation of lignin starts from about 160°C and continues until 400°C. The cleavage of bonds in the aromatic rings of the lignin takes place at higher temperatures [59]. Lignin on thermal degradation produces higher char than that of cellulose. Thus higher lignin content in a plant fibre generally shows higher flame resistance but lower oxidation resistance, while higher cellulose content shows lower flame resistance.

High level of crystallinity in the cellulose content of a plant fibre produces higher levoglucosan during pyrolysis and consequently increases the flammability. Higher crystallinity also increases the activation energy for thermal degradation and raises the thermal degradation temperature. For example, the activation energy of amorphous cellulose is about 120 kJ/mol, whereas it is about 200 kJ/mol for crystalline cotton and ramie [60,61]. The degree of polymerization and fibrillar orientation of cellulose significantly influence the flammability of the plant fibres. The higher the orientation, the lower the oxygen permeability into the fibres and this has a direct effect on flammability [54,61].

The thermal degradation behaviour of plant fibres restricts their use in combination with high temperature curing thermosetting resins or in situ polymerizable thermoplastic resins like polyamide 6. The fibres undergo discoloration and degradation during in situ composite manufacturing [62].

Fig. 1.6 Images of (A) flax twill weave in a cone calorimeter and (B) a burnt flax unidirectional fabric sample.
Reproduced with permission from Chai MW, Bickerton S, Bhattacharyya D, Das R. Influence of natural fibre reinforcements on the flammability of bio-derived composite materials. Compos Part B 2012;43:2867–74, Elsevier.

An interesting study was conducted by Chai et al [63] where the flammability of flax fibre-reinforced epoxy composite was compared with an equivalent glass fibre-reinforced epoxy composite. Cone calorimetry and burning tests revealed that the flax fibre composite ignited earlier with higher heat release, higher time to extinguish and higher smoke production rate when compared to the equivalent glass reinforced one. The poor flame resistance of flax composites was attributed to the poor flame resistance of the flax fibres which are highly susceptible to combustion with vigorous heat release. The flax fibres were deformed during combustion while the glass fibres remained in integrated form. The flax fabrics, twill and UD, are shown in Fig. 1.6.

A large number of studies have been done on the flammability of cotton fibres [64–67], but very few studies have been reported on the flammability of plant fibre reinforcements like flax, jute, or hemp. Very recently some new approaches have been patented for improving the fire resistance of cellulosic materials, especially when the cellulosic material is to be used in polymer composites [68]. In this invention the cellulosic material was treated with an aqueous mixture of alkali metal or ammonium hydroxide and alkaline-earth or aluminium metal salt simultaneously with or within a short period of time of preparing the mixture. The treated cellulosic material became self-extinguishing and exhibited improved thermal stability, improved interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents, improved resistance to damage by ultra-violet light and/or reduced negative impact on fibre strength and/or modulus. It was also mentioned that these fire-resistant cellulosic materials may be further treated with a layered nanoparticulate material for additional enhancement of the fire resistance property. Polymer composites produced from cellulosic material treated according to this invention showed significantly improved fire-resistance with small negative impact on the mechanical performance of the composite. A lot more research activity is required in this field to minimize this inherent drawback of the plant fibres.

1.3.6 Cost

Plant fibres are generally called ‘low cost’ materials, but this is not always applicable. The biofibres in reinforcement forms like UD, plain weave, twill, or biaxial are sometimes more expensive than conventional synthetic fibre reinforcements like glass [69], although it depends on the reinforcement type, order quantity, supplier, etc. The high cost of plant fibre reinforcement fabrics does not always justify their performance and industries go for safer, lower cost, and higher performance synthetic reinforcements for commercial products. Hence efficient and cost effective processing and weaving techniques are required for plant fibres which will help to make them more competitive in price.

1.4 Commercially available plant fibre reinforcements

Table 1.4 shows commercially available plant fibre reinforcement types.

Table 1.4 **Examples of some commercially available plant fibre reinforcement forms**

Company	Reinforcement types
Flaxcomposites [70]	• Flax UD • Flax Balanced Twill • Flax Biaxial • Flax Braids • Flax fibre nonwoven mats • UD Flax/Epoxy Prepreg • Balanced Twill 2/2 Flax/Epoxy Prepreg
Lineo [71]	• FlaxTape (UD, 50–200 g/m^2) • Flaxpreg (Flax/Epoxy prepreg) (UD and Balanced fabric) • FlaxPly (flax UD and Balanced fabrics) • FLAXPREG T-UD Preimpregnated material based on an epoxy resin system and FlaxTape
Bcomp [72]	• Bcomp PowerRibs PowerRibs composite reinforcement materials ensure extremely light shell element solutions with high stiffness and damping properties for less cost • Bcomp ampliTex Fabrics Noncrimp, Biaxial

Continued

Table 1.4 Continued

Company	Reinforcement types
Composites Evolution [73]	• Biotex Flax Yarn, UD tape, Twill 100–400 g/m^2 • Biotex Jute Twill 400 g/m^2 • Biotex Flax/PLA Commingled Twill (400 g/m^2) • Biotex Flax/PP Commingled Twill (400 g/m^2) *New developments* Carbon/flax hybrid
EcoTechnilin Products [74]	• FibriMat LCM Flax nonwoven mat 300 and 450 g/m^2 • FibriPlast Natural fibre or glass fibre combined with thermoplastic (PP, PLA, PA) • FibriBoard Preconsolidated sheets produced from FibriPlast nonwoven mats after an additional precompression step, which bestows the rigidity of a thermoplastic composite (1000–2400 g/m^2) • FibriPreg 100% natural, nonwoven mats preimpregnated with 100% bio-sourced thermoset resin dedicated to hot moulding processes
Terre de Lin [75]	• Bioreinforts Composed by 0 and 90 degrees unidirectional fibre fabrics and also 45 degrees bi-axial fibre fabrics, all with different weights. This line is available in 100% flax for thermosetting uses and in fibre blend for thermocompressed applications
SAFILIN France [76]	• Rovings: TEX 200–2000 • Low twist yarns: TEX 68 and 105

1.5 Applications of plant fibres

The main advantages of using plant fibres are their low cost, low density, and high specific strength. They are easy to handle and do not cause any skin irritation. Less energy (~80% less energy) is required for the production of plant fibre textiles and fabrics than that of E-glass fibres and fabrics [2,3]. Plant fibres are used in wide range of applications, which include geotextile, automotive, textile, paper making, building and construction industries, etc. Hemp fibres are used in the sealing of pipes—coir fibres as the filling materials for seat upholstery—in transport packaging, furniture industries, cement reinforcements [77–81]. Yarn-based fabrics (from flax, hemp, cotton, jute, sisal, abaca) are used as furniture materials, in carpets, bags, geotextiles, and tarpaulins. Hemp- or flax-based needle nets or fleeces find applications in thermal insulating industries. In Europe mainly wood, flax, or hemp are used in insulating fleeces [82].

Jute, coir, and sisal are important materials in geotextile industry because of their smoothness, well adaptability with the ground unevenness and also due to their biodegradable nature [83]. Plant fibre-reinforced composites are used in many low-strength applications, such as biodegradable flower pots, disposable golf tees, table tops, chairs, garden furniture, etc. Automotive industries have shown their interests in plant fibre-reinforced composites for applications like instrument boards, indoor panels, car body components including gear encapsulation in bus [84], spare wheel cover of the Toyota RAUM [5], bonnet, boot lid, and roof of the BioConceptcar [5]. Overcoming the flammability problem, plant fibre-reinforced composites have also been used in seat box and seat back cladding [85]. Plant fibres have potentials to be used in aircraft industries, although fire safety has to be ensured [86].

1.6 Future prospects

In Europe plant fibres are traditionally used in paper and textile industries. Over the past few decades the use of plant fibres is increasing in different sectors because of economic and environmental issues. Plant fibres, having advantages in cost, properties, energy efficiency, renewability, biodegradability, and neutral carbon balance over the synthetic fibres, are of significant interests to many industries [87]. In industrialized countries efforts are being made to introduce plant fibre-reinforced composites in the market in replacement of synthetic FRPs because of the European ‘end-of-life vehicles regulation (ELV)’, the ‘European Composite Recycling Concept’, and other waste management laws [2,3]. According to a report by JEC [87] the market share for plant fibre-reinforced composites is 0.1%–0.5% depending on their applications and their development is at an emerging stage currently. The production of plant fibre-based composites reached 650,000 metric ton (MT) in 2015 and it is expected to rise up to 1,150,000 MT in 2030 in France according to the study by ADEME (Agence de l'environnement et de la maîtrise de l'énergie) in 2007. An effective synergy is required between the industries and the R&Ds to fulfil this target [87]. Focus should be given to improve the fibre properties, mastering their reproducibility and adaptability to specific technical applications, processing technologies, extraction methods, and to aid better adhesion with the polymer matrices. Technologies are being developed by National Research Council Canada (NRC; Ottawa, ON) to mitigate some of the intrinsic drawbacks of plant fibres, which are sensitive to moisture, inflammable, and can generate volatile organic compounds upon processing [88]. A good effort is being made by ADEME for the structural development of the plant fibre composite industries by providing global support, bringing together all the researchers, technologists, plant fibre producers, processors and users, and arranging the technical or brainstorming sessions on the new uses of the plant fibres in market. In future major steps have to be taken to support the plant fibre-based research, such as development of waste management guidelines like biodegradability, recycling, and reuse in developing countries, encouraging appropriate policy responses from governments to the problems faced by the plant fibre industries. Currently in Asia composite market is rapidly growing than that in Europe and North America and this is leading to the development of cheaper green composites because of the profound local cultivation of the plant fibres [2,3]. But certain limitations are still hindering the growth of industrial applications of these fibres. There is still lacking of an international organization or association which can represent the interests of plant fibres as a whole [5]. In textile industry cotton is mostly used, and sometimes flax, jute, ramie, hemp, and sisal, but applications of straw fibres are limited only to paper industry [2,3]. Continuous production of high quality fibres and their availability in large quantities at competitive prices are of high demand for industrial applications [2,3]. The demands of the modern industries are very far to reach by using only conventional processing techniques. Examples of few industrial demands are shown in Table 1.5.

Research efforts are therefore required to develop new technologies to fulfil these demands. For the production of consistent quality fibres research attention should be given on genetics and biotechnology. Economic viability is another factor. Processing of high quality fibres often increases the fibre cost. Poor fire resistance properties and weak fibre/matrix adhesion hinder the commercialization of plant fibre-based composites. Recent research activities to improve the flame resistance property include developing environmentally friendly, nontoxic fire retardants with higher efficiency,

Table 1.5 **Some examples of demands of the manufacturing industries on the fibres [2,3]**

Industrial criteria of acceptance of the final product (*1 tex = 1 g/1000 m of a fibre)						
Fibre length (mm)	**Fineness (tex)**	**Shive content (%)**	**Moisture content (%)**	**Fungal attack**	**Tensile strength (cN/tex)**	**Final product**
70–90	3–18	≤2	≤10	No	≥40	Internal boards and mats for cars, vehicles, trains, and aircrafts
50–70	3–10	≤4	≤12	No	≥40	Heat insulation mats for buildings
30–40	2–4	≤0.5	≤12	No	≥40	Yarn (spinning machines)
30–60	2–8	≤1	≤12	No	≥40	Coarse yarn composites
2–4	2–6	≤2	≤12	–	≥25	Pulp and paper industries
2–8	<18	<12	≤14	–	≥20	Air-placed concrete
≤2	2–20	≤15	≤8	–	–	Adsorption materials for various industries

chemical or biochemical modification of lignocellulosic fibres or plant fibres using enzymes, functionalization of plant fibres by chemical substitution of the reactive groups and employing irradiations like plasma, corona, and microencapsulation, incorporation of nanostructured flame retardants, etc. [89]. Farmers should be encouraged and motivated with low taxable infrastructures and other allowances for the production of renewable fibres and other biomass from renewable resources [5]. Moreover awareness should be developed among consumers, governments, and industries about the importance of sustainable technology and the products [2,3]. In a recent project report [90] the market entry barriers for general bio-based products have been discussed in great detail. This project identified three types of barriers stemming from norms and standards: (1) General product specifications are not addressing favourable bio-based properties. (2) The product specifications focus properties that are not really related to product functionality and are not fulfilled by the bio-based products. (3) Acceptance of bio-based products is not happening due to ‘old thinking’ in terms of conventional products. The report also highlighted a multitude of nontechnical barriers, mostly in the fields of political framework, communication, marketing, and finance. Huge efforts are therefore required to raise the performance level of existing plant fibres, biocomposites, and to win the confidence of the manufacturers and users.

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Man-made cellulose fibre reinforcements (MMCFR)

2

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2.1 Introduction

The concept of man-made cellulose fibre reinforcements (MMCFR) was first coined by the inception of rayon synthesis. Man-made cellulose fibres are developed from plant cellulose after processing it into a pulp and then extruding similar to synthetic fibres. Rayon or viscose is one of the most commonly ‘manufactured’ cellulose fibres, and it can be made from wood pulp [1].

Cellulose is the main component of plant cell walls and constructional unit for many natural fabric and paper. The purest natural form of cellulose is cotton and ashless filter paper in the laboratory. The monomer unit of cellulose is β-d-glucopyranose. Two monomer units are joined to form the disaccharide cellobiose eliminating a water molecule. The length of the chain varies greatly, from a few hundred sugar units in wood pulp to over 6000 for cotton.

There are a huge number of polar –OH groups in the cellulose chain (Fig. 2.1) which form intermolecular hydrogen bonding in between the chains forming highly crystalline structure. Cellulose is a natural polymer which is found in large amounts in nearly all plants, and also a major component of food resource. Cellulose and its derivatives are widely applicable in the field of food, textile, fibre, cosmetics, pharmaceuticals, etc.

Environmental awareness and the depletion of fossil fuels are raising the demands for man-made cellulose fibres. MMCFR are dominating the textile field for more than 70 years and can be of various types, e.g., Viscose (CV), Modal (CMD), Lyocell (CLY), Cupro (CUP), and cellulose derivative fibres, e.g., Acetate (CA) and Triacetate (CTA) [2].

The most important MMCFR are Viscose, Modal, Lyocell, Cupro, and Acetate fibres which are produced as staple fibres like Lenzing Viscose, Lenzing Modal, and TENCEL or as filaments like viscose tire cords and viscose yarns. The structures of the fibres are given in Table 2.1.

2.2 MMCFR source and manufacturing

Today rayon is the generic term for all of the manufactured naturals, while viscose implies a specific process and materials—so viscose is rayon, but not all rayons are viscose.

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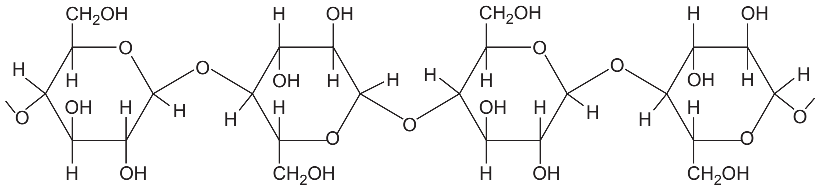
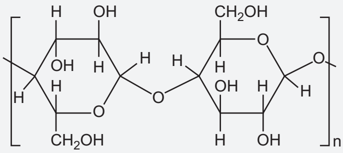
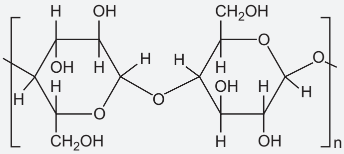
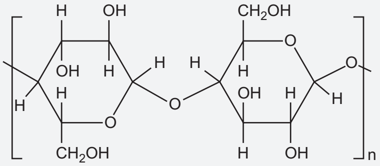
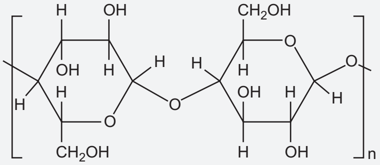


Fig. 2.1 Structure of cellulose.

Table 2.1 **The structure and code of common MMCFR [ISO 2076:1999(E)]**

Fibres with code	About the fibre	Molecular structure
Viscose (CV)	Cellulose fibre obtained from the cellulose pulp by viscose process	
Modal (CMD)	Cellulose fibre possesses a high breaking force and high wet modulus	
Lyocell (CLY)	Cellulosic fibre obtained from organic solvent spinning process	
Cupro (CUP)	Cellulose fibre obtained by the cuprammonium process	
Triacetate (CTA)	Cellulose acetate fibre in which at least 92% of the hydroxyl groups are acetylated	$-\!\left[C_6H_7O_2-(OX)_3\right]_n\!-$
Acetate (CA)	Cellulose acetate fibre in which less than 92%, but at least 72% of the hydroxyl groups are acetylated	$-\!\left[C_6H_7O_2-(OX)_3\right]_n\!-$

2.2.1 Rayon

The oldest commercially available man-made fibre is rayon. It is generally made from wood pulp and depending upon the process employed for generation of the fibre there are three types of rayons: viscose rayon, cuprammonium rayon, and saponified cellulose acetate.

2.2.2 Methods of preparation of rayon

Three types of rayons are now available in the market depending on their method of preparation. However, there are four methods by which rayon can be produced. Out of these four methods, one is completely obsolete and two are still practiced. 'Viscose Process' is used on a large scale as it is very inexpensive.

(a) Nitrocellulose Method
(b) Viscose Method
(c) Cuprammonium Method
(d) Acetate Method

(a) Nitrocellulose Method: Nitrocellulose is readily soluble in organic solvents, such as ether and acetone by which Georges Audemars developed the first 'artificial silk' in about 1855 but the method was impractical for commercial use. Commercially the fibre was produced first in 1891, which was flammable and more expensive than acetate or cuprammonium rayon. It was briefly known as 'mother-in-law silk'. The production was ended before World War I because of its flammability and expensiveness and now totally obsolete.

(b) Viscose Method: First wood pulp is treated with aqueous sodium hydroxide to form 'alkali cellulose'. The alkali cellulose is then treated with carbon disulphide to form sodium cellulose xanthate. The xanthate is dissolved in aqueous sodium hydroxide (typically 2%–5% w/w) and allowed to depolymerize to a desired extent, indicated by the solution's viscosity. The rate of depolymerization called ripening or maturing depends on temperature and is affected by the presence of various inorganic and organic additives, such as metal oxides and hydroxides. Rayon fibre is produced from the ripened solutions by treatment with a mineral acid, such as sulphuric acid. In this step, the xanthate groups are hydrolyzed to regenerate cellulose and release dithiocarbonic acid that later decomposes to carbon disulphide and water.

Rayon fibres are highly absorbent. Moisture content of cotton is 6% at 70°F and 65% RH, and for viscose rayon it is 13% under the same conditions. The fibre is soft, breathable, comfortable to wear, can easily be dyed in vivid colours, possess fair abrasion resistance. Like other cellulosic fibres, it is not resilient, that is it wrinkles exhibiting poor crease recovery and crease retention and the fabric shrinks appreciably when washed. Rayon withstands ironing temperatures slightly less than that of cotton. It does not build up static electricity, nor will it peel unless the fabric is made from short, low-twist yarns. It may be attacked by silver fish and termites, mildew, moulds, fungus, bacteria affecting the colour, strength, dyeing properties and the lustre. Clean and dry viscose rayon is rarely attacked by moulds and mildew [3].

The higher the crystallinity and orientation of rayon, the lower is the drop in tenacity upon wetting with a decrease in elongation-at-break. The tensile strength of the fibre is 1.5–2.4 grams per denier (gpd) and 0.7–1.2 gpd in the wet state whereas for high tenacity variety the values are 3–4.6 gpd and 1.9–3.0 gpd. The %elongation-at-break seems to vary from 10% to 30% dry and 15% to 40% wet. The density of normal viscose rayon is 1.53 g/cc with other variety of 3.0 and 4.5 g/cc. Viscose rayon loses strength above 149°C; chars and decomposes at 177–204°C. It does not melt or stick at elevated temperatures. As a cellulosic fibre, rayon will burn, but flame retardant finishes can be applied [4]. Strong acids like H_2SO_4 and HCl breaks the cellulose chains but cold acid solutions for a short time do not attack viscose rayon. Rayon reacts with hot dilute acids, bleaches at very high concentrations and by mildew under severe hot and moist conditions whereas bases do not seem to significantly attack rayon. Strong oxidizing agents like $Na(OCl)_2$, bleaching powder, and permanganate form oxycellulose. Prolonged exposure to sunlight causes loss of strength because of degradation of cellulose chains due to moisture and ultraviolet light of the sunlight. At 149°C or more the fibre loses its strength and begins to decompose at 177–204°C.

Rayons are available in different forms like yarns, woven, and non-woven fabrics. Rayon is the fibre of choice in many medical applications such as surgical packs, drapes, and gowns where hand, absorbency, and sterilizability are important [4]. In the form of yarn rayon fibres are predominantly used as embroidery thread, chenille, cord, novelty yarns, and industrial textiles. High tenacity rayon yarn is used as reinforcement in rubber goods (tires, conveyor belts, hoses), in applications within the aerospace, agricultural, and textile industries, as braided cords, tapes, etc. Rayon in woven form is used as fabric in crepe, gabardine, suiting, lace, outerwear fabrics and linings for furcoats and outerwear, apparel, home furnishing material. Wipes represent the largest non-wovens market for rayon [3].

(c) Cuprammonium Rayon Method: The fibre was first discovered by the Swiss chemist Matthias Eduard Schweizer dissolving cellulose in tetraamine copper dihydroxide. During manufacturing, a solution of cellulosic material in cuprammonium hydroxide solution was made at low temperature in a nitrogen atmosphere, followed by extrusion through a spinnerette into a sulphuric acid bath. This reaction of the fibre with the acid is necessary to decompose cuprammonium complex to cellulose. This is a more expensive process than that of viscose rayon and used on low scale. Its fibre cross-section is almost round [5]. BEMBERG, for example is a trade name for cupramonium rayon that is only produced in Italy.

The fibre has very fine texture with a soft silk-like feel. Filaments as fine as 1.33 deniers are produced regularly (as compared to viscose rayons which have a usual denier of around 2.5, cross-sections are round and smooth, being occasionally oval. The average tensile strength of cuprammonium rayon is 1.7–2.3 gpd in dry and 0.9–2.5 gpd in wet state. Moisture content at 27°C and 65% RH is about 11% as in case of viscose rayon. It has an elongation at break of 10%–17% when dry. It burns rapidly and chars at 180°C and on ignition, it leaves behind ash containing copper. It degrades and weakens on exposure to sunlight in the presence of oxygen and moisture.

(d) Acetate Method: The method was first discovered by Paul Schützenberger. This acetate was first used as a coating on cotton fabric used in early aeroplanes or as a film similar to cellophane or plastic wrap. Triacetate fibres were developed later until the availability of safe solvents in sufficient quantity to make production economically profitable. Applications of both acetate and triacetate fibres are only for selected types of fabrics and have continued to decline over the years.

Cellulose, generated from wood pulp or purified cotton, was first steeped with acetic acid for swelling of cellulose and making it more reactive. The pre-treated cotton is acetylated with excess of glacial acetic acid and acetic anhydride in the presence of sulphuric acid to form cellulose triacetate which is only soluble in chloroform making the method expensive. The cellulose triacetate formed is then aged for 20 h to carry out partial hydrolysis for the conversion of triacetate to diacetate and the resultant mixture is poured into water to precipitate out the cellulose acetate with a DP of 350–400 and 2.35–2.4 unit of acetyl group per anhydro glucose unit. The solution is filtered and spinning of the fibre is done from the solution of cellulose acetate in acetone [6].

Fibres are lustrous, soft, pliable, drape well, easy to handle, quick drying, dimensionally stable, good conductor of heat, fairly resistant to dilute acids, and poor resistance to concentrated acids. Concentrated organic acids cause swelling and also resistant to mildew, moths, and bacteria. Tenacity and elongation at break of acetate rayon is 1.4 gpd and 25% at dry state whereas 0.9 gpd and 35% at wet state, respectively. It can also withstand treatment with soap or alkali solution with a pH of not more than 9.5 at temp up to 100°C [7]. It begins to weaken at 93°C and at 175°C it becomes sticky and melts at 260°C. Some degeneration takes place when this fibre is exposed to light but not severely and is stable to hot water.

Typically acetate fibres are combined with other fibres such as rayon and polyester to produce ladies' apparel. In particular, as triacetate fibre has a soft texture and drapes well most ideal for use in luxury couture for women. Diacetate fibre is also used for sleepwear, lining for clothes, gift box lining, labels and tags attached to clothes, ribbons, packing tape, and other sundry goods. The most unique industrial use is as cigarette filters.

2.2.3 Lyocell

The cellulose fibres with the generic name of Lyocell and code CLY is produced by direct dissolution of cellulose. The research on generation of MMCFR is diversified with the use of different solvents of cellulose and many attempts have been made among which N-methyl morpholine-N-oxide (NMMO) hydrate was found to be the best solvent. Commercially these cellulose fibres are successfully marketed under the trade name of Tencel by Courtaulds since 1994. There are other process variations which generate the fibres Lenzing Lyocell and TITK Alceru [8]. These processes are advantageous over the viscose generation because NMMO hydrates are non-toxic and environmentally benign with respect to toxic carbon disulphide, which can be almost completely recycled.

The Lyocell fibre exhibits good wet strength as well as excellent dry strength due to its highly crystalline structure with continuous crystalline domains dispersed along the fibre axis. This makes Lyocell water-washable. Further, it offers less shrinkage on wetting than other cellulose fibres such as cotton and viscose rayon. Lyocell fibres exhibit the following properties:

Lyocell has moisture absorption property 50% more than cotton and even more than wool. The combination of this extremely smooth surface of Lyocell with the presence of nanofibril and excellent moisture absorption property makes Lyocell fibre soft and pleasant to the skin, making this versatile fibre ideal for active wear, clothing for sensitive skin as well as to upholstery fabrics and home fashions in sheets and towels. Blends of Lyocell complement those of wool, cotton, linen, silk, polyester, and nylon, and enhance their inherent properties such as introducing new softness in wool and drape; with cotton and linen, it increases suppleness and luster. Staple fibre is used in apparel items such as denim, chino, underwear, other casual wear clothing, and towels. Filament fibres are used in items that have a silkier appearance such as women's clothing and men's dress shirts. Non-woven products of the Lyocell fibres include the area which require absorbency, purity, softness, strength, and biodegradability, i.e. wipes specially spun-laced wipes, medical and hygiene as well as filtration application. Ecologically friendly carpets can be made from Lyocell fibres in sustainable process and is 100% biodegradable. Lyocell 'fill' for bedding has excellent moisture and temperature regulation to provide a pleasant and dry feel during sleeping.

2.2.4 Modification of lyocell to lyocell LF

Lenzing with Lyocell LF has developed a fibre, in which the fibrillation tendency is arrested somehow by chemical cross-linking at the production stage and the production of fibre is based on the principle of solvent spinning. This fibre is readily controllable and no additional finishing steps are required to suppress fibrillation. The difference between the processing of Lyocell and Lyocell LF is after dissolving the pulp in the NMMO (*N*-methylmorpholine-*N*-oxide) solvent, a highly viscous solution is obtained by water evaporation and then extruded through spinnerets. Cross-linking of this fibre is made in an additional finishing step in a dried condition to maintain the typical fibre properties of Lyocell followed by the soft finishing which is necessary for spinning and the fibre is dried.

2.2.5 Modal

Modal is a generic name for a modified rayon fibre that has high tenacity and high wet modulus and is coded as CMD. Modal is a type of rayon, a semi-synthetic cellulose fibre made by spinning reconstituted cellulose, in this case often from beech trees. First developed by the Austria Lenzing company, who trademarked the fabric's name, modal is now made by many manufacturers. Modal is classified as a bio-based textile. Modal fibres were initially developed in the 1930s for industrial uses in tires, conveyor belts, and hose pipes. Changes in the rayon processing, such as the spinning conditions, chemical solutions, and stretching sequences, produced rayon fibres with increased crystallinity and thus, greater strength.

Modal fabric has good moisture regain capacity as it is about 50% more hygroscopic or water absorbent per unit volume than cotton fabric. Air permissibility is often considered better than cotton but needs ironing after washing like cotton. They are even softer than mercerized cotton such that mineral deposits from hard water like lime do not stick to the fabric surface, i.e. does not show dry rigidity after repeated washing. Modal fibres are dimensionally stable and do not shrink or get pulled out of shape when wet like many rayons. They are also wear resistant and strong.

Due to its properties, modal is also a favourite fibre in lingerie, loungewear as well as kids clothes and baby wear. It is a good material for exercise clothing and health suit, which can serve to benefit physiology circulation and health of the body. Modal is used alone or with other fibres (often cotton or spandex) in household items such as towels, bathrobes, bed sheets, etc. Modal fabric is very soft and is often found in underwear, bedding, and towels. It is often blended with cotton, spandex, or other fibres. It is cool to the touch and very absorbent. It takes and holds dye easily. Modal is less resistant to shrinkage than cotton and tends to peel less as a result of friction on the surface. The textile has particularly taken off in Indian companies. In the United States, it is most often seen in bed sheets, towels, and robes, but it is slowly gaining ground as a clothing material as well. In Europe, where the fabric originated, it is already widely used in clothing as a replacement for cotton.

2.3 Viscose rayon and other MMCFR

Various MMCFR have been discussed in previous sections. Commercial fibres [9,10] are mostly viscose fibres (tire cord viscose, polynosic fibres), modal fibres, cupro fibres (Asahi Kasai), and lyocell fibres (Tencel) differing in DP of cellulose (source), spinning process, and post-spinning treatment. Their fibre properties vary over a wide range. Nevertheless, further diversification needs the use of other solvent systems and are based on cellulose derivatives such as *Fortisan fibres* (saponified cellulose acetate from acetone, Celanese Corp., Grenoble, France); *“Fibre B” (Bocell)* (dissolution of cellulose in superphosphoric acid spun via air-gap into acetone and saponification in water/soda, Akzo Nobel); *Celsolfibres* (cellulose is dissolved in sodium hydroxide and regenerated in water, Institute of Chemical Fibres, Lodz, Poland). Bocell is very uniform and highly oriented fibre whereas Celsol contains presumably fibres having lower quality than viscose. A comparison of the fibre properties is given in Table 2.2.

The variation in tenacity of different MMCFR versus crystallinity parameters is given in Figs. 2.2 and 2.3. Apart from the CV tire cord the fibres showed more or less a linear correlation between tenacity and fibre orientation.

Table 2.2 Comparison of fibre properties [11–14]

Fibre type	Density (g/cm^3)	Tenacity (wet) (cN/tex)	Tenacity (dry) (cN/tex)	Water retention (%)	Melting point (°C)
Viscose (Lenzing Viscose)	1.52–1.54	10–13[15]	24–26	90–100	n/a
(Lenzing Modal)	1.52–1.54	19–21	34–36	60–65	n/a
Lyocell (Tencel)	1.50	34–36	40–42	60–70	n/a

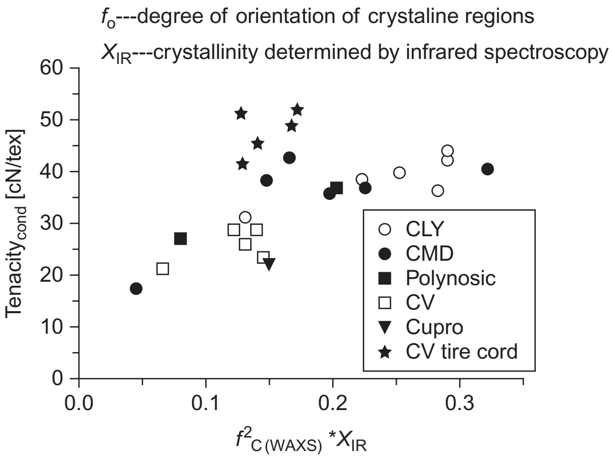


Fig. 2.2 Correlation between tenacity (conditioned state) and structural parameters—degree of crystalline orientation and crystallinity [2].

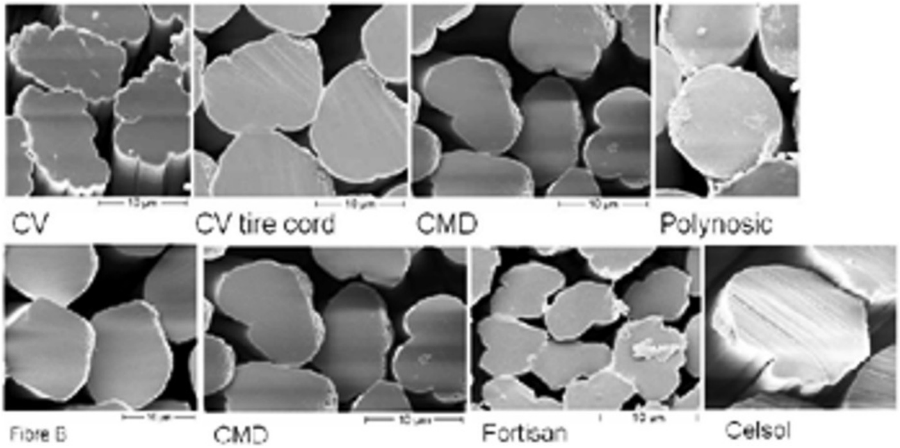


Fig. 2.3 SEM images of different viscose types of fibres [2].

Morphology of the different MMCFR is shown in Fig. 2.3 which indicates that fibre cross-sections also change with the fabrication process.

2.4 MMCFR for industrial-scale manufacturing of biocomposites

In reality fabrication of commercially viable biocomposite materials has proven to be a daunting challenge. Natural fibres are mostly inferior in strength compared to their synthetic counterparts—glass, aramid, and both biofibres and bio-based resins

Table 2.3 **Commercially available MMCFR [2]**

Sl. no.	Type of fibre	Manufacturer	Trade name
1	Cupramonium rayon	Asahi Kasai	Bemberg, ecological Bemliese
2.	Lyocell	Lenzing AG	Tencel, Modal
3.	Rayon	Kelheim Fibres	Galaxy, Danufil, and Viloft
4.	Cellulose acetate	Celanese Corp	Fortisan
5.	Regenerated cellulose from superphosphoric acid as solvent	Akzo Nobel	Bocell
6.	Regenerated cellulose from Caustic soda as solvent	Institute of Chemical Fibres, Lodz, Poland	Celsol

are more costly. Continuous research is offering new commercial or near-commercial biofibres and bioresins comparable with the synthetic products in terms of price and performance. The most important source is cellulose based. The problem of variation in diameter and length for natural fibre is solved by generation of MMCFR obtained by dissolution of cellulose pulp and then made into uniform-sized filaments by means similar to those used in the manufacture of glass and other synthetic fibres. Most of the commercially available MMCFR which can be used as reinforcements in biocomposites are listed in Table 2.3.

In October 2012, Engineered Natural Composites Corp. (aka ENC International, Seoul, South Korea) manufactured a continuous-filament cellulose fibre known as BioMid for the North American market and GS Consulting (aka Gordon Shank Consulting, Burnaby, British Columbia, Canada) retains the exclusive marketing and sales rights. The first commercial grade of BioMid is a 1650-denier yarn, comprising 900 'extremely highly crystalline' cellulose filaments, each with a diameter of about 11 μm. It has a tenacity of 8–9 gpd and a modulus of 350 gpd, properties that put it roughly on par with some E-glass yarns (typically 6–11 gpd) but below S-glass and aramid [16]. The company also has a 2200-denier yarn under development. BioMid is made in South Korea by dissolving cellulose and spinning the solution from a spinneret. BioMid fibre's density is close to that of aramid fibre and its specific tensile strength is comparable to Innegra Technologies' (Greenville, S.C.) 8 gpd high-modulus polypropylene (HMPP) fibre. BioMid is translucent when wet out and has very high degree of crystallinity (95%), permitting fibre processing at temperatures as high as 360°C/680°F in comparison to 150°C/302°F for most natural fibres. Hence BioMid is a more suitable option as the processing temperature for commercial resin systems is around 200°C/392°F. Unlike the discontinuous natural fibres with variation in length from inches to a few feet, BioMid fibres are continuously spun and need not be twisted into bundles. Spinning can achieve the smallest filament diameter of any natural fibre—10–11 μm (0.39–0.43 mil) in case of BioMid consistently and repeatedly which is impossible with plant-based fibres. On the other hand they can be used

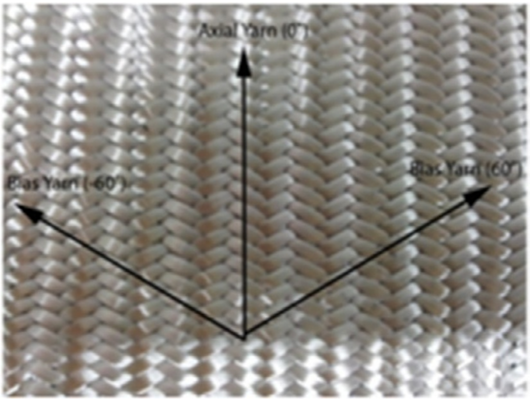


Fig. 2.4 Triaxially braided BioMid preform showing axial and bias yarns [17].

in parallel, enabling much higher properties and producing thinner fabrics than twisted yarns reducing resin puddling at the warp-weft interstices, resulting in a more even resin-to-fibre distribution [16].

BioMid maintains a smaller carbon footprint than other natural fibres as the raw material is obtained from wood pulp and paper-industry waste in Canada. The product does not compete with food crops for land and requires no water or fertilizer for its production. Shank Consulting claims that BioMid fibre manufacturing generates 0.88 kg (1.94 lb) of carbon dioxide (CO_2) emissions per metric tonne of fibre, compared to 55 kg (121 lb) for flax fibre and 500–600 kg (1102–1323 lb) of CO_2 emitted per metric tonne of produced glass fibre.

Development of commercial biocomposites has also begun with BioMid, and the company is exploring reactive sizings that will optimize the fibre–matrix interface and is developing a range of linear densities that can be optimized for specific end-uses. Eco-friendly surfboards with zero-glass are fabricated by E-Tech Boards (Hawthorne, CA) with an array of recycled and bio-based materials, including recycled expanded polystyrene (EPS) foam core and the woven fabric for the boards is a 5.1-oz, 100% BioMid, supplied in a 45-in./1140-mm width. Two prototype boards have successfully passed field testing [16]. Qamhia [17] has fabricated composite panels from triaxially braided BioMid fibre (Fig. 2.4) with a braiding angle of 60° and a high-bio-content epoxy resin system.

2.5 Plant fibres and MMCFR—mechanical properties, moisture absorbance, thermal stability, flammability, cost, and ecological impact

A single plant fibre consists of several layers. These layers or cell walls differ in their composition (ratio between cellulose and lignin/hemicellulose) and in the orientation of the cellulose microfibrils. The characteristic values for these structural parameters

Table 2.4 Mechanical properties of plant-based natural fibres in comparison with MMCFR [15,18]

Fibre	Density	Elongation	Tensile strength (MPa)	Young's modulus (GPa)
Cotton	1.55	7.5	290–590	5.6–12.5
Hemp	–	1.6	691	–
Flax	1.5	2.9	350–1030	27.5
Jute	1.25	1.65	395–770	26.1
Sisal	1.51	2.25	515–630	9.5–21.5
Ramie	–	3.7	405–935	61.5–125
Coir	1.21	30.0	176	4.5–5.9
Viscose (cord)	–	11.2	595	11.0

vary from one natural fibre to another [15]. The spiral angle of the fibrils and the content of cellulose determine generally the mechanical properties of the cellulose-based natural fibres [15,18]. Natural fibres can be processed in different ways to yield reinforcing elements having different mechanical properties. The elastic modulus of bulk natural fibres such as wood is about 10 GPa. Cellulose fibres with moduli up to 40 GPa can be separated from wood, for instance, by chemical pulping processes. Such fibres can be further subdivided by hydrolysis followed by mechanical disintegration into microfibrils which are estimated to have an elastic modulus of as high as 138 GPa [15,19]. Mechanical properties of natural fibre in comparison with conventional reinforcing fibre are presented in Table 2.4.

Regenerated cellulose fibres have long been made according to various processes yielding fibres with a wide range of mechanical properties. They include textile fibres with a low modulus and tenacity but high elongation at break, fibres for technical applications such as tire cords with an intermediate modulus and strength, and fibres with a high modulus and tenacity but low elongation at break. There are several processes for the production of cellulose yarns, both for textile and industrial applications. The commercial types, Viscose-Rayon, Cupro, and Lyocell, all have a limited tenacity [20].

Recently, there has been a report of a highly oriented cellulose fibre with high modulus and tenacity properties spun from an anisotropic solution in phosphoric acid using an air gap. Liquid crystalline solutions are known to be good precursors for high modulus/high tenacity yarns. The backbones of most of the polymers used for the preparation of these strong fibres comprise aromatic units, e.g., poly(*p*-phenylene terephthalamide) or PPTA, polybenzoxazole or PBO, polybenzothiazole or PBT, and also poly{2,6-di-imidazo[4,5-b:4′5′-e]pyridinylene-1,4-(2,5-dihydroxy)phenylene} or PIPD. The advantage of using a liquid crystalline solution for fibre production is that the local orientational order of the chains is already at such a level that they can be transformed into highly oriented fibres without the necessity of an after-treatment, which is required in spinning from isotropic melts or solutions of flexible polymers [20,21]. The mechanical properties of the major regenerated cellulose fibres and plant fibres such as flax and hemp are listed in Table 2.5.

Table 2.5 Mechanical properties of the major regenerated cellulose fibre types, including flax and hemp [22]

Sample	Fibre diameter (μm)	Young's modulus (GPa)	Tensile strength (MPa)	Breaking strain (%)
Cordenka EHM	9.4	32.2	710	3.9
Enka Viscose	18.0	9.4	220	17.2
Cordenka 1840	12.9	16.9	660	12.7
Alternative cellulose	15.6	30.6	1010	7.0
Cordenka 700	13.1	20.0	660	10.7
Lyocell	12.3	15.2	540	7.0
Hemp	17.1	43.5	270	5.5
Flax	31.2	19.1	270	0.8

MMCFR are a unique solution to develop novel bio-based composites that can unhook the widespread dependency on fossil fuel [23,24]. Regenerated cellulose fibres have good potential and there is a rise in the interest for these fibres [25–29] though they are inferior to glass fibres in mechanical performance. However, the low density and non-abrasiveness of cellulose are strong advantages of regenerated cellulose fibres. Natural fibres may also be the solution to the environmental problem but still less preferred because natural fibres are inherently dependent on their locality, part of the plant from where they are collected, maturity of the plant and how the fibres are harvested, etc. [30–33]. Also there is wide property variation when natural fibres are used as reinforcement in biocomposites. Using MMCFR as reinforcement gives a good balance of mechanical properties [34] compared to the natural fibres, though both natural fibres and MMCFR have similar extent of heat sensitivity and flammability. A comparison of cotton and flax fibres with most common MMCFR is presented in Table 2.6.

There are reports where the poor mechanical properties of natural fibre-reinforced composites have been improved by incorporating MMCFR. Mieck et al. [35] studied the effects of the admixture of Lyocell fibre and flax fibre reinforcements on the mechanical properties of polypropylene matrix composites. Further investigation was carried out by Graupner [36]. Composites of the fibre mixtures of hemp/Lyocell were investigated [36].

2.6 Reinforcement forms (unidirectional, woven and non-woven fabrics, hybrid fabrics, commingled fibres)

The regenerated fibres or filaments can be twisted or plied together or they remain as a continuous filament yarn. Large numbers of continuous rayon filaments that give the appearance of untwisted rope is known as tow. Such regenerated cellulose fibre tows are then interlocked into a long continuous length of fibres known as yarns which have

Table 2.6 Comparison of cotton and flax fibres with MMCFR

Sl. No.	Name of the fibre	Mechanical properties	Moisture absorbance/feel	Cost and ecological impact
1.	Cotton	Strong in wet condition	Absorbent	Ample supply, economic
2.	Flax (Linen)	Strong both in dry and wet condition	Absorbent, smooth, lustrous	Wrinkles, limited supply, mildews
3.	Modal	Dry strength fairly good—better than that of standard viscose; loses less strength in wet	Absorbent	Economical to produce
4.	Lyocell	Good strength, loses some strength in wet	Absorbent	Wrinkles, swells in water (fabric shrinks), mildews
5.	Acetate	Weak, much weaker in wet	Drapes well; soft, silky to hand; smooth	Low abrasion resistance, economical to produce
6.	Triacetate	Weak, much weaker in wet	Permanent heat set	Low abrasion resistance, economical to produce

Fig. 2.5 MMCFR forms from wood.

consistent properties and increased suitability in engineering composite applications. The fibre tows when cut into shorter lengths become staple fibres (Fig. 2.5). Thread is a type of yarn intended for sewing by hand or machine. Said regenerated cellulose fibres may comprise one or more of rayon, viscose rayon, lyocell, regenerated bamboo fibres, or cellulose acetate.

Different forms of MMCFR used as reinforcing agent are listed in Table 2.7 with their mechanical properties.

Table 2.7 Commercial grades of MMCFR [37]

Material	Average strength (MPa)	Elongation (%)	Modulus (GPa)
Cordenka 700	833	13	20
Viscose sliver	338	12	11
Tencel sliver	552	11	23
Carbamate	365	8	22

Cordenka 700 is a rayon tire cord yarn provided by Cordenka GmbH (Obernburg, Germany) and is produced by a special variant of the viscose process. Enka viscose is a typical viscose fibre for textile applications produced by Enka GmbH and Co. KG (Oberbruch, Germany). Viscose sliver was kindly provided by KelheimFaser GmbH (Germany) and taken from the staple fibre production line (non-wovens applications) by separating a sliver of approximately 2 ktex. In contrast to the former three, the filament yarn NewCell is spun using a non-derivatizing Lyocell process with N-methyl morpholine-N-oxide/water as the solvent. The fibre was manufactured by Akzo Nobel NV (The Netherlands), but is out of production at present. Another Lyocell fibre is Tencel (Lenzing AG, Austria), again separated from a staple fibre sliver suited for incorporation into the composite matrix [37]. Finally, Carbamate is a cellulose fibre spun via the CARBACELL process [38], an environmentally friendly alternative to the viscose process using urea as the derivatizing agent.

Yarns of MMCFR may further be available in either knitted or woven form. Knitted fabrics are produced by knitting machines that 'knit' different yarns together using exactly the same hand knitting method to make fabric. Woven fabrics are produced on huge looms that 'weave' different yarns together by interlacing threads both horizontally and vertically. These are expressed in Fig. 2.6.

Fabrics made from weaving and knitting yarns constitute the largest part of textiles manufactured around the world. But the woven form may also be used in composite manufacturing way in a commingled form. Suresh et al. [39] studied the influence of different layering pattern on the thermal and mechanical properties of

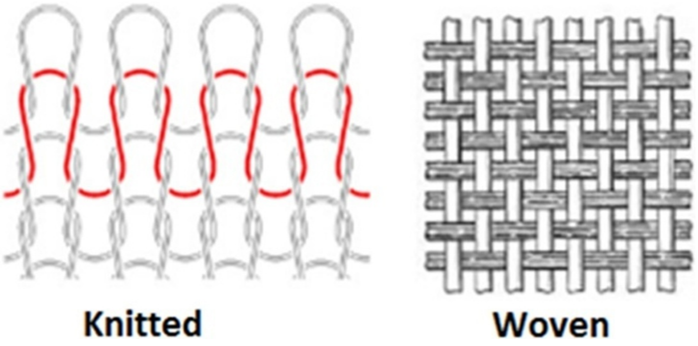


Fig. 2.6 Yearn in different forms of weaving.

the hybrid lyocell/rayon woven fabric-reinforced polyester composites. The rayon/rayon/lyocell pattern reinforcement in the composites has the best tensile and flexural properties exhibiting an increase in tensile and flexural strength by 36.5% and 43.79%, respectively, with reference to neat resin followed by a reduction of 31.1% in tensile modulus. On the other hand rayon/lyocell/rayon hybrid or commingled form of reinforcement achieved only 8% increase in tensile properties in comparison to the neat resin due to rayon fabric placed as a skin rather than core. A 6%–26% reduction in tensile strength was observed in the samples with different patterns or commingled reinforcements which was due to fibre and inter fibre (matrix) fracture. The impact properties for the lyocell/lyocell/lyocell reinforcement showed the best impact strength of 3.36 kJ/m^2 compared to rayon/rayon/rayon and other tri-layer composites. Thermal analysis showed higher thermal stability for the rayon/rayon/lyocell pattern reinforcement.

Many thermoplastic matrices are used to fabricate biocomposites but show inadequate fibre–matrix adhesion and the problem of lack of adequate resin penetration into the fibre tow or into the pores generated by the fibre interlacement are important issues. Dealignment of the reinforcing fibres is another problem caused by high matrix viscosity during consolidation. Among different fabrication processes like hot melt, solution, slurry, emulsion, film, surface polymerization, powder coating, and commingling, only powder coating and commingling are effective to produce prepregs with substantial flexibility [40–42]. So this thermoplastic commingled/hybrid yarns are one of the possible intermediate products, 'dry prepregs', applied for continuous fibre-reinforced thermoplastic composites and hence become the cost-effective solution for manufacturing different complex-shaped parts. Hybrid yarns can be prepared by different methods including co-wrapping, core spinning, and commingling.

In co-wrapping method, a core of twistless reinforcing fibres and thermoplastic filaments (Fig. 2.7A) are usually wrapped by thermoplastic fibres surrounding the core [43]. However, the yarn has poor impregnation due to inhomogeneous distribution of the reinforcing and matrix yarns and requires higher pressure and processing temperature [44] for good impregnation and adhesion.

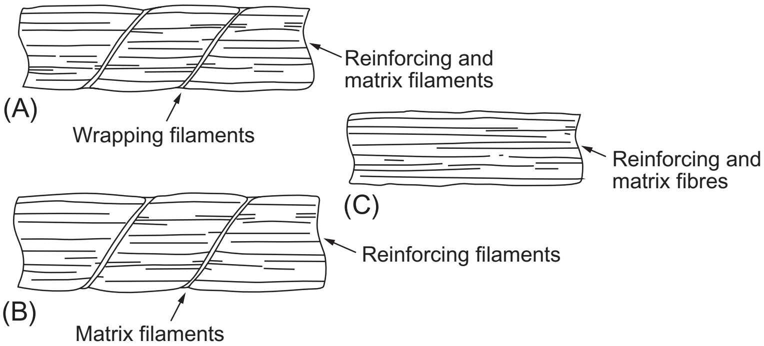


Fig. 2.7 Structures of (A) wrap spun hybrid yarn, (B) friction spun hybrid yarn, and (C) commingled hybrid yarn.

Short staple fibres of thermoplastic matrix are spun around a core of high-performance continuous reinforcing fibres in the core spinning (friction spinning) technique as represented in Fig. 2.7B producing a flexible yarn and making further processing easier [45].

Commingling is most effective hybridization technique for the matrix and reinforcing fibres by which soft, flexible, and drapable yarns [46] are produced where both are mixed in a nozzle with the help of compressed air (Fig. 2.7C). However, there will be tendency for these yarns to demingle under load and during preforming operations [47].

Braided composites can also be produced in 2D and 3D fabric textures for improving the out-of-plane resistance, shape retention capacity, and impact resistance. The fibre preform produced by the braiding is unique and can be easily impregnated with a thermosetting resin using various techniques such as resin transfer moulding, vacuum assisted resin transfer moulding, or in pre-impregnated forms. They are less susceptible to delamination [48] resulting in wide applications [49]. Besides the woven form various non-woven technologies constitute the fastest growing sector of textiles. Non-wovens are engineered textile substrates that are made directly from fibres bonded together by chemical, mechanical, heat, or solvent treatments. There is an increasing number of new non-woven products produced related to medical and personal care, filters and electronics, clothing/household textiles, padding/laminated textiles, geotextiles, and other technical textiles.

The term composite non-wovens, refers to a category of materials different from non-woven composites, which consist of a resinous matrix reinforced with an embedded non-woven fabric. Combination of different non-woven preforms prepared either by employing a variety of process technologies or by combining non-woven preforms with traditional textile preforms into a consolidated structure can also result in the creation of composite non-wovens. Composite non-wovens can provide an engineered solution by creating multifunctional products as well as an economical solution by eliminating manufacturing processes and replacing two or more products by a single product. Business activity in the field of composite non-wovens is therefore expected to grow substantially. These are developed by employing non-woven technologies and using a combination of fibres of different origins, different characteristics, or a combination thereof [50]. Non-wovens are assemblages of fibres that are soft, porous, and voluminous, but, at the same time, offer resistance to mechanical deformation. Fibres in the webs are bonded mechanically, thermally or chemically, or by a combination of all to impart structural integrity and stability. Originally, non-wovens were used as low-cost replacements for traditional textiles, but now they are a feature of medical, technical, and consumer products in their own right, and are engineered fabrics offering cost-effective solutions for a wide variety of applications. The definitive definition of non-wovens as given in Textile Terms and Definitions is as follows: Fabrics normally made from continuous filaments or from staple fibre webs are strengthened by bonding using various techniques. These include adhesive-bonding, mechanical interlocking by needling or fluid jet entanglement, thermal-bonding, and stitch-bonding [51]. Sodden et al. [52] have reported new developments in the design, manufacture, and testing of 3D-reinforced natural fibre woven composites with structural strength potential. It discusses the 3D weave architectures used, details of the VARTM composite

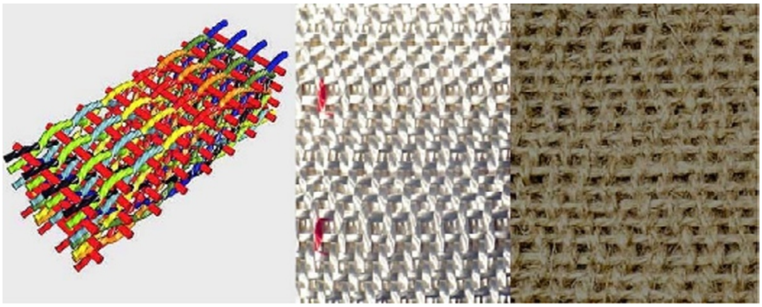


Fig. 2.8 3D Angle interlock design simulation (left), viscose preform (centre), and flax preform (right) [52].

processing method and highlights the challenges of producing structural thermoset composites from naturally variable yarns. They have used both flax and viscose rayon yarns. Viscose rayon yarns were already modified by the manufacturer to produce good thermal and adhesion compatibility with the resin matrix. Attributes such as consistency in production and fibre properties, small batch supply, comparable cost, and quality certification, demonstrated the potential of a yarn to be investigated in this research. Spun flax yarns can retain their cross-sectional shape and resist deformation in the preform due to their bulky and textured nature. Viscose rayon yarns are slippy in nature and are prone to distortion and flattening to an elliptical shape within the preform. This is reflected in the varying preform thickness between the fabric types and is pronounced in the cross-sectional micrographs in Fig. 2.8. Due to the slippage experienced within the viscose yarns, additional tension is applied during the manufacture and this can affect the weft pick density values.

They have used a two-part epoxy resin system consisting of Araldite LY-564 epoxide and an Aradur HY 2954 curing agent. For a comparative study a novel thermosetting bioresin (BioRez) from Trans Furans Chemicals was also employed as a matrix material which is a furan resin, based on furfuryl alcohol derived from Hemi-cellulose C5 sugars produced from agricultural waste. Vacuum Assisted Resin Transfer Moulding (VARTM) was used to manufacture the composites. The disadvantages of flax fibres such as batch variabilities, need for pre-treatment, and availability at low cost can be solved with the use of viscose rayon. Viscose–epoxy and viscose–furan composites with a much reduced fibre volume fraction V_f, reached 65% and 50%, respectively, of the properties of glass fibre composites. Flax composites demonstrate a robust yarn that resists deformation but requires a higher density preform and fibre surface treatment if performance is to improve.

2.7 Literature review on MMCFR-based composites

One class of natural fibres is regenerated cellulose fibres which are produced by dissolving cellulose, then regenerating it by extrusion and precipitation. Regenerated cellulose fibres have generally less variable properties compared to other natural fibres and have more uniform shape, diameter, tensile strength, and failure stress [53]. There are many reports on MMCFR as reinforcement in biocomposites. Lyocell fibres have been impregnated with PHBV powder averaging a particle size of 600 nm in a fluidization chamber. The impregnated rovings (fibre tow) consisting of 3500 filaments each, resulted in unidirectional composites with a modulus of 5.8 GPa (at 10 vol.% fibre content) and 11.4 GPa (at 27 vol.% fibre content) after consolidation [54]. Nickel et al. [55] fabricated a starch-Lyocell non-woven composite with approximately 30% fibre volume content and with tensile strength and Young's modulus values of 80 MPa and 5.5 GPa, respectively. The solution-pre-pregging of high modulus Lyocell fibre tow with cellulose acetate was made by Seavey et al. [56,57] to produce unidirectional panels with tensile strength, modulus, and strain at failure values of approximately 250 MPa, >20 GPa and 3%–4%, respectively, at fibre volume contents of approximately 60%. The composite tensile fracture surface is shown in Fig. 2.9.

They also incorporated another type of continuous regenerated cellulose fibres, rayon in matrix like cellulose acetate propionate (CAP), and several cellulose acetate butyrates (CAB) with different butyryl contents, having different molecular weights and different methods of plasticization. The effects of fibre modification by acetylation and varied consolidation conditions on the interfacial adhesion and composite properties were also studied [56–58]

Shibata et al. [59] used biodegradable polymers such as poly(butylene succinate) (PBS), poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and poly(lactic acid) (PLA) with Lyocell fabric reinforcement and prepared samples by compression moulding method. The tensile moduli and strength of all the biodegradable polyester/ Lyocell composites increased with fibre content as shown in Table 2.8. The PLA/ Lyocell composites showed unexpectedly high biodegradability in soil burial tests.

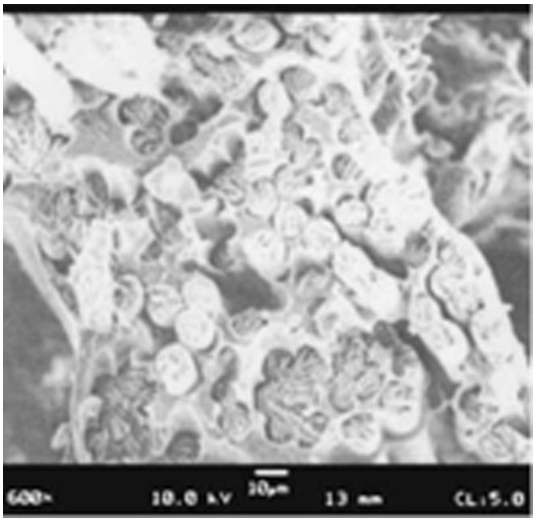


Fig. 2.9 Tensile fracture surface of the Lyocell fibre-reinforced cellulose acetate butyrate (CAB) composite [56,57].

Table 2.8 **Tensile properties of biodegradable polymers/Lyocell composites moulded at various conditions [59]**

Biodegradable polymer	Fibre content	Tensile strength (MPa)	Elongation (%)	Tensile modulus (GPa)
PHBV	17.6	38	14	0.9
PHBV	36.7	79	14	1.7
PHBV	63.2	108	10	2.4
PLA	24.8	48	9	3.4
PLA	38.7	76	8	4.6
PLA	62.1	100	6	5.5
PBS	25.4	80	14	1.4
PBS	40.0	107	12	2.6
PBS	60.0	114	9	3.3

Adusumali et al. compared single fibres of different types of regenerated cellulose fibres to glass and flax fibres for modulus of elasticity, tensile strength, and interfacial shear strength with polypropylene [27]. They found that regenerated cellulose fibres could exceed both flax and glass fibres in their strain to failure; making them particularly useful for composite applications in which a higher fracture toughness is required. Cheng et al. [28,60] investigated the effects of the process and source of cellulose fibrils by measuring its elastic modulus using atomic force microscopy on the fibrils. The research estimated the elastic modulus of Lyocell (Tencel; Lenzing Fibers Inc., Axis, Alabama, USA) to be approximately 98 ± 6 GPa for fibrils with diameters ranging from 150 to 180 nm. The modulus, however, drops dramatically for fibrils with diameters exceeding 180 nm. Gindl and Keckes studied the strain hardening of Lyocell and viscose forms of regenerated cellulose fibres by straining fibres under cyclic tensile tests and observing the increase in tensile modulus [53]. The strain hardening was larger for Lyocell that showed more crystallinity and orientation of cellulose chains in addition to a 47% increase in its modulus compared with only 28% for viscose. Research on regenerated cellulose-based composites has also been reported in the literature as well as research has been conducted using recycled cellulose for the generation of regenerated cellulose [29]. A surface selective dissolution method to prepare high modulus all-cellulose composites from Lyocell and Bocell fibres was investigated by electron microscopy, tensile testing, and X-ray diffraction [24]. The fibres were found to have excellent mechanical properties that can be tuned depending on the processing parameters. The use of regenerated fibres for composites was also addressed by several studies. Regenerated cellulose fibres, on the other hand, possess all the advantages of man-made industrial fibres in terms of supply, quality control, and uniformity, maintaining the advantages mentioned above for natural fibres. At moderate price they offer remarkable mechanical properties (strengths can be above 50 cN/tex (750 MPa), moduli up to 2000 cN/tex (30 GPa)) which make them a promising candidate for reinforcing thermoplastic matrices. Single fibres of several types of regenerated cellulose fibres were compared to glass and flax fibres with respect to modulus of elasticity, tensile strength, and interfacial shear strength with polypropylene [61] concluding that cellulose fibres could exceed both flax and glass fibres with respect to strain to failure. Thus they are particularly useful for composites with higher fracture toughness. Research using recycled cellulose for its generation has also been reported in the literature [29]. Graupner and Mussig [25] used compression moulding to prepare cellulose composites with Kenaf and Lyocell in PLA and poly(3-hydroxybutyrate) matrices. The Lyocell–PLA composites showed high tensile and impact strength with the highest Young's modulus (9.3 GPa) at 30% Lyocell loading whereas Lyocell–poly (3-hydroxybutyrate) had the highest impact strength at 70 kJ/m^2 [34]. During the study of the chopped Lyocell (produced with steam exploded wood fibres)–polypropylene composites prepared by wet layup and compression moulding a retention of 90% of the flexural strength and 98% of the tensile modulus at 41.2% of the cost of the reference-based Lyocell composite was observed [62]. Raman spectroscopy of the molecular deformation of regenerated cellulose fibres in epoxy and polyester has shown the presence of large interfacial shear stress between the fibres and the resin [63]. Use of biocompatible resins has been found to result in higher tensile strength when incorporating regenerated cellulose fibres [64]. A wide range of moulding technique could be considered for composites manufacturing [65–67]; compression moulding technique was adopted in this study. Qamhia [17] have investigated unidirectional regenerated cellulose-based composites, triaxially braided regenerated cellulose-based composites. Bio-based epoxy–Lyocell composite model was first simulated following FE approach using p-FEA incorporating the bilinear constitutive response of Lyocell and predicted the composite behavioural response. The results justified the loading behaviour of these composites under different fibre contents in dry conditions making the proposed model successful. Composite fabrications were made by various techniques and the most effective one for higher loading of Lyocell was the resin-infusion process (Fig. 2.10).

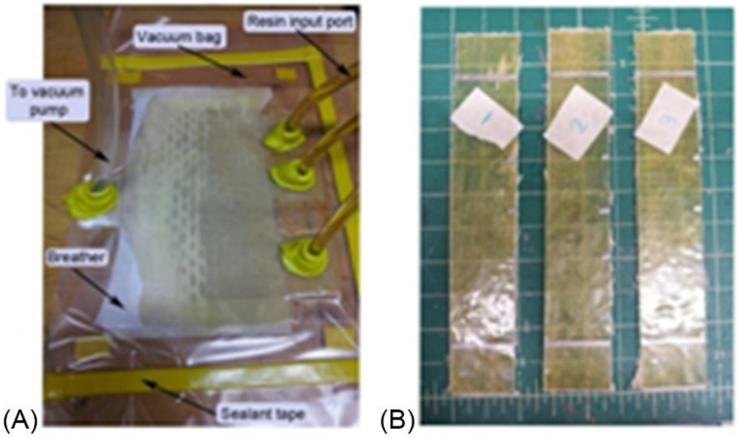


Fig. 2.10 Fabrication techniques for Lyocell/epoxy composites showing (A) a resin infused panel and (B) specimens prepared by hand layup [17].

Resin infusion process allowed higher fibre loading but some unwetted areas were seen even under high vacuum pressures which were overcome by the use of wet layup technique followed by degassing. However, wet layup technique is not very suitable for thicker parts and complex geometries. Similarly Qamhia [17] has tried manufacturing braided regenerated cellulose fibre, BioMid, composites where again resin infusion technique was found to be the most useful one.

The nonlinear variation of longitudinal and transverse elastic modulus with respect to the fibre volume fraction predicted by the analytical model corroborates with the experimental data. The initial elastic stiffness results are approximately 20% higher in the longitudinal direction when compared to the transverse direction. The acoustic emission study was done to predict the damage initiation and propagation through the braided composite. The results showed that damage initiation have started at lower stresses in the transverse direction compared to the longitudinal specimens, i.e. more energy is dissipated due to damage in the longitudinal direction due to the breaking of fibres in the axial yarn [68] which is evident from Fig. 2.11 exhibiting the damage progression in longitudinal and transverse direction of the samples. The strain patterns in the transverse specimens show a significant effect of the microstructure, especially at the edges.

The notched specimens appear to provide better estimates of the Young's modulus for the triaxially braided regenerated cellulose composites (Fig. 2.12).

Dynamic mechanical analysis is a thermo-mechanical technique to measure the total energy stored and dissipated in the material due to dynamic stimuli and separates the viscoelastic properties into an elastic part and a viscous part which are measured by the storage modulus (E') and the loss modulus (E''), respectively. Soykeabkaew et al. [24] used dynamic mechanical analysis to investigate the effect of temperature on the storage modulus of three different types of regenerated cellulose composites; namely: low draw ratio Lyocell, high draw ratio Lyocell, and Bocell fibres. Bocell

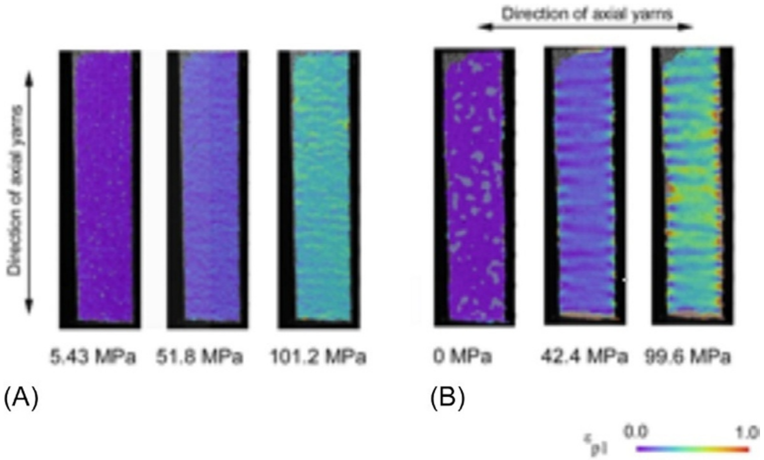


Fig. 2.11 Progression of principal strain distribution in (A) longitudinal specimen and (B) transverse specimen [17].

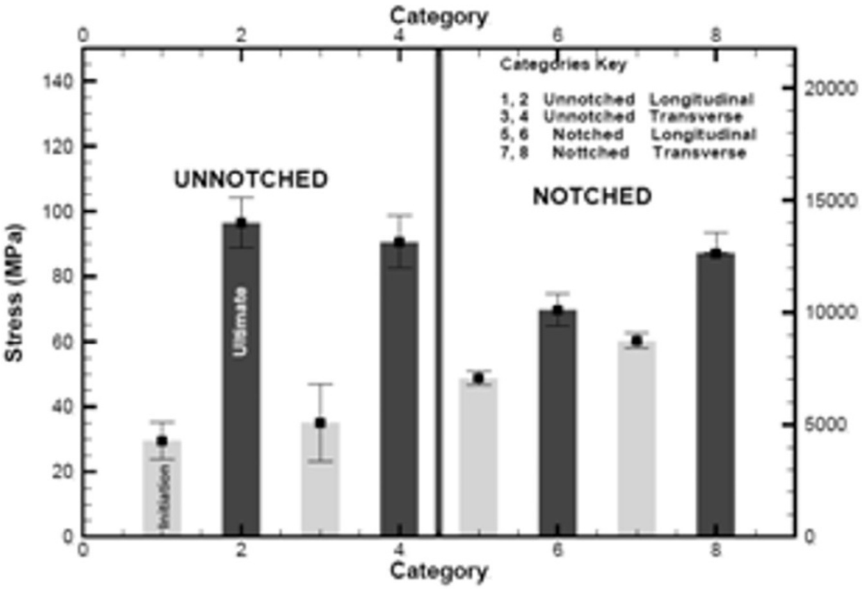


Fig. 2.12 Initiation and ultimate failure of unnotched and notched BioMid-epoxy specimens [17].

composites were found to have outstanding mechanical and thermal performances over Lyocell; seen by a higher elastic modulus over the tested temperature range. Incorporation of regenerated cellulose in epoxy matrix by Qamhia [17] shifted the glass transition to higher temperatures and lowered the damping property. Exposure to a humid environment results in reduction of the glass transition temperature and mechanical property. T_g may be further improved by heating but some of the elastic properties are permanently lost like the storage modulus which did not recover. The DMA approach was able to capture the variation in the modulus in the axial and transverse directions of the triaxially braided composites.

Jaszkiewicz et al. [69] investigated the utilization of cellulosic fibres, Cordenka 700 manufactured by Cordenka GmbH, in a biogenic matrix PLA and compared to PP-based composites, to improve the mechanical parameters while the primary target was to improve the impact strength of the brittle polylactide composites. They also studied glass and abaca fibre for comparison. Besides, somewhat lower E-modulus value of MMCFR-reinforced composites corresponded to almost the same tensile strength as their GF equivalents. Furthermore, PLA composites displayed a noticeably higher performance than their PP counter parts with an improved stiffness. MMCFR not only increased properties like stiffness and strength, but, at the same time, allowed larger deformations. PLA matrix has an inherent drawback of poor impact strength which can easily be avoided by tailoring the interphase. Improvement in impact properties are tabulated in Table 2.9. The impact strength can be doubled at a low additive content, evidently exceeding the impact resistance of PP-based composites. Abaca fibre, also improved the mechanical properties, such as the tensile or impact strength

Table 2.9 Mean values of A-notch Charpy impact strength (fibre content 30 wt.%) [69]

Parameter	PLA				PP			
	–	Cell	GF	Abaca	–	Cell	GF	Abaca
Mean value of A-notch Charpy impact strength (kJ/m^2)	1.65	8.25	3.71	10.12	1.95	16.5	3.9	8.7

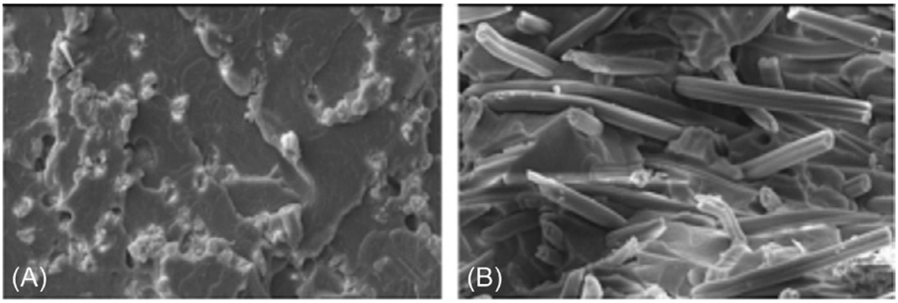


Fig. 2.13 Exemplary micrographs of PLA Cell 20 (A) and PLA Cell 20 with 3 wt.% of Joncryl 3229 (B) [69].

with significant impact in composite's stiffness. Mechanical property can also be considerably enhanced if the appropriate processing parameters are used.

Further addition of the maleinated additive Joncryl 3229 which is originally a maleinated chain extender based on styrenic–acrylic copolymer with moderate polarity influences the interfacial region so that fibre pull-outs become the dominant mode of failure as evident from SEM micrographs (Fig. 2.13). As a consequence, the impact energy increases from 6.7 kJ/m^2 to 9.1, 12.7, and 12.8 kJ/m^2 for 0, 1, 3, and 5 wt.% of Joncryl 3229, respectively.

This observation was further supported by the findings of Bax and Mussig [70] during the study of injection moulded flax and man-made Cordenka fibre-reinforced PLA composites. The impact strength of pure PLA was improved by adding Cordenka but the values of flax/PLA composites were inferior to the pure matrix. Stiffness and strength of the injection moulded Cordenka fibre-reinforced PLA with a fibre mass content of 25% could be approximately doubled compared to the pure matrix while the impact strength could be tripled [37].

In a work by Erdmann and Ganster [71] the mechanical properties such as tensile strength and impact strength of polylactic acid (PLA) and polyhydroxybutyrate (PHB) reinforced with 20 wt.% MMCFR (rayon, tire cord yarn) were evaluated. The sample preparation has been made by drying all the components overnight under vacuum at 50°C and 100°C, respectively, until moisture levels reached 0.025 and 0.1 wt.%. Then the polymeric resin was compounded thoroughly with additives like anti-coupling agent MAH-g-PP (3 wt.%) and coupling agent HMDI (1 wt.%) with the help of a *Brabender W 350* kneader at approximately 180°C for 5 min. Subsequently pultrusion technique was applied to cover a number of continuous cellulose fibre filament tows with the molten anti-coupling agent mixture with a conventional co-rotating twin screw extruder (*Haake Rheocord 9000 PTW 25*) at 170°C. Then the coated filament tows were cooled with water and cut into pellets. The pellets were then dried overnight at 50°C in the presence of P_2O_5 and extruded further with the same extruder under the same conditions for more uniform fibre–matrix mixture. The filament from the extruder was cut into pellets of lengths between 3 and 5 mm after cooling and standard test specimen were prepared by injection moulding technique.

By fibre surface modification with hexamethylene diisocyanate (HMDI) a strong interface was achieved with the matrix which resulted in improved mechanical properties (Fig. 2.14A). On the other hand for PLA matrix composites the Charpy notched impact strength can be improved by about 200% from 8 to 26 kJ/m^2 with 20 wt.% of fibre content and 3 wt.% of MAH-g-PP as surface modifier (Fig. 2.14B). This is obvious from SEM fracture micrographs. HMDI containing two highly reactive isocyanate end groups reacts simultaneously with the hydroxyl groups of the cellulose surface chains on the one hand, and also with the hydroxyl or carboxyl groups at the PLA or PHB chain ends on the other, forming either covalent urethane or amide bonds. In this way HMDI acts as a successful coupling agent improving the wetting of fibre by the matrix resin. By achieving strong interfacial adhesion, the tensile strength improved by 50% from 36 to 54 MPa and unnotched Charpy impact strength increased by 90% from 30 to 55 kJ/m^2. In the scanning electron micrograph no gaps between the fibre and matrix were observed and the fibres were completely covered with the matrix material.

In the contrary MAH-g-PP acts as an anti-coupling agent in cellulose fibre-reinforced PLA or PHB composite which was evident from the morphology showing an extreme fibre pull-out with its typical cylindrical voids and long fibre ends which is even inferior than the interface between fibre and matrix without any additive (Fig. 2.15).

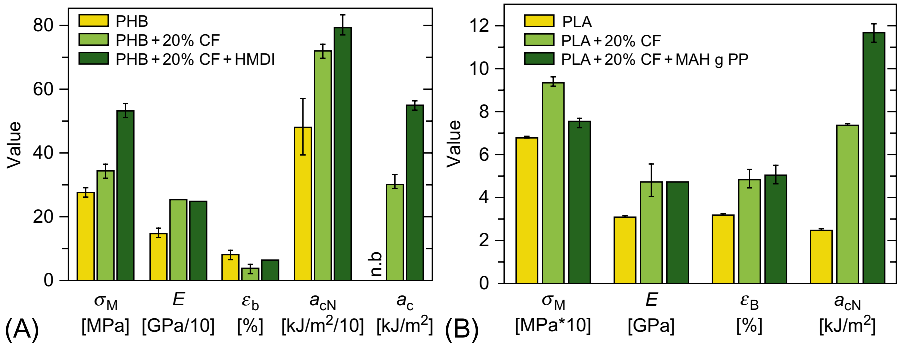
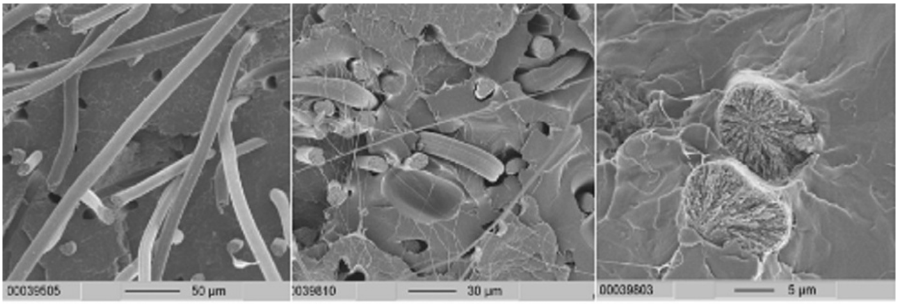


Fig. 2.14 Influence of cellulose fibre reinforcement on the mechanical performance of PHB-based composites (A) improved fibre–matrix adhesion (through coupling agent HMDI); (B) decreased fibre–matrix adhesion (through anti-coupling agent MAH-g-PP) [71].



a1) weak interface through anticoupling agent MAH-g-PP

a2) moderate interface without any additive

a3) strong interface through coupling agent HMDI

Fig. 2.15 SEM tensile fracture surface micrographs of PLA/cellulose fibre [71].

Tensile strength was not much higher than that for unreinforced PLA or PHB but notched Charpy impact strength was increased by 400% for 20 wt.% cellulose fibre content due to frictional fibre pull out mechanism. HMDI is suitable as an efficient coupling agent in cellulose fibre-reinforced PLA and PHB composites whereas MAH-g-PP acted as a very efficient impact modifier. Through the use of MMCFR reinforcement and anti-coupling agent MAH-g-PP it was possible to generate bio-based PLA composites with mechanical properties above the level of PP/GF.

The potential of short-cut rayon fibre as reinforcement in polypropylene matrix was studied by Amash et al. [72,73]. With the same matrix Lyocell fibre application was investigated by Lützgendorf et al. [74]. Seavey et al. [56] evaluated unidirectional Tencel fibre-reinforced cellulose ester composites with respect to both the processing route and fibre surface modifications. A further attempt was made by Paunikallio et al. [75,76] to fabricate injection moulded spun cellulosic fibre-reinforced polypropylene composite. Injection moulded composites with rayon tire cord yarn and a polypropylene block copolymer were first reported by Weigel et al. [77] and Fink et al. [78]. Ganster et al. [79] studied reinforcing effect of spun cellulose fibres of various origin (viscose, lyocell, carbamate) to reinforce thermoplastic matrices, i.e. polypropylene, polyethylene, high impact polystyrene, poly lactic acid, and a PP-based thermoplastic elastomer. The matrix polymers with its coupling agent (3 wt.% coupling agent with respect to the matrix polymer) used in this study as well as some important characteristics as given by the producers are listed in Table 2.10.

Injection-moulded standard test specimens were evaluated with respect to their strength, stiffness, impact strength, and heat distortion temperature (HDT) and morphology were revealed by SEM. High tenacity tire cord rayon gives excellent composite strength and impact strength, often doubling or tripling the original matrix values with a strong reinforcing effect in all cases. Lyocell fibres in PP enhanced the stiffness and heat deflection temperature (HDT) while the combination of both fibre types leads to a balanced composite property profile. The PE exhibits very similar results to PP. For HIPS mainly strength and stiffness is increased, while for TPE the property profile is changed completely. For all the matrix materials other than the PLA small

Table 2.10 Matrix resins with producers and coupling agents [79]

Sl. No.	Name of the matrix resin	Producer	Strength [MPa] (yield)	Modulus [GPa]	Coupling agent
1	PP	Sabic	26	1.55 (bend)	Maleic anhydride-grafted polypropylene (MAPP) (graft level >1 wt.%)
2	PE	Basell	30	1.35 (tesile)	Fusabond E MB-100D (Du Pont) with a graft level >1 wt.%
3	HIPS (yield)	Atofina	26	2 (bend)	Poly(styrene-*co*-maleic anhydride) with 25 wt.% maleic anhydride
4	PLA	Cargill Dow	53	3.5	No compatibilizer
5	TPE	Ravago	4	0.02	Maleic anhydride-grafted polypropylene

amounts of maleic anhydride grafted or copolymerized matrix material is added in the composite with the cellulose fibres to increase the interfacial adhesion. With biogenic and biodegradable PLA matrix excellent mechanical properties is obtained without coupling agent [79].

From Fig. 2.16A, a clear reinforcing effect is observed for 25% fibre loading with all types of fibre; tensile strength, tensile modulus are increased considerably, while the elongation is reduced, as expected. Highest value for strength is obtained with Cordenka, 74 MPa followed by 66 MPa with Tencel. Tencel and jute and give the best effects in terms of modulus 3.6 and 3.3 GPa, respectively. On the contrary Cordenka, shows the highest elongation of 10% among all reinforced materials.

Ganster et al. [79] have also tried mixed reinforcement in order to obtain a balanced property profile in terms of stiffness/HDT and strength/impact strength. The classic stiffener talcum has also been used to reach this goal. The composition of the composites with mixed reinforcement and 3 wt.% of MAPP coupling agent in PP matrix were as follows: Cord./talc. (25 wt.% Cordenka + 10 wt.% talcum), Cord./Jute (22 wt.% Cordenka + 8 wt.% jute), Cord./Tencel (18 wt.% Cordenka + 7 wt.% Tencel). The results for hybrid composites have been presented in Fig. 2.16B from which it is clear that for all composites a combination of good stiffness (around 3 GPa), HDT (>100°C) and high strength (>65 MPa) along with high impact strength (>70 kJ/m^2 for unnotched and >12 kJ/m^2 for notched Charpy test were achieved. Cord./Jute composite exhibited higher notched Charpy impact strength values than that for pure Cordenka.

High impact polystyrene has good impact properties, but a rather low modulus and, in particular, tensile strength which has been improved by incorporation of 25% of Cordenka both with and without a coupling agent. The styrene–maleic anhydride copolymer was used as a coupling agent. Improvement is therefore expected by (a) decreasing the MA concentration and (b) using a grafted product instead of a copolymer to improve the accessibility. A biogenic and biodegradable polymer matrix PLA with

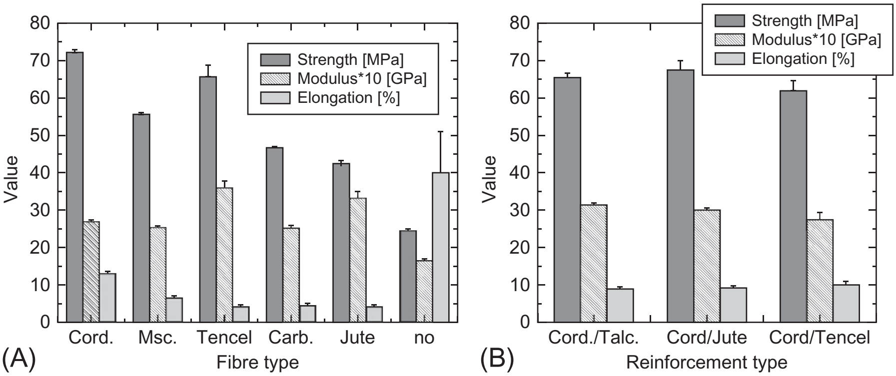


Fig. 2.16 Strength, modulus, and elongation for injection moulded composite test bars with 25% fibre loading as a function of (A) single fibre type and for the pristine polypropylene; (B) with mixed fibre type [79].

remarkable mechanical properties is available in various grades (mostly thermoforming and extrusion) at moderate prices. Reinforcement of 25% Cordenka fibre in the PLA matrix without any coupling agent increasing the strength and modulus by 50% also proved to be an excellent impact modifier: unnotched impact strength is doubled and notched Charpy values tripled. However, care must be taken to avoid the presence of water during processing to prevent degradation of the polyester backbone by hydrolysis.

PLA is the most commercially relevant bio-based polymer to develop biocomposites mainly replacing commodity polymers in packaging [80]. The production volume of PLA was 180 kt in 2012 which will be raised to over 800 kt by 2020 [81]. It has very high modulus and ultimate strength but low impact strength and heat deflection temperature (HDT), slow crystallization hence slow cooling is required for injection moulding. In a work by Sobczak et al. [82] 100% biocomposites were generated using two PLA grades by Nature works LLC with man-made regenerated cellulose fibres Tencel FCP by Lenzing AG as reinforcement to overcome the drawback of PLA. At 25°C, introduction of Tencel lead to a significant reduction in cycle time for both PLA matrix polymers. The results show that FCP acts as a nucleating agent, and allows a reduction of injection moulding cycle time. Based on a more than 75% amorphous PLA matrix, Young's modulus and impact strength were improved significantly with an increasing crystallinity and a reduction in injection moulding cycle time of up to 50% at a tool temperature of 25°C, and of over 80% for a tool temperature of 120°C [82].

2.8 Application and future scope of MMCFR

Increasing market demand placed on technical textiles for a wide range of composite applications has resulted in strong business value worldwide. In the textile sector, technical textiles have demonstrated great scope and considerable demand because of their diverse applications. Non-woven biocomposites include automotive, geotextile, packaging, and biomedical applications. Almost in all sectors, disposable and durable non-woven applications demonstrate high demand and consumption of composite non-wovens. These types of biocomposites in the form of non-woven composite are very much in demand for a wide range of medical and technical applications including, but are not limited to hygiene and healthcare, automobile, geotechnical, acoustical, agricultural, industrial, consumer, and apparel. They also have high demand in filtration and purification application. As result there is a high rate of consumption of MMCFR. There are a number of large companies involved in the production of composite non-woven products [83]. Dupont is primarily focussed on selective barrier technology, and almost all of their products, such as Tyvek, Sontara, Suparel, and HMT, are based on composite non-wovens. Other manufacturers include Kimberley-Clark, Polymer Group Inc., Ashlstorm, Hollingsworth&Vose, 3M, etc. Steadily growing demand of MMCFR and limited availability of cotton have opened a great opportunity for different MMCFR which is known as the Cellulose Gap. The major replacement of cotton is still polyester. There is a wide scope for MMCFR to take up a major role in filling the 'Cellulose Gap'.

2.9 Future needs

Cellulose, the most abundant renewable organic material on earth, exhibits outstanding properties and useful applications, but also presents a tremendous challenge with regard to economical and environmentally friendly chemical processing. The viscose process, more than 100 years old, is still the most widely used technology to manufacture regenerated cellulose fibres and films. Viscose fibres are produced today worldwide on a 5 million ton scale with various fibre types ranging from high-performance tire yarn to textile filaments and staple fibres with excellent properties close to that of cotton. At Fraunhofer IAP, the technical equipment for viscose preparation, wet spinning of fibres, hollow fibres, and tube-like films is available on a mini-plant scale. Research should be focused on raw materials testing, process optimization with regard to economic and ecological aspects, structural analysis of cellulose during processing, and structure–property relations of fibres and films. There is scope to develop methodologies by which MMCFR can be produced via cellulose carbamate in an environmentally friendly route. The use of N-methylmorpholine-N-oxide (NMMO) as a solvent may be the non-derivatizing commercial alternative to the still dominant viscose route. Fraunhofer IAP has already been employing NMMO-water solution to precipitate cellulose fibres and manufacturing melt blown non-wovens technology first time for cellulosics on a pilot plant scale. Overall, MMCFR are likely to play a key role in the development of green composites for future provided eco-friendly manufacturing routes are successfully learned and implemented.

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Thermosetting bioresins as matrix for biocomposites

3

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3.1 Introduction

The depletion of the nonrenewable resources and increasing environmental pollution motivated researchers to focus on the development of environmentally friendly biobased materials from renewable resources. In this context biocomposites made of bioresins and natural fibre reinforcements are interesting materials. Bioresins are greener alternatives to the synthetic ones, as these are produced from plant oil-based triglycerides and other natural resources.

3.2 Thermosetting bioresins

Natural resins are viscous materials mainly derived from plants. Due to unstable nature they cannot be used for commercial purposes [1] and synthetic resins dominate all over the market. Unsaturated polyester, epoxy, vinylester, and phenolic are the common thermosetting resins used in various industries and are not environmentally friendly materials. To address these environmental problems bioresins are developed from vegetable oil resources, e.g., castor oil, soybean oil, rapeseed oil, etc. However, very few bioresins are available commercially in large scale for industrial applications (Table 3.1).

Apart from the vegetable oils, there are several other natural compounds, such as tannins, lignins, proteins, triglycerides, bioalkyds, waxes, etc., which can be used as precursors for bioresins.

3.2.1 Thermosetting bioresins from vegetable oils

Vegetable oils (e.g. rapeseed, soybean, sunflower, tung, Cashew Nut Shell Liquid or CNSL) are important raw materials for the synthesis of bioresins. These vegetable oils consist of triglycerides in which the main components are saturated and unsaturated fatty acids of varying compositions depending on the plants or crops. These triglycerides contain several reactive sites which can undergo various chemical reactions and synthetic transformations [3,4]. There are three main approaches for preparing polymers from the plant triglycerides, presented in Fig. 3.1 [4].

One route to polymerize the vegetable oil is the direct polymerization of the C=C bond in the vegetable oil structure. But this direct polymerization of C=C is critical

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Table 3.1 **Examples of few commercially available biobased resins [2]**

Resin type	Resin base	Type of resin	Trade name
Acrylated epoxidized soybean oil (AESO)	Soybean oil	Thermoset	Ebecryl 860
Epoxidized soybean oil	Soybean oil	Thermoset	Vikoflex 7170
Epoxidized pine and vegetable oils	Pine and vegetable oils	Thermoset	Super Sap 100 Epoxy
Polyester bioresin	Soy	Thermoset	Envirez 5000
Epoxidized linseed oil	Linseed oil	Thermoset	Vikoflex 7190

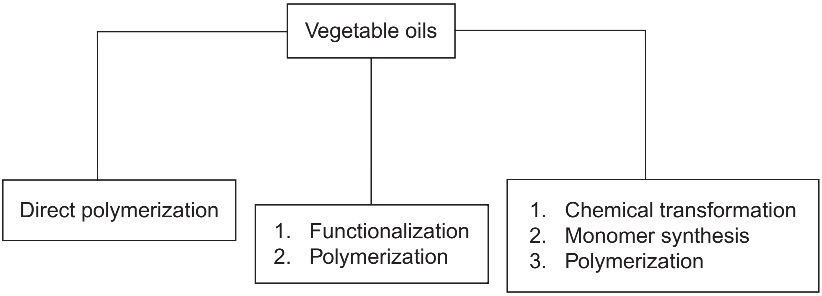

Fig. 3.1 Schematic representation of the synthesis of biopolymers from vegetable oil [4].

and using high temperature for polymerization results poor product yield. Some vinyl monomers, such as styrene, divinyl benzene, norbornadiene, etc., are used with the plant oils for thermal or cationic copolymerization. Microwave-assisted polymerization is also possible [4–6]. Functionalization of the triglyceride C=C bond and development of the cross-linked structure is another route to obtain thermosetting biomaterials. The allylic positions present in the vegetable oil can be converted into allylic hydroperoxides which can easily undergo various organic transformations to form different cross-linked bioresins, shown in Fig. 3.2 [5,6].

The third approach is to produce monomers from vegetable oils by chemical transformation. Ronda et al. [4] synthesized difunctional monomers via acyclic dienemetathesis polymerization and thiol-ene coupling reactions from 10-undecenoic acid. These two methods are helpful in synthesizing tailor-made telechelic polyesters with controlled structure and molecular weight.

3.3 Biocomposites based on bioresins

Bakare et al. [7] synthesized cellulose fibre-reinforced biocomposites from lactic acid resin by hand lay-up method. The synthesis and properties of this lactic acid-based bioresin are discussed in Section 3.5. Behera et al. [8] worked on nanobiocomposites prepared from soy resin, jute felt, and nanoclay. Soy resin was prepared from

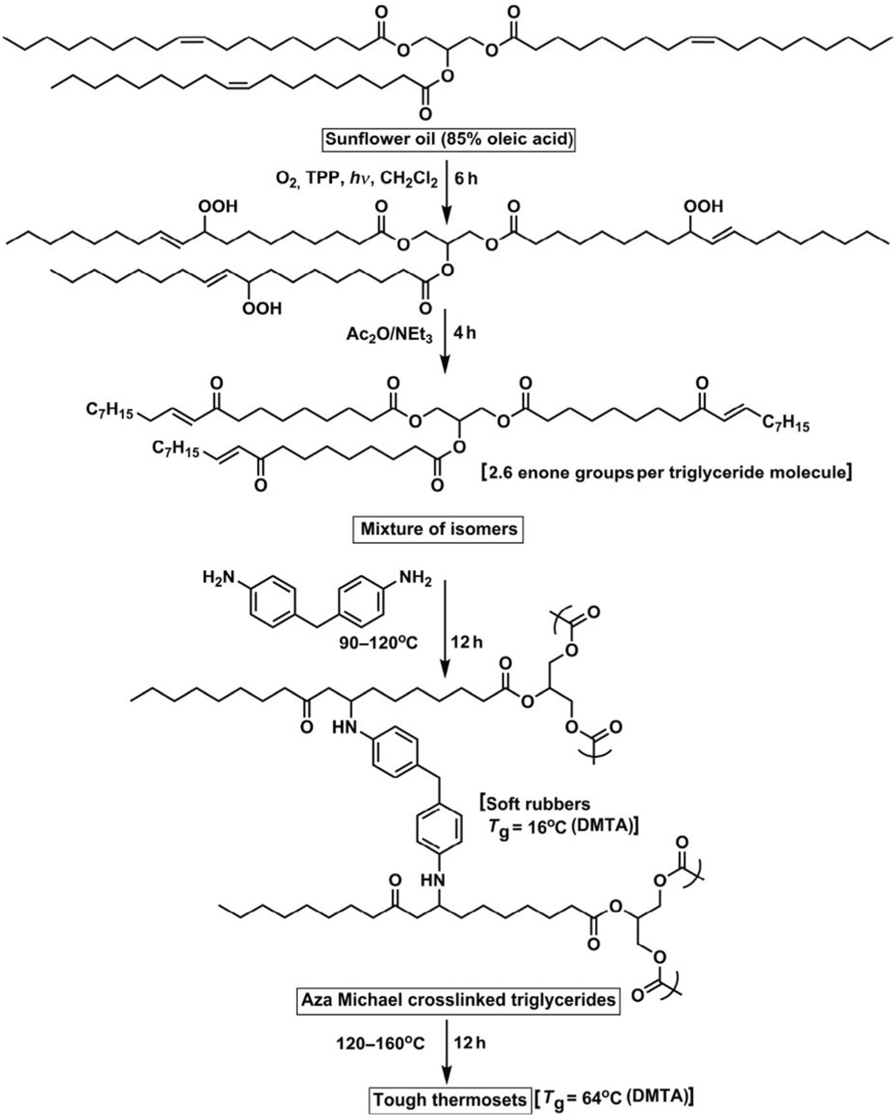

Fig. 3.2 Synthesis of cross-linked thermoset bioresin from high oleic sunflower oil via aza-Michael addition.
Adapted from Ronda JC, Lligadas G, Galià M, Cádiz V. Vegetable oils as platform chemicals for polymer synthesis. Eur J Lipid Sci Technol 2011;113:46–58.

soy milk, extracted from soy seed. The soy milk was mixed with different weight% of glutaraldehyde (GA) (1, 5, 10, 15, and 20) and glycerol and stirred for 30 min to prepare the soy resin. Nanoclay was used as the resin modifier. Glycerol and GA were used as the plasticizer and cross-linking agents, respectively. Resin was cured at 130°C for 20 min.

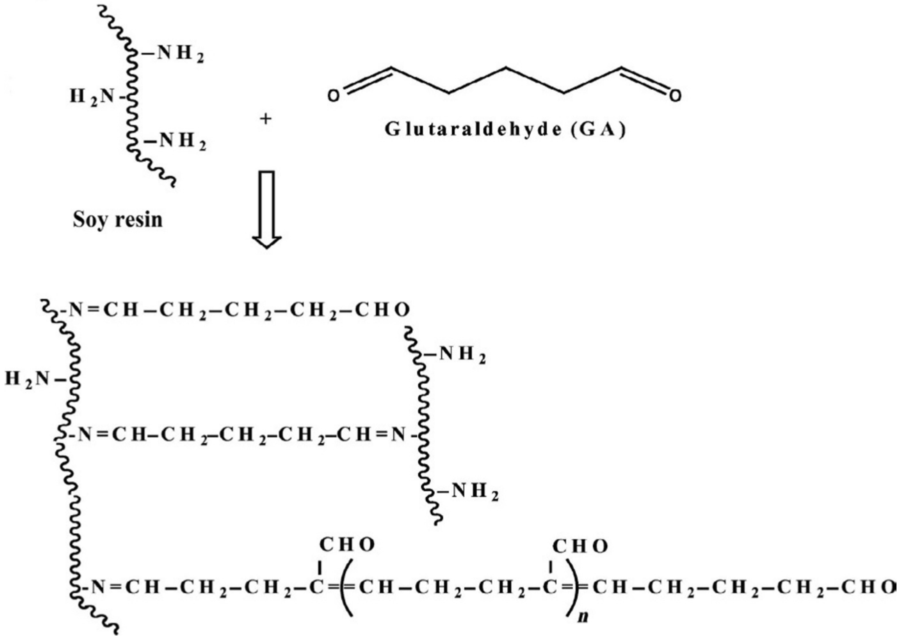

Fig. 3.3 Cross-linking reaction between glutaraldehyde (GA) and soy resin films. Reprinted with permission from Chabba S, Netravali AN. "Green" composites part 1: characterization of flax fabric and glutaraldehyde modified soy protein concentrate composites. J Mater Sci 2005;40:6263–73.

Chabba and Netravali [9] used three-step curing process for the soy resin. First the mixture was cured at 70°C for 15 min followed by 20 h at 35°C and finally in hot press at 120°C for 25 min with 7 MPa pressure [9]. Tensile strength of the resin depended on the cross-linking between GA and soy milk protein. Soy resin film with 10% GA content showed enhanced tensile strength ~1.98 MPa than the noncross-linked soy resin films. The cross-linking reaction is shown in Fig. 3.3.

Published data on bioresin-based biocomposites are given in Table 3.2.

3.4 Commercial bioresins

3.4.1 Envirez (bio-unsaturated polyester resin)

Ashland's Envirez resin is the first commercially available biobased unsaturated polyester resin (UPE) which comprises of renewable materials. The product line has been expanded to include resins with recycled content to provide with more sustainable resin options. Envirez 1807 is UPE produced from corn-derived ethanol and soybean oil via a new patented technology where low reactive soybean oil was transformed into highly reactive resin and 25 wt.% grain-derived organic raw materials were used [19]. Envirez resins meet the same performance and processing

Table 3.2 Various bioresin-based biocomposites

Reinforcements	Bioresin matrices	Refs.
Jute and glass fibre	Epoxidized and acrylated epoxidized bioresin from hemp oil	[10]
Kenaf fibre	Polyfurfuryl bioresin	[11]
ZnO nanoparticles	Epoxidized soybean oil	[12]
Chitosan-modified ZnO nanoparticles	Derivatives of castor oil	[13]
Glass fibre	Biobased polyurethane from soy oil-derived polyol	[54]
Glass fibre	Furfuryl alcohol	[55]
Nanoclay and hemp fibre	Unsaturated polyester (UPE) and epoxidized soybean oil	[56]
Jute fibre	Epoxidized hemp oil	[14]
Non woven hemp mat with 10% PET as filler	Ortho unsaturated polyester resin (UPE) and blend of UPE and epoxidized vegetable oil	[15]
Montmorillonite (MMT) nanoclay (Cloisite 30B)	Blend of unsaturated polyester resin (UPE) and epoxidized palm oil	[16]
Surface treated regenerated cellulose fibre	Lactic acid thermoset resin	[17]
Jute felts	Furfuryl ester of palmitic acid	[18]

requirements of 100% petroleum-based UPE products and are used in a wide variety of processes and applications within the construction, marine, and transportation industries [20]. The Envirez resins are currently used in several commercial processes, and provide surface finishes when used in press moulding, resin transfer moulding (RTM), and resin infusion. Specific liquid resin properties and cured resin properties are given in Table 3.3.

3.4.2 Super Sap (bio-epoxy resin)

Super Sap CLR epoxy is a clear-modified liquid epoxy resin [48]. As opposed to traditional epoxies that are composed primarily of petroleum-based materials, Super Sap formulations contain bio-renewable materials sourced as co-products or from waste streams of other industrial processes, such as wood pulp and biofuels production. These natural components have excellent elongation and exceptionally high adhesion properties. Super Sap CLR epoxy is water clear, UV-stabilized resin system for applications that require a low-colour, low-yellowing resin. It has a viscosity suitable for a wide range of processing applications ranging from hand lay-up to resin infusion. Super Sap can be processed using a range of different hardeners, like, clear fast (CLF), clear slow (CLS), casting slow (CCS), infusion fast (INF), and infusion slow (INS); the physical and mechanical properties are shown in Tables 3.4 and 3.5.

It is important to note here that the cure cycle for the resin is generally 7–10 days which is not favourable for high-production rate required in industrial manufacturing.

Table 3.3 Properties of Envirez 1807 [19]

Specifications		Typical physical properties		Typical cured resin properties	
Acid value (mg KOH/g)	27	Viscosity at 25°C (mPa s)	850	Tensile strength (MPa) (ASTM D638)	40
Styrene content (%)	29.5	Gel temperature (°C) (with 1 wt.% benzoyl peroxide)	82.2	Tensile modulus (MPa) (ASTM D638)	3000
Density (g/cc) at 25°C	1.10	Gel time (min)	7.5	Elongation at break (%) (ASTM D638)	1.56
		Time to peak exotherm (min)	11.4	Flexural strength (MPa) (ASTM D790)	57
		Temperature to peak exotherm (°C)	213	Flexural modulus (MPa) (ASTM D790)	3000
				Heat distortion temperature (°C)	135

Table 3.4 Physical properties of Super Sap bioresin in liquid form [48]

	Physical properties				
Super sap resins based on hardeners	**Viscosity (cPs @ 25°C)**	**Biocontent by mass (%)**	**Gel time (min, 150 g @ 25°C)**	**Cure cycle (days) @ 25°C**	**Post curing**
Clear fast (CLF 01)	2000–4000	21–30	25	7–10	Recommended
Clear slow (CLS 02)	2000–4000	21–30	50	7–10	Recommended
Casting slow (CCS 01)	500–750	21–30	360	3	3 h @ 120°C
Infusion fast (INF 02)	500–1000	21–30	45	7–10	Recommended
Infusion slow (INS 01)	500–1000	21–30	90	7–10	Recommended

Table 3.5 Mechanical and thermal properties of Super Sap bioresin in cured form [48]

Super sap resins based on hardeners	Mechanical and thermal performances					
	Tensile strength (psi)	Tensile modulus (psi)	Flexural strength (psi)	Flexural modulus (psi)	Elongation at break (%)	Glass transition temperature (T_g, °C)
Clear fast (CLF 01)	9410	5×10^5	13,534	4.4×10^5	5	115.6
Clear slow (CLS 02)	9410	5×10^5	13,534	4.4×10^5	5	115.6
Casting slow (CCS 01)	8100	4×10^5	–	–	6	82.2
Infusion fast (INF 02)	10,100	6.2×10^5	16,000	5.5×10^5	2	115.6
Infusion slow (INS 01)	10,100	6.2×10^5	16,000	5.5×10^5	2	115.6

Table 3.6 **Properties of Aropol S604 INF-60 Infusion resin [21]**

Typical liquid resin properties		Typical cured resin properties	
Viscosity at 25°C (mPa s)	220	Tensile strength (MPa)	45
		Tensile modulus (MPa)	3100
Styrene content (%)	36	Elongation at break (%)	1.6
		Hardness (Barcol)	40
Gel time (min)	60	Heat deflection temperature (°C)	85
		Water absorption in 28 days (mg/sample; sample dimension: 50×50×4 mm)	76

3.4.3 Aropol S604 INF-60 infusion resin

This is a dicyclopentadiene-based polyester resin with low styrene content. This type of resin is mainly used for the infusion process. In this resin styrene content is ~36%. Some of the physical properties of the resin along with the cured properties are mentioned in Table 3.6 [21].

3.4.4 Biorez and furolite

These two are furan-based resins developed by TransFurans Chemicals. These resins are developed from prepolymers of furfuryl alcohol derived from biomass such as, sugarcane bagasse [22]. Biorez resin is curable at elevated temperature and this is obtained as moulding resin or water soluble impregnation resin. Application areas of this resin include: wood modification, preparation of wood-based panels, boards, glass insulation materials, etc. Because of its adhesive properties and compatibility with natural fibres, Furolite resins are used where stability is required under heat, fire, and corrosive environment. These resins are used to prepare fibre-reinforced plastics, polymer concrete, ceramic or carbon aggregate binder, etc. [23].

3.5 Bioresin research activities in lab

3.5.1 Bioresin from banana sap

Banana sap (BS) obtained from *Musa Cavendish* was used for the synthesis of bioresins [24]. BS was added in varying concentrations ~30%–65% to the synthetic polyester resins and processed for 12–35 h with additives and curing agents. BS containing 97% water underwent esterification reaction in the presence of maleic anhydride (MA) and propylene glycol (PG) producing the hybrid bioresin system. The reaction mechanism is shown in Fig. 3.4.

Viscosity is an important property of the thermoset resins as it influences the processing. A low viscosity is desirable for manufacturing composites [25]. Hybrid bioresin produced from BS and polyester resin [24] showed viscosity of 110 Pa s and molecular

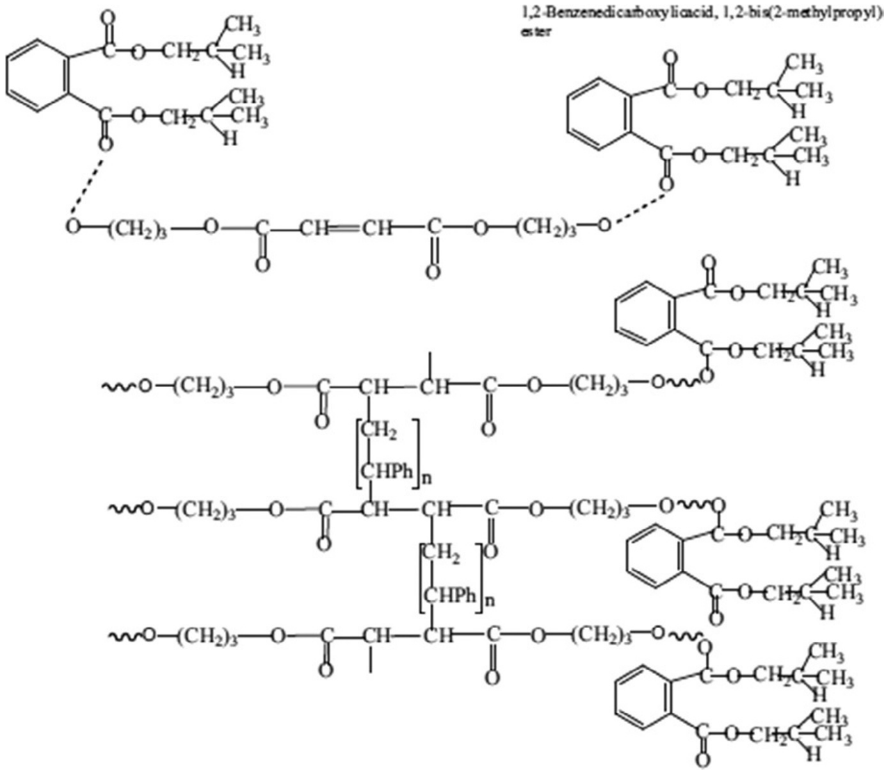

Fig. 3.4 Proposed mechanism of ester from banana sap (BS) with polypropylene glycol (PG). Reprinted with permission from Paul V, Kanny K, Redhi GG. Formulation of a novel bio-resin from banana Sap. Ind Crops Prod 2013;43:496–505.

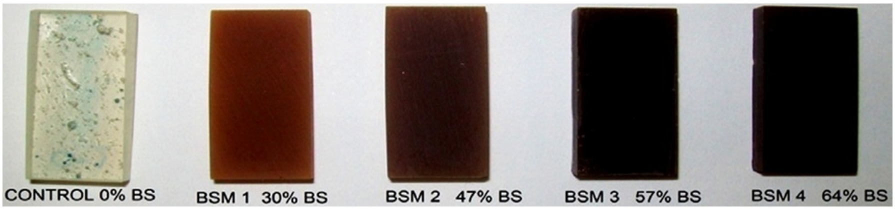

Fig. 3.5 Image of control sample and samples prepared from varying concentrations of BS. Reprinted with permission from Paul V, Kanny K, Redhi GG. Formulation of a novel bio-resin from banana Sap. Ind Crops Prod 2013;43:496–505.

weight of 2179. Acid value of the resin decreased gradually with time, whereas, the viscosity and molecular weight increased. At the end of the reactions, sudden rise in viscosity and molecular weight indicated that chain transfer predominated over the acid-glycol esterification reaction. Fig. 3.5 shows the prepared bioresin samples from BS.

The BS-derived bioresin showed some interesting mechanical properties, as shown in Table 3.7 [24]. Dynamic stiffness increased with 47% and 57% BS contents.

Table 3.7 Mechanical properties of BS bioresin [24]

Banana sap maleate (BSM) bioresin samples	Stiffness (GPa)	Tensile strength (MPa)	Flexural modulus (MPa)	Tensile stress–strain (%)
Control sample	0.4	12	870	16.5
BSM 1 (i.e. 30% BS content)	0.62	12.6	1571	21
BSM 2 (i.e. 47% BS content)	0.79	27	1677	23
BSM 3 (i.e. 57% BS content)	1.20	21.7	2528	19
BSM 4 (i.e. 64% BS content)	0.64	25	1727	12.6

Mwesigwa et al. [26] prepared bioresin from raw banana peel using varying ratios of glycerol. The density of the resin was determined to be 0.83 g/cm^3, which is comparable with the tapioca resin and polypropylene.

3.5.2 Bioresin from lactic acid

Thermoset bioresin can be prepared from lactic acid. Development of cross-linked structure is advantageous in improving the heat stability and mechanical properties of the biopolymers. There are two ways of developing cross-linked structures in lactic acid: (1) by introducing C=C bonds or functionalizing the telechelic or star-shaped PLA monomer by introducing some groups which undergoes free radical polymerization during cross-linking reaction and (2) by using free radical initiator with small amount of cross-linking agent or some irradiation on linear PLA monomer [25]. Some examples of the thermosetting resins prepared from lactic acid are given below.

Åkesson et al. [27] prepared thermoset bioresin using star-shaped lactic acid oligomer, pentaerythritol, itaconic acid, and methacrylic anhydride. Lactic acid was polymerized first via condensation reaction between itaconic acid and pentaerythritol followed by the functionalization with methacrylic anhydride to obtain the thermoset resin (shown in Fig. 3.6). The synthesized resin was highly viscous (7000 Pa s) at room temperature (25°C), but on heating up to 80°C the viscosity decreased to 4 Pa s showing its suitability for high temperature processing. The completion of the cross-linking reaction was confirmed by DSC study which revealed complete curing at 170°C and the curing time was ~6.5 min. The cured resin showed a T_g at 83°C and was thermally stable up to 200°C. The thermal degradation peak was evident only at 319°C.

Lactic acid oligomers with different chain lengths ($n=3$, 7, and 10) were reacted with glycerol via direct condensation and then the product was end functionalized with methacrylic anhydride. The use of glycerol was quite advantageous here, as glycerol is an inexpensive, renewable raw material and a by-product from biodiesel production [28]. The reaction mechanism is shown in Fig. 3.7. The viscosity for the cured resin at room temperature was 1.09 Pa s for $n=3$ which is much lower compared to $n=7$ and 10. Upon heating the viscosity dropped to 0.0361 Pa s for $n=3$. The high viscosities of the resins with $n=7$ and 10 made them unsuitable for impregnation into

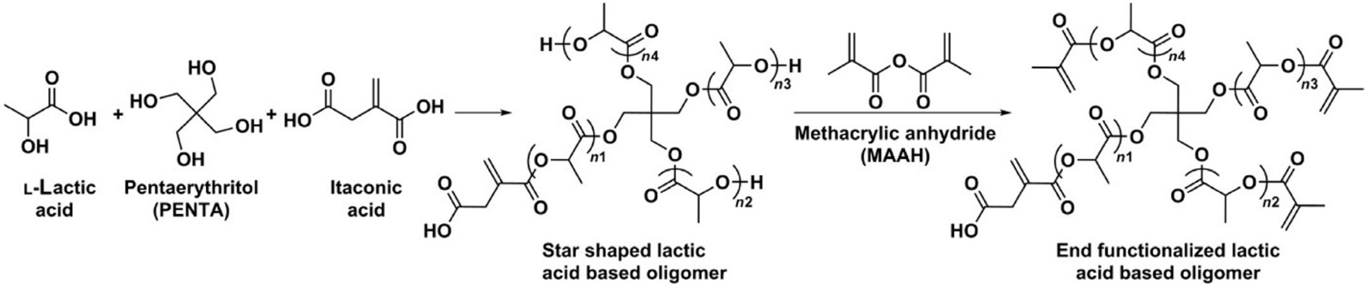

Fig. 3.6 Reaction scheme for the synthesis of star-shaped lactic acid-based oligomer and end-functionalized lactic acid-based oligomer. Adapted from Åkesson D, Skrifvars M, Seppälä J, Turunen M, Martinelli A, Matic A. Synthesis and characterization of a lactic acid-based thermoset resin suitable for structural composites and coatings. J Appl Polym Sci 2010;115:480–486.

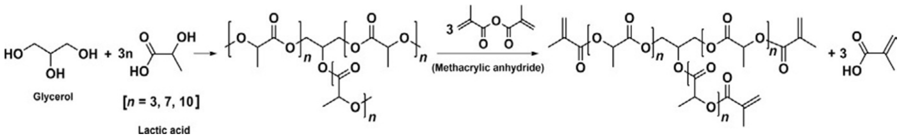

Fig. 3.7 Reaction scheme for the synthesis of methacrylate-functionalized glycerol–lactic acid resins (GLA).
Adapted from Bakare FO, Skrifvars M, Åkesson D, Wang Y, Afshar SJ, Esmaeili N. Synthesis and characterization of bio-based thermosetting resins from lactic acid and glycerol. J Appl Polym Sci 2014;131:40488(1–9).

fibre reinforcements. The resin with $n=3$ showed improved T_g (97°C) compared to neat PLA and commercial polyester resin (CPR).

The resin with $n=3$ displayed higher storage modulus (~4314 MPa) in the glassy state than the resin with $n=7$ (storage modulus ~3766 MPa) and $n=10$ (storage modulus ~1766 MPa) [28]. Because of the higher storage modulus in the glassy state, the resins with $n=3$ and 7 showed enhanced polymer chain packing compared to CPR. In the rubbery region CPR and the resin with $n=3$ exhibited almost similar behaviour indicating their comparability.

Bakare et al. [29] synthesized thermoset bioresin from lactic acid oligomers. They first introduced C=C bond to the lactic acid by reacting it with allyl alcohol in order to develop cross-linked structure through free radical polymerization. The oligomer prepared with allyl alcohol and lactic acid (ALA) was end functionalized with methacrylic anhydride to synthesize methacrylated lactic acid resin (MLA). Methacrylated pentaerythritol lactic acid resin (PMLA) was synthesized by reaction between the mixture of ALA-pentaerythritol and methacrylic anhydride. Fig. 3.8 describes the scheme of the synthesis of PMLA.

The PMLA resin had very low viscosity (0.02 Pa s) at room temperature compared to MLA, methacrylate functionalized glycerol–lactic acid resins (GLA) and UPE as shown in Fig. 3.9, which further decreased to 0.01 Pa s with rise in temperature. At room temperature PMLA and MLA had nearly similar viscosities indicating their suitability for room temperature processing. These two resins also showed improved thermal and mechanical properties compared to others as shown in Table 3.8.

3.5.3 Plant oil-based alkyd resins

Alkyd resins draw significant attention of the chemical industries for their immense use in paint and coating applications. Alkyd resins comprise fatty acid-modified polyester resins [30]. They are derived from the chemical reactions of polycarboxylic acids, polyols, and fatty acids, which come from vegetable oils [1].

Das et al. [31] synthesized sunflower oil-modified hyperbranched polyurethane (HBPU) and linear polyurethane (LPU) (shown in Fig. 3.10).

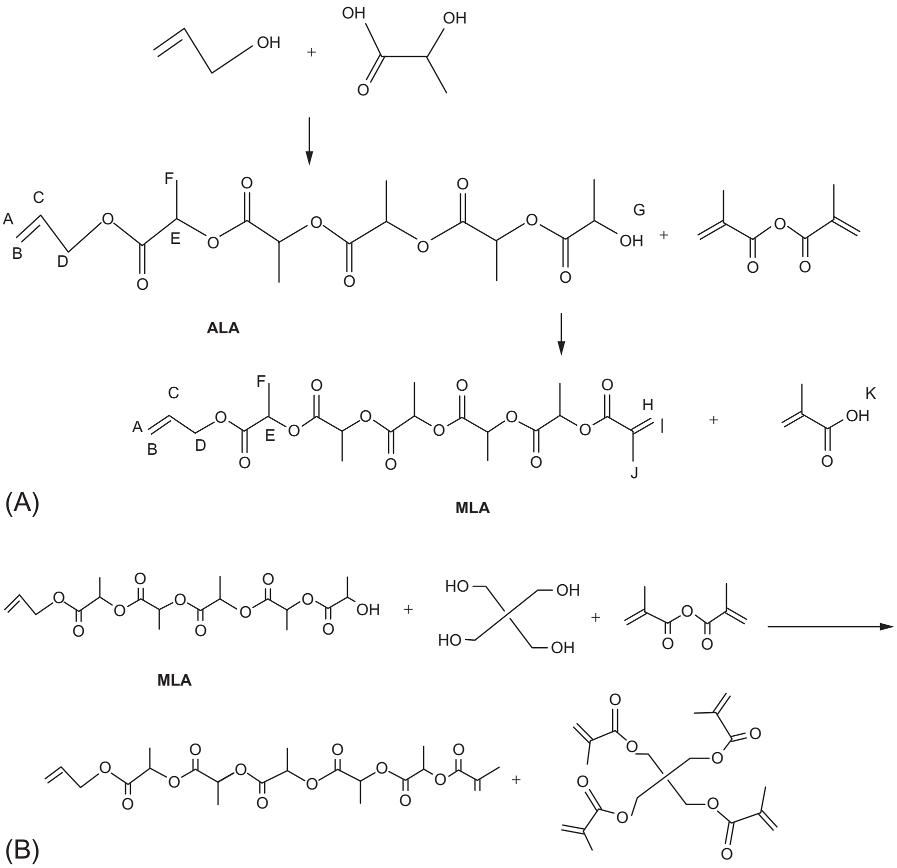

Fig. 3.8 (A) Reaction scheme for alcohol and lactic acid (ALA) resin and MLA resin. (B) Reaction scheme for PMLA resin.
Reprinted with permission from Bakare FO, Åkesson D, Skrifvars M, Bashir T, Ingman P, Srivastava R. Synthesis and characterization of unsaturated lactic acid based thermoset bio-resins. Eur Polym J 2015;67:570–582.

Physico-chemical, thermal, mechanical, and biodegradation properties of the synthesized materials were evaluated. HBPU showed higher tensile strength (~23 MPa) than LPU (~18 MPa) due to more polar groups and higher hydrogen bonding, polymer chain entanglements, and reactivity of the multifunctional groups. This also resulted in a higher thermal stability in HBPU than that in LPU. Such improved thermal, mechanical properties, chemical resistivity, and biodegradability made the synthesized material ideal for thin film applications. The SEM images of the biodegraded samples are shown in Fig. 3.11.

Uzoh et al. [32] synthesized alkyd resin from nondrying palm oil. Self-cured resin was obtained by the modification of palm oil with glycerol via alcoholysis and then

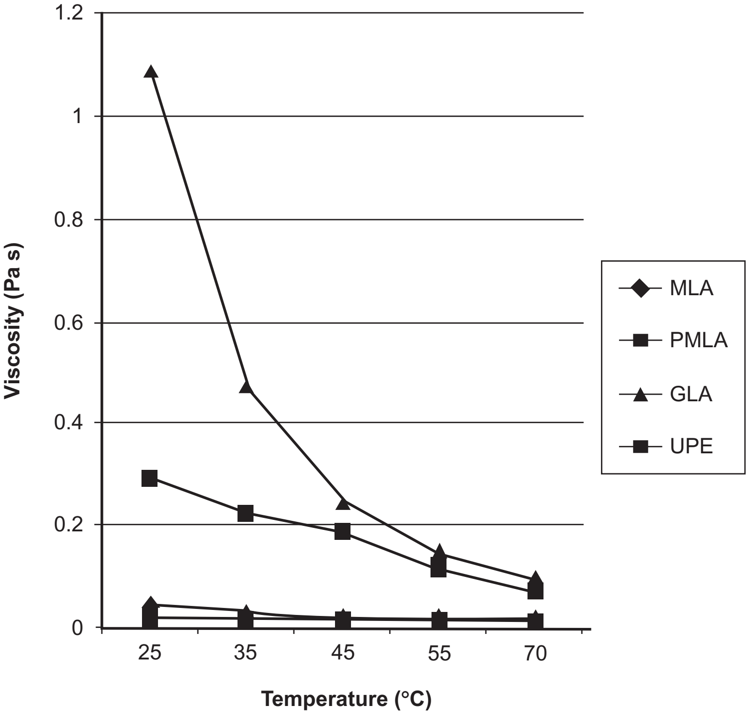

Fig. 3.9 Viscosity of MLA and PMLA resins at different temperatures.
Reprinted with permission from Bakare FO, Åkesson D, Skrifvars M, Bashir T, Ingman P, Srivastava R. Synthesis and characterization of unsaturated lactic acid based thermoset bio-resins. Eur Polym J 2015;67:570–582.

polyesterification process was performed with phthalic anhydride (PA). The polyesterification reaction was optimized by varying reaction time, temperature, catalyst concentration, etc. Palm oil-based alkyd resin was also synthesized by Islam et al. [33]. They performed an alcoholysis reaction between palm oil and glycerol using calcium oxide as the catalyst followed by an esterification reaction with the PA and MA. Three types of resins (Resin A, B, and C) were prepared and their properties were analysed. Among the three, Resin C showed marginally higher thermal stability (shown in Fig. 3.12) and lower curing time. Resin A showed higher chemical resistivity than others. High gloss, hardness, chemical resistivity, and temperature sustainability proved their applicability in the surface coating area.

Nahar seed oil is another potential source for the preparation of polyester resin. Dutta et al. [49] synthesized three types of resins (resin A, resin B, and resin C) via alcoholysis of Nahar seed oil followed by esterification with varying contents of PA and MA. The curing time and viscosity of the synthesized resins were dependent on the MA content in the resins. Some of the resin properties are shown in Table 3.9.

Table 3.8 Resin properties

	DSC			DMA			TGA	
Name of the resin	**Heat of exotherm for uncured resin (J/g)**	**Heat of exotherm for cured resin (J/g)**	T_g **(°C)**	**Storage modulus (MPa)**	**Loss modulus (MPa)**	**Tan** δ **(°C)**	**Degradation temp. (°C) at 10 wt.% loss**	**Highest degradation temp (°C)**
MLA	194	1.40	79	3269 (±199)	400 (±145)	109	290	346
PMLA	26	0.03	100	3663 (±173)	123 (±27)	113	302	344
GLA	227	0	76	4312 (±157)	354 (±48)	97	258	375
UPE	198	0.45	71	2955 (±5)	135 (±22)	83	308	362

Reprinted with permission from Bakare FO, Åkesson D, Skrifvars M, Bashir T, Ingman P, Srivastava R. Synthesis and characterization of unsaturated lactic acid based thermoset bioresins. Eur Polym J 2015;67:570–582.

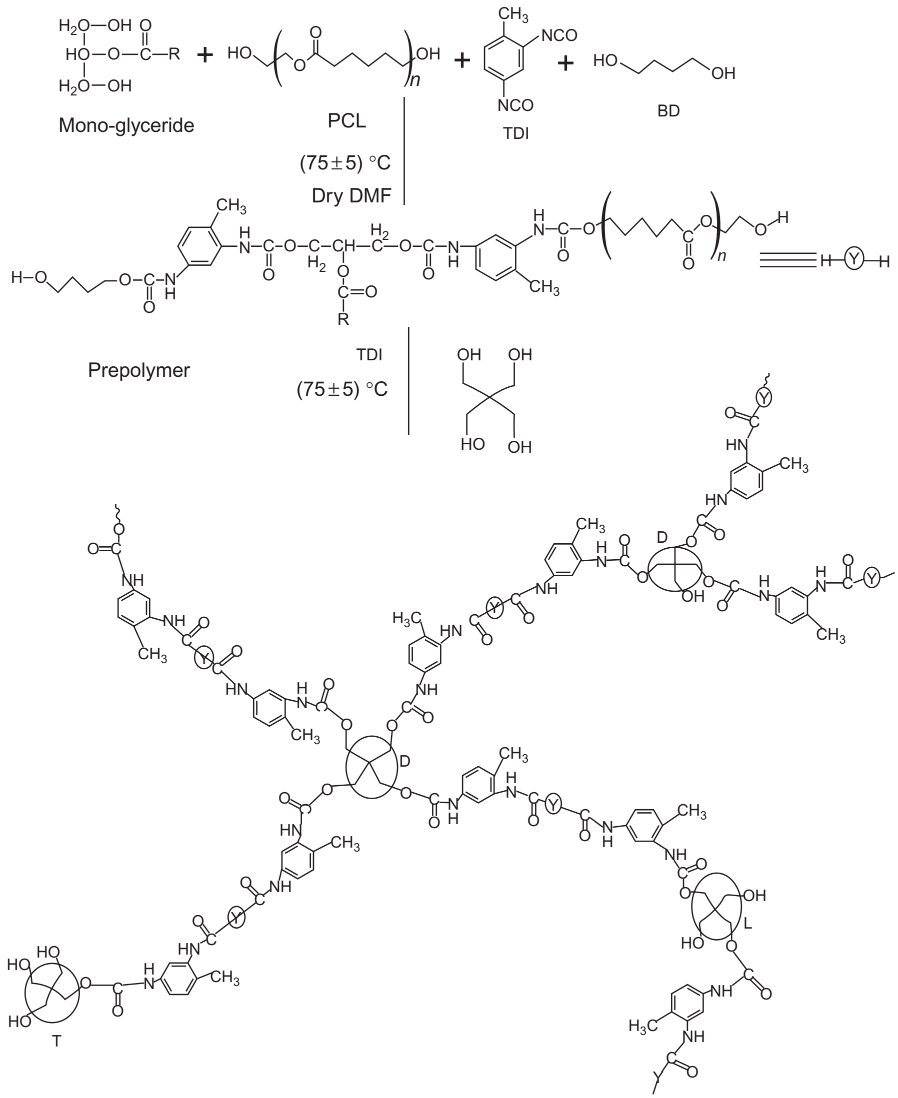

Fig. 3.10 Synthesis of hyperbranched polyurethane (HBPU).
Reprinted with permission from Das B, Konwar U, Mandal M, Karak N. Sunflower oil based biodegradable hyperbranched polyurethane as a thin film material. Ind Crops Prod 2013;44:396–404.

CNSL, lignin, and tannin are other important sources of bioresins. Ferreira et al. [50] synthesized bioresin using CNSL, lignin, and furfuraldehyde. The prepared bioresin showed chemical similarity with the oil and the experimental results showed that this bioresin can be used for removal of oil spilled on water.

Lagel et al. [34] synthesized bioresin from condensed tannin and furfuryl alcohol.

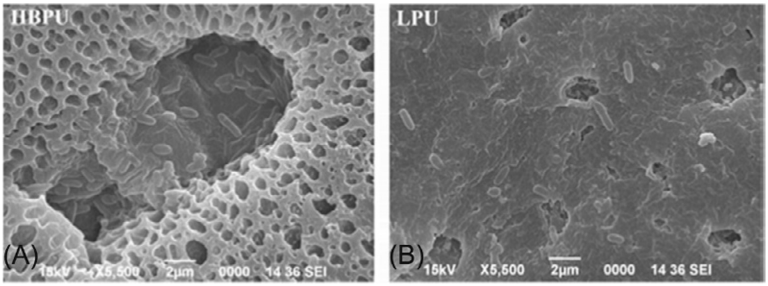

Fig. 3.11 Representative SEM images for the biodegraded (A) HBPU and (B) LPU by *Bacillus subtilis*, MTCC73 after 4 weeks.
Reprinted with permission from Das B, Konwar U, Mandal M, Karak N. Sunflower oil based biodegradable hyperbranched polyurethane as a thin film material. Ind Crops Prod 2013;44:396–404.

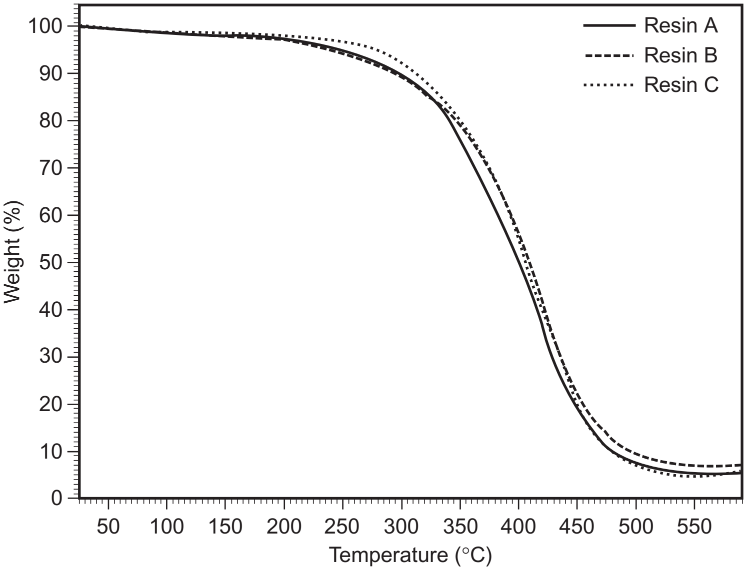

Fig. 3.12 Weight vs temperature curves of different resins.
Reprinted with permission from Islam MR, Hosen Beg MD, Jamari SS. Alkyd based resin from non-drying oil. Procedia Eng 2014;90:78–88.

Table 3.9 Composition and physical properties of resins prepared from Nahar seed oil [49]

Resin name	Composition (MA and PA content)	Curing time and temperature	Viscosity (cP)	Acid value (mg KOH/g)
resin A	100% PA	9h at 175°C	540×10^3	19.34
resin B	50% PA + 50% MA	7h at 150°C	410×10^3	34.10
resin C	25% PA + 75% MA	6h at 15°C	245×10^3	23.44

3.6 Comparative study: Bioresins in market and bioresins synthesized in laboratories

Although many academic research has been carried out on different bioresins, but very few of them have been commercialized. Longer processing steps, higher curing times, and poor performance make them industrially unacceptable. A comparative study among some bioresins synthesized in laboratories, commercial grades of bioresins, and commercial grades of synthetic resins is presented in Table 3.10.

In Western Europe and the United States, 145,000 tonnes of formaldehyde-based phenolic resins are used per year according to the report by Celluwood [40]. Attempt to move away from these petrochemical-based resins has already been started in North America. Though there are number of bioresin producers but they are characteristically small enterprises. Among those, Cambridge Biopolymers Ltd., Foreco BV, Baxenden Chemicals Ltd., etc., are developing some cost effective, high-performance materials from renewable resources via patent-protected technologies [40]. Much effort on research is required in this field as commercial bioresins are really small in number compared to the petroleum-based ones with lower properties.

3.7 Advantages and disadvantages of bioresins

Biobased products from renewable resources are of high demand in recent times due to their environment friendliness [41]. They also have the advantages of low density and low abrasiveness [42]. The environmental benefits of bioresins include:

i. They are sustainable and renewable in nature. They help to fix the amount of CO_2 in the environment. Replacement of petroleum-based synthetic resin with bioresin can reduce the amount of CO_2 in the environment [43].

ii. Petroleum-based synthetic resins may produce hazardous or carcinogenic gases. But bioresins are generally free of such carcinogenic materials.

Besides these environmental benefits bioresins have some commercial advantages also [43], such as:

i. The properties of some of the bioresins are comparable with that of the traditional petrochemical resins. Burke et al. [44] showed that the manufacturability and properties of lactic acid-based bioresin in making biodegradable bottles for packaging of water and beverages are comparable to PET bottles.

ii. The use of plant oils creates polymers with a greater intra-chain length than traditional resins which impart flexibility to the structure increasing the impact resistance of the composites.

3.8 Application areas and future pathways

Research on developing biobased products is raising our hopes towards the development of a sustainable world. Lactic acid-based bioresins have been found to be suitable for preparing biodegradable bottles (water and beverages packaging bottles) which may decrease the use of PET bottles [44]. According to Cambridge biopolymers, bioresins

Table 3.10 Comparisons between properties of commercial grades of bioresins, bioresins synthesized in laboratories, and equivalent synthetic resins

	Physical properties				Mechanical properties					
	Bio content%	**Viscosity (mPa s) @ 25°C**	**Curing**	**Post curing**	**T.S (MPa)**	**T.M (MPa)**	**F.S (MPa)**	**F.M (MPa)**	T_g	**Refs.**
Bioresins (laboratory synthesized)										
Banana sap maleate resin (BSM)	47	110×10^3	24 h @ 25°C	3 h @ 80°C	25		1727		71	[24]
GLA resin (lactic acid-based resin)	78	1.09×10^3	1 h @ 25°C	20 min @ 150°C	–	–	–	–	97	[28]
PMLA resin (lactic acid-based resin)	90	$.02 \times 10^3$	1 h @ 25°C	1 h @ 160°C	–	–	–	–	100	[29]
M4sPLA-5 (lactic acid-based resin)	–	–	196 s @ 120°C	–	57.29 ± 2.56	–	138.05 ± 5.32	–	75	[25]
Palm oil-based alkyd resin	–	99.6	9 h 23 min @ 140°C	–	–	–	–	–	–	[33]
Nahar seed oil-based alkyd resin	–	540×10^3	9 h @ 175°C	–	–	–	–	–	–	[49]
Tung oil-based unsaturated co-ester resin	–	1750	3 h @ 110°C	2 h @ 150°C	36.3 ± 0.9	1700	–	–	127	[35]
Bioresins (commercial grades)										
Envirez1807 Unsaturated polyester resin	18	850	–	–	40	3000	57	3000	–	[19]
Super Sap (CLF 01) Epoxy resin	21–30	2000–4000	7–10 days@ 25°C	Recommended	64.88	3447.38	93.31	3033.69	115.6	[48]
Aropol S604 INF-60 Polyester resin	–	220	–	–	45	3100	–	–	–	[21]

Continued

Table 3.10 Continued

	Physical properties				Mechanical properties					
	Bio content%	**Viscosity (mPa s) @ 25°C**	**Curing**	**Post curing**	**T.S (MPa)**	**T.M (MPa)**	**F.S (MPa)**	**F.M (MPa)**	T_g	**Refs.**
Synthetic resins (commercial grades)										
Epon Epoxy resin	–	$(110–150) \times 10^2$	–	–	69	2750	–	–	–	[36]
D.E.R. 331 Epoxy resin	–	11,000–14,000	–	–	79	–	96	3000	–	[37]
Crystic VE671 Vinyl ester resin	–	425	24 h @ 20°C	3 h @ 100°C	80	3300	–	–	–	[38,39]
Crestapol 1212 Urethane acrylate	–	.0156	24 h @ 20°C	3 h @ 80°C	119	6200	186	5300	–	[38,39]

have application potential in different areas, like timber boards, laminates, furniture, mouldings, glass-fibre insulation, foundry sands, etc. [45]. Bioresin, prepared from CNSL, furfuryl, and lignin, is used as petroleum absorber from water [50]. Tannin-based bioresin is used for the preparation of grinding disks [34]. Furan-based resins, like biorez and furolite, are used in some interior panels [22]. Furan-based resins exhibit a range of excellent properties, including high intrinsic fire resistance, and hence are extensively used in fire proof applications in public transport, construction, etc. Plant oil-based resin matrix composites have drawn the attention of composite industry, e.g., Ford motor company first used the idea of blending phenol-formaldehyde resin and soybean meal for automotive applications [46]. Cellulose fibre-reinforced acrylated epoxidized soybean oil resin mat was found to have mechanical strength suitable for housing and automotive applications [51]. Soybean oil-based thermoset resins are suitable in sheet moulding compound (SMC) applications. Such SMC-based composites find application in electrical, automotive, construction, aircraft, civil infrastructure, trucking, and military industries [46].

Several works have been carried out on bioresins [52], but production of very few bioresins have actually been translated to an industrial scale. Poor mechanical performance, inadequate processing technique, longer curing time, poor interfacial bonding with the biofibres, lack of investigation on long-term durability hinder their applications for outdoor purposes. Like many of the petroleum-based resins, styrene, which is not environmentally friendly is used as the reactive diluent in bioresins [53]. Research has shown that fatty acid-based monomers can be used instead of styrene as done with acrylated biopolymers [47]. Further research is required to overcome these obstacles. Focus should be given on:

- Identifying the appropriate processing techniques. Conventional processing equipment/techniques used for synthetic resins such as VARTM, RTM, hand lay-up, etc., should be equally suitable for bioresin processing to facilitate industrial-scale manufacturing. Viscosity, curing time, and temperature are important parameters which will control the success of bioresins in industrial level.
- Looking for environmentally friendly reactive diluents, curing agents, hardeners and catalysts. The use of CNSL-amine (PAA5012) as curing agent was reported by Manthey [47] for Epoxy/epoxidized hemp oil (EHO) blends. Investigating their effects on the fundamental properties, like, curing kinetics, mechanical and thermomechanical properties, moisture absorption, etc., is required.

It is therefore a challenging research field with plentiful opportunities for future development. Focus should be given on developing renewable resource-based new monomers and curing agents for the synthesis of new bioresins, which can successfully compete with the petroleum-based products in coming years.

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Thermoplastic biopolymer matrices for biocomposites

4

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4.1 Introduction

In recent years biopolymers or biobased polymers have attracted increased attention with the twofold objective of substituting for currently used synthetic polymers whilst providing new combinations of properties for innovative applications. Nowadays polymers represent essential constituents in a great host of industrial applications and it is difficult to conceive a future without them. All aspects of our life are totally dependent on materials in general and on polymers in particular, but it is interesting to note how this dependence evolved from a simple reliance on renewable materials (stone, wood, natural fibres, and so forth) to one that supplanted renewables in favour of resources that cannot be replaced. This is particularly true for synthetic polymers, whose ascent during the 20th century led to the development of advanced and cost-effective materials which replaced natural polymers. Biopolymers account for about 1% of today's plastic production but there has been a resurgent interest in biobased polymers in recent years due to several reasons that can be summarized in the dwindling oil supply, in the growing concerns of people towards global warming, and in the environmental regulations that support the development of materials and processes with a low carbon footprint [1]. In 2014 the global production capacity amounted to circa 1.7 million tons but by 2019 it is expected to reach 7.8 million tons [2]. In this regard, the aim of the present chapter is to review the main biopolymers to be used as matrices for biocomposites with a focus on properties, technological, and future challenges.

4.1.1 Terminology

This section is believed to be necessary because in the available literature on the subject there is no general agreement on the definition of several terms such as biobased, biodegradable, biopolymer, and compostable that are often used, incorrectly, to indicate similar concepts. A polymer material can be defined as a biopolymer (or bioplastic) only if it meets at least one of the following criteria: biodegradable and biobased, which refer to the biodegradability and to the origin of the raw materials, respectively. As regards the biodegradability, this is a feature that applies to those polymers able to undergo a degradation process up to final products (water, carbon dioxide) due to the action of microorganisms over a determined period of time and in a specific environment. Biodegradable polymers are certified in accordance with international standards such as: ISO 17088:2012, EN 13432:2000, EN 14995:2006, and ASTM D6400-12. Biobased is a term meaning that a particular material is derived from renewable

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resources and even though there are no standards defining a biobased product, there are standards that allow to quantify the biobased content of materials by carbon isotope analysis, such as ASTM D6866-12. Compostability differs from biodegradability only in the rate of biodegradation and toxicity and in fact all compostable polymers are by definition biodegradable but it is not true the vice versa. In an attempt to summarize, it can be said that biopolymers are defined as polymers obtained from renewable resources along with fossil-based biodegradable polymers.

4.1.2 Classification of biopolymers

In view of the definitions reported in Section 4.1.1, biopolymers can be divided into three groups [2,3]:

1. biopolymers made from renewable raw materials (biobased) and biodegradable, such as poly(lactic acid) (PLA), polyhydroxyalkanoates (PHAs), starch, chitosan;
2. biopolymers made from renewable raw materials (biobased) but not biodegradable, such as biobased polyethylene (bio-PE), biobased polypropylene (bio-PP), biobased poly(vinyl chloride) (bio-PVC), biobased polyethylene terephthalate (bio-PET);
3. biopolymers made from fossil resources but biodegradable, such as polycaprolactone (PCL), poly(butylene succinate) (PBS), poly(butylene adipate-*co*-terephthalate) (PBAT).

In the following section, the attention will be focused on biopolymers that are already commercially available in different grades and that appear more promising as matrices for natural fibre composites (NFCs). The chapter will not cover non-biodegradable biopolymers such as bio-PE, bio PP, and so forth.

4.1.3 Types and chemistry of biopolymers

Nowadays biodegradable polymers exhibit a large range of properties that allow them to compete with traditional polymers in several fields (packaging, textile, biomedical, etc.). The most investigated family of biopolymers is represented by polyesters, particularly by the linear aliphatic ones, and two main groups can be recognized depending on the type of bonding of the constituent monomers: (i) polyesters synthesized from hydroxy acids and/or esters or by ring opening polymerization of cyclic esters and (ii) polyesters obtained from the polycondensation of diols and dicarboxylic acids [3]. The hydroxy acids include the hydroxyalkanoic acids that can be in turn differentiated on the basis of the position of the hydroxyl group with respect to the carboxyl group. In the field of poly(α-hydroxyalkanoic acids), an important role is played by lactic acid, glycolic acid and their mixtures which have given rise to well-known and common polymers such as PLA and poly(glycolic acid).

4.1.3.1 Poly(lactic acid)

Among these biopolyesters, PLA is at present one of the most exploited biopolymers and has been the subject of extensive literature [4–9]. The synthesis of PLA is a multistep process starting from the production of lactic acid and ending with its polymerization. An intermediate step is often the formation of the lactide. Lactic acid is the simplest hydroxy acid with an asymmetric carbon atom and exists in two optically active configurations. The L(+) isomer is produced in humans and other mammals whilst both the D(−)- and L(+)-enantiomers are produced by the bacterial fermentation of carbohydrates, using homolactic organisms mainly belonging to the genus *Lactobacilli.* Several types of carbohydrates can be used in the fermentation depending on the particular strain of *Lactobacillus*. Usually most of the simple sugars are obtained from agricultural byproducts, including (a) glucose, maltose, and dextrose from corn or potato starch; (b) sucrose from cane or beet sugar; and (c) lactose from cheese whey [7]. Two different paths can be followed to synthesize lactic acid into high-molecular-weight PLA. Lactic acid is condensation polymerized to yield a low-molecular-weight, brittle glassy polymer, which is almost unusable unless coupling agents are used to increase the molecular weight of the polymer. The azeotropic condensation polymerization is an alternative method to obtain high-molecular-weight polymer without the use of chain extenders. The second route of producing PLA is to ring-open polymerize lactide to yield high-weight average molecular weight ($M_w > 100{,}000$) PLA. Lactide can be obtained by the depolymerization of low-molecular-weight PLA under reduced pressure to give a mixture of L-lactide, D-lactide, or meso-lactide. Due to the strict control of residence time and temperatures, the desired ratio and sequence of isomer units in the final polymer can be designed, provided that adequate catalysts and concentration of reactants are selected. The various types of PLA can be classified as follows: (i) poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), syndiotactic poly(D,L-lactide), atactic poly(D,L-lactide), isotactic stereocomplex PLA (csPLA), stereoblock copolymer PLA (sbcPLA) but most commercially available PLA is represented by PLLA. The mechanical, thermal, and degradation properties of commercial PLA depend on the molecular weight, the degree of crystallinity and the purity and relative amount of enantiomers. Amorphous PLLA has melting temperature in the range of 160–185°C and glass transition temperature in the range of 50–65°C whilst meso-PLA obtained by the polymerization of meso-lactide shows glass transition temperature in the range of 40–45°C with melting temperature around 150°C. As regards the mechanical properties, PLA usually exhibits a brittle behaviour with Young's modulus ranging from 2 to 5 GPa, tensile strength in the range of 30–65 MPa, and strain at break from 1% to 7%. These properties are comparable if not superior to the corresponding ones of many commodity polymers.

4.1.3.2 Poly(glycolic acid)

Poly(glycolic acid) (PGA) is a biodegradable polyester which has the simplest molecular structure among aliphatic polyesters. This polymer can be obtained by dehydration polycondensation of glycolic acid or ring opening polymerization of glycolide, which can be synthesized from the dimerization of glycolic acid. PGA has high gas barrier properties (O_2, CO_2, and moisture vapour) and outstanding mechanical properties with tensile strength as high as 117 MPa, tensile elongation of 13%, flexural strength of 195 MPa, and Izod impact strength of 29.2 J/m. A drawback of this polymer, at least considering the envisaged use as matrix in NFCs, is represented by the high density (~1.5–1.6 g/cm^3) and especially the high melting temperature ($T_m \sim 220°C$) which would degrade natural fibres during the processing steps.

4.1.3.3 Poly(3-hydroxybutyrate)

PHAs are an important class of biopolymers and, on a chemical basis, are polyesters of β-, δ-, ε-, γ-hydroxyalkanoic acids that are naturally produced by microorganisms. PHA monomers can have only three carbon atoms (3-hydroxypropionate) up to 14 carbon atoms (3-hydroxytetradecanoate) and the chain length is known to significantly affect the behaviour of PHAs, moving from a brittle behaviour to an elastomeric one with increasing chain length. A host of microorganisms [10–12] accumulate PHA as storage polymers for carbon and energy sources and they appear as discrete inclusions that are typically 0.2–0.5 μm in diameter localized in the cell cytoplasm. Depending on the carbon substrates of the microorganisms, different monomers, and therefore copolymers, can be obtained but they can also be synthesized chemically. The simplest PHA is polyhydroxybutyrate (PHB or P3HB), which is, along with its copolymer with polyhydroxyvalerate, at present, the most relevant for practical applications even though there are several additional commercially available PHAs including poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV), poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB), and poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) P(3HB3HH).

Bacterial synthesis is considered to be the most important process for PHA preparation at present but also the chemical synthesis of PHB via the ring-opening polymerization of butyrolactone is possible. The bacterial synthesis can be described as a two-step process where the first step is the fermentative step during which the microorganisms metabolize the sugar available in the medium and accumulate the P3HB in the cell interior as reserve whilst the second step is the extraction step during which the accumulated polymer is extracted and purified to obtain the P3HB granules [3]. These polymers can be isolated from the biomass through the destruction of the cell membrane by mechanical, chemical, or enzymatic means [13], followed by the dissolution of the polymer in a suitable solvent, for example, chloroform, methylene chloride, 1,2-dichloro ethane, or pyridine. The remnants of the cell walls are removed by filtration and/or centrifugation. Extraction, using mixed solvents, for example water/organic solvent, is the last step used for the final purification. It is to be emphasized that the number of bacteria capable of producing PHAs is really impressive and in this regard the *Pseudomonas genus* is considered the most versatile accumulator of PHAs [14]. PHB has a perfectly isotactic structure with high crystallinity (55%–80%), a glass transition temperature around 4°C whilst the melting temperature is close to 180°C. The densities of crystalline and amorphous PHB are 1.26 and 1.18 g/cm^3, respectively [12]. This biopolyester exhibits mechanical properties comparable with those of isotactic PP, in terms of Young's modulus (3.5 GPa) and tensile strength (43 MPa). A drawback of PHB is its brittle character with strain at break around 5%, which can be solved through several approaches including plasticization, copolymerization with 3-hydroxyvalerate, or annealing treatment after initial crystallization. It has been observed [15] that embrittlement of PHB tends to occur during storage after initial crystallization from the melt and that an annealing treatment [16] can effectively toughen the polymer by promoting a change in the lamellar morphology, thus reducing both the amorphous–crystalline interface area and the constraint imposed on the amorphous chains by the crystals.

4.1.3.4 Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) is a copolymer characterized by 3-hydroxyvalerate (HV) units in the PHB backbone added during the fermentation step. Compared to the homopolymer, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV or PHBV) exhibits improved ductility, toughness and processability at lower temperatures, which is particularly helpful in avoiding thermal degradation. Usually the crystallization rate and crystallinity are depressed, but this problem can be overcome through the addition of suitable nucleating agents such as boron nitride or thymine [17]. P(3HB-*co*-20 mol% 3HV) shows a melting temperature as low as 145°C, a Young's modulus of 800 MPa, a tensile strength of 20 MPa, and a strain at break of around 50%, properties similar to those of low-density polyethylene.

4.1.3.5 Poly(ε-caprolactone)

PCL is a biodegradable fossil fuel-based aliphatic polyester belonging to the general family of poly(ω-hydroxyalkanoate)s. It is usually manufactured by ring opening polymerization of ε-caprolactone. Despite the growing amount and demand of bioplastics, a large-scale application of PCL has been hindered so far by its cost and intrinsic inferior mechanical properties [18]. PCL is a tough and ductile (elongation at break ~ 600%–800%) semicrystalline polymer with low glass transition temperature (~−60°C) and melting temperature (~60°C). The tensile strength (~18–25 MPa) and Young's modulus (~300–500 MPa) are lower than those of low density polyethylene. The low melting temperature of PCL can limit the use of this polymer even though it finds applications especially in the medical field.

4.1.3.6 Poly(butylene succinate)

Polyesters obtained only from aliphatic dicarboxylic acids, also known as poly(alkylene alkanoate)s, are synthesized from a dicarboxylic acid containing from 4 to 10 carbon atoms and a diol with 2–6 carbon atoms. In recent years, one of the emerging polymers belonging to this class is PBS mainly due to its biodegradability. PBS is commercially available under several trade names and is traditionally synthesized by polycondensation of 1,4-butanediol (BDO) and succinic acid. The monomers can be obtained from fossil-based or renewable resources. Succinic acid is currently produced by hydrogenization of maleic anhydride to succinic anhydride followed by hydration to succinic acid. Another opportunity is the fermentation of microorganisms on renewable feedstocks (glucose, starch, and so forth) [19] including *Actinobacillus succinogenes*, *Anaerobiospirillum succiniciproducens*, *Mannheimia succiniciproducens*, and recombinant *Escherichia coli*. As regards the production of 1,4-butanediol, in addition to traditional petrochemical feedstocks, other routes from renewable feedstocks have been recently proposed, such as the biocatalytic routes to BDO from renewable carbohydrate feedstocks, leading to a strain of *E. coli* capable of producing 18 $g L^{-1}$ of this chemical [20]. As a whole, PBS exhibits a low melting temperature (~115°C) with a heat distortion temperature of about 94–97°C. The tensile strength is similar to the one of PP (30–35 MPa) whilst the Young's modulus (300–800 MPa) is in between the one of LDPE and HDPE.

4.1.3.7 Poly(butylene adipate-co-terephthalate)

This polymer is a random biodegradable copolymer of butylene adipate and terephthalate obtained by melt polycondensation of 1,4-butanediol, dimethyl terephthalate and adipic acid and belongs to the family of aliphatic–aromatic copolyesters [3]. It is the aliphatic part that imparts degradability to the copolymer, whilst the aromatic component controls the mechanical behaviour of the polymer. This polymer shows high elongation (~700%) but low tensile strength (~30 MPa) and Young's modulus (60–80 MPa) and finds many applications as toughening agent in other biopolyesters, such as PLA and PHA [21–23].

4.2 Properties

It is customary to divide the properties of polymers in three main classes which are referred to as intrinsic properties, processing properties, and product properties. Intrinsic properties represent those properties that are directly related to the chemical composition and structure of a well-defined polymer, such as density, crystallinity, transition temperatures, mechanical properties, and so forth. Processing properties include those properties linked to the forming step of a polymer, including viscosity, melt strength and so forth, whilst product properties are those related to the polymer as an entity. In the following, only intrinsic and processing properties will be presented and discussed.

4.2.1 Intrinsic properties

Table 4.1 compares the density values of several biopolymers with those of traditional non-biopolymers.

It is evident that most biodegradable polymers exhibit higher densities compared to traditional polymers.

The properties of polymers depend not only on their molecular characteristics but also on the presence of ordered structures, such as crystallinity degree, spherulite size, morphology, and degree of chain orientation. The low crystallization ability and degree of PLA, which are typical features of polyester polymers, are limiting its widespread industrial use. In particular, the crystallization behaviour of PLA is highly affected by the stereochemical makeup of the backbone that can be modified by polymerization with D-lactide, L-lactide, D,L-lactide, or mesolactide. The amount of crystallinity plays a role in controlling the hydrolytic degradation of the polymer with highly crystalline PLA being very difficult to be hydrolyzed [24]. PLA can be produced as totally amorphous or with up to 35%–40% crystallinity. PLA containing more than 93% of L-lactic acid are semicrystalline, but if the content drops in the range of 50%–93% it is entirely amorphous. Similarly to PET, PLA can be oriented by processing and chain orientation improves the mechanical strength of the polymer. If orientation is performed at low temperature, the resulting PLLA has a higher modulus without any significant increase in crystallinity. Typical PLA glass transition temperature ranges from 50°C to 80°C, whereas its melting temperature

Table 4.1 **Densities of the main biopolymers versus non-biopolymers**

Polymer	Commercial grade/ name	Density (g/cm^3)	Manufacturer
P3HB	Biocycle 1000	1.20	PHB Industrial S/A
P3HB	Biocycle 189D-1	1.30	PHB Industrial S/A
P3HB	Biomer P209	1.20	Biomer
P3HB	Biomer P226	1.25	Biomer
PHBV	ENMAT Y1000P	1.25	TianAn Biologic Materials Co., Ltd.
PHBH (3-hydroxybutyrate-*co*-3-hydroxyhexanoate)	Kaneka PHBH	1.19	Kaneka Corporation
PHBHV	Mirel P1003	1.40	Metabolix, Inc.
PHBHV	Mirel P1004	1.30	Metabolix, Inc.
PLA	Ingeo Biopolymer 2003D	1.24	NatureWorks LLC
PLA	Ingeo Biopolymer 3260HP	1.24	NatureWorks LLC
PLA	TE-2000	1.25	Unitika Ltd.
PGA	Kuredux	1.50–1.60	Kureha Co.
PCL	Capa 6200	1.07	Perstorp
PBS	Bionolle 1001MD	1.26	Showa Denko
PBSA(polybutylene succinate/adipate)	Bionolle 3001MD	1.23	Showa Denko
PBAT	Ecoflex F Blend C1200	1.25–1.27	BASF
PP	Metocene MF650W	0.91	Lyondell Basell
HDPE	Alathon H6012	0.96	Lyondell Basell
LDPE	Lupolen 1800P	0.918	Lyondell Basell
UHMWPE	Lupolen UHM 5000	0.931	Lyondell Basell
ABS	Lustran ABS1146	1.03	Ineos
PC	Makrolon 2405	1.20	Bayer
PA66	Zytel 101 NC010	1.14	DuPont

ranges from 130°C to 180°C. Annealing is a strategy commonly used to improve the crystallization behaviour of PLA thus leading to enhanced performance [25,26]. Other limitations of PLA are represented by the relatively low heat distortion temperature and poor thermal stability, both of which can be overcome with a postprocessing annealing step that tends to favour crystallization. An alternative approach is the use of nucleating agents to speed up crystallization. In literature several types have been suggested, such as talc and ethylene bis-stearamide [27], titanium dioxide [28], calcium sulphate [29], calcium lactate and sodium stearate [30], and organoclays [31,32]. The mechanical properties of lactic acid-based polymers can be varied to a large extent ranging from soft and elastic plastics to stiff and high strength materials depending on several parameters, such as crystallinity, molecular weight, material formulation (plasticizers, blends, composites, etc.), and processing (e.g. orientation) [9]. Semicrystalline PLA is the material of choice when higher mechanical properties are desired, having an approximate tensile modulus of 3 GPa, tensile strength of 50–70 MPa, flexural modulus of 5 GPa, flexural strength of 100 MPa, and an elongation at break of about 4% [9]. In attempt to improve specific properties of PLA, several PLA-based composites containing both micro- and nanofillers have been investigated: calcium carbonate [33], basalt fibres [34–36], organomodified layered silicates [37–41], carbon nanotubes [42–45], and graphene [46–50]. A host of studies dealt with use of PLA as a matrix for NFCs. In this regard, PLA proved to be a suitable matrix often exhibiting properties comparable if not higher than those of commodity plastics. Oksman et al. [51] reported superior (~50%) tensile strength of a PLA/flax composite compared to similar PP/flax composites with stiffness increase over the neat PLA from 3.4 to 8.4 GPa due to addition of 30 wt% of flax fibres. Also the thermal properties of PLA, which are considered its drawback, were found to improve with the addition of flax fibres. It is almost impossible to summarize all the natural fibres investigated as potential reinforcement of PLA. Just to name the most important ones: hemp [52–57], flax [58–61], jute [62,63], kenaf [64–66]. In these studies, a special care has been always devoted to the optimization of the fibre/matrix interface through suitable chemical treatments. Over the last years cellulose nanofibres (CNFs) and nanowhiskers (CNWs) derived from renewable biomass have attracted great interest as an alternative to micron-sized reinforcements in composite materials especially for enhancing the barrier effect of PLA to be used in the packaging sector [67,68]. The improvements that can be achieved are impressive if the low filler content is taken into account. Jonoobi et al. [69] reported a significant increase in tensile modulus and strength from 2.9 to 3.6 GPa and from 58 to 71 MPa, respectively, for nanocomposites with 5 wt% CNF extracted from kenaf pulp. In Fig. 4.1 it is possible to observe an example of CNFs isolated from kenaf pulp [69].

PHAs made of relatively short chains with 3–5 carbon atoms, such as P3HB and PHBHV, usually exhibit a brittle behaviour and some grades of PHB show mechanical properties comparable to those of PP. The significant brittleness is mainly associated

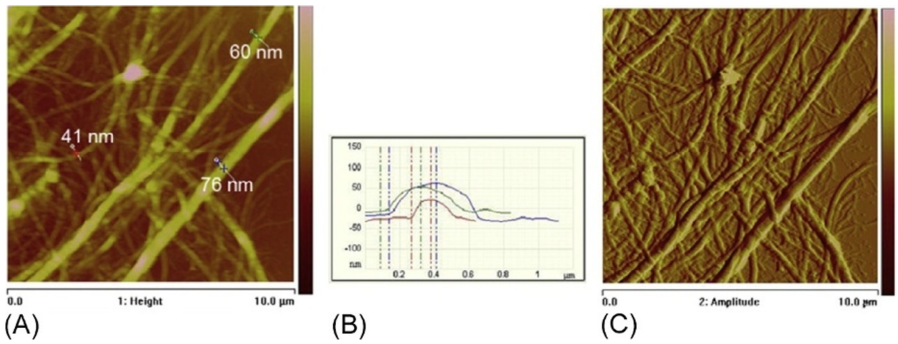

Fig. 4.1 AFM images of isolated nanofibres after grinding process: (A) height image with measured fibre dimensions, (B) fibre diameter measurements, and (C) amplitude image. Reprinted with permission by Elsevier [69].

to the presence of large crystals in the form of spherulites and to the recrystallization with ageing at room temperature [15]. This explains why many research and industrial efforts are mainly focused on plasticizers and nucleating agents able to decrease the crystallization process and to enhance the final ductility of the product. Table 4.2 summarizes some physical and mechanical properties of PHAs and of other biopolymers.

Another issue to be considered when dealing with PHAs is the fact that the decomposition temperature of PHB is very close to its melting point and this can cause a severe degradation of the polymer through random chain scission reactions [70,71]. This phenomenon can be mitigated by the use of lubricants that hinder the degradation of the chains and allow the PHB to be processed at temperatures around 170–180°C, thus causing a decrease in the molecular weight and in the melt viscosity whilst the crystallization temperature moves to lower values, and crystallization takes longer time. Another successful and common way to improve the properties of PHB is the production of derivatives based on PHB containing PHB units with other 3-hydroxyalkanoates units such as poly (3-hydroxybutyrate-*co*-hydroxyvalerate), or poly (3-hydroxybutyrate-*co*-3-hydroxyhexanoate) [72]. The introduction of natural fibres in PHAs is considered another effective strategy to improve their brittle behaviour and the related low impact resistance. This approach has been validated and supported by many studies on a great deal of natural fibres, including flax fibres [73], jute fibres [74,75], wheat straw [76,77], wood flour [78, 79], bamboo fibres [80–82], pineapple leaf fibres [83], kenaf fibres [84,85]. As a general comment, the resulting biocomposites were found to have enhanced Young's modulus, tensile strength, and thermal properties (such as, e.g. heat deflection temperature, as reported in [86], where it increased from 105°C to 131°C for composites with 40 wt% of recycled cellulose fibres) with increasing fibre amount. Also in the case of PHAs, the attainment of higher mechanical properties is hindered by the weak fibre/matrix interface due to the hydrophobicity of PHAs compared to the strong hydrophilicity of natural fibres. In this regard Anderson et al. [87] reported on the effects of four modifiers, namely maleated PHB (PHB-*g*-MA), a low-molecular-weight epoxy (having an epoxide equivalent of 590–630 g/eq), a low-molecular-weight carboxylic-terminated polyester, and polymethylene-diphenyl-diisocyante (pMDI). PHB-*g*-MA was prepared by reactive compounding of MA (5 parts), PHB (95 parts), and dicumyl peroxide (0.5 parts) in a Haake Mixer at 180°C and 50 rpm for 40 min. The MA content was found to be 0.3 wt%. The composites consisted of PHB (35 parts), wood flour (57 parts), talc (8 parts), boron nitride (0.2 parts), lubricant (3 parts), and interfacial modifier (0–4 parts). All ingredients were premixed using a kitchen mixer for a few minutes and then melt mixing was accomplished using a corotating twin screw extruder. The most effective interfacial modifier was pMDI. The addition of 4% pMDI resulted in a 57% increase in ultimate strength, and in a 21% increase in modulus. Similarly, water resistance increased with the addition of interfacial modifiers, particularly with pMDI showing the greatest improvement. Using maleic anhydride-grafted PHBV (PHBV-*g*-MA) as a reactive compatibilizer, Avella et al. [84] showed that the modulus of the PHBV/kenaf composites was significantly increased whilst tensile strength and impact strength were increased to a lesser extent. Srubar et al. [79] also utilized PHBV-*g*-MA as compatibilizer for the PHBV/oak wood flour composites to achieve improved strength. MA grafting was obtained

Table 4.2 A comparison of the physical and mechanical properties of PHAs with those of other polymers

	PHB[a]	PCL[b]	PGA[c]	PLA[d]	PBAT[e]	PHBV[f]	PP[g]	HDPE[h]	LDPE[i]
Melting temperature (°C)	170–175	65	220	152	110–115	170–176	176	137	108
Glass transition temperature (°C)	117	−61	40	58	−30	0	−10	–	–
Young’s modulus (MPa)	2200 (flex)	190	7600 (flex)	2000	52	2800–3500	1710 (flex)	1450 (flex)	130 (flex)
Tensile strength (MPa)	32	15–18	117	62 (Yield)	–	39	36.9 (Yield)	30 (Yield)	10 (Yield)
Strain at break (%)	4	>500	13	9	>500	2	142	400	–

[a] Biocyle1000.
[b] CAPA680.
[c] Kuredux.
[d] Nature Works3001D.
[e] Eastman (Eastar bio 14766).
[f] ENMAT Y1000P.
[g] IneosH05H-01.
[h] Eraclene MP90U.
[i] Riblene MP20.

via reactive extrusion in a single-screw extruder. The reactive extrusion was performed at a melt temperature of 160°C and an extruder screw speed of 20 rpm, which corresponded to a residence time of 150 s. The graft percentage of MA-grafted PHBV in the extracted material was determined to be 0.8%, similar to the values generally used for PHA-based polymers (from 0.2% to 1.18%) [88]. In other studies, Jiang et al. [80,89] demonstrated that using polymeric diphenylmethane diisocyanate (pMDI) or PHB-g-MA as compatibilizer resulted in significant increases in strength and elastic modulus of PHBV/bamboo fibre composites. Mohanty et al. [90] also demonstrated that the composites of switchgrass and PHBV/poly(butylene adipate-*co*-terephthalate) exhibited increasing strength and modulus with pMDI concentration (0.5, 0.75, and 1 phr). Zini et al. [91] investigated the improvement of fibre/matrix adhesion in a P(3HB-*co*-3HH)-flax fibres system through chemical modification of the flax surface by acetylation or by short-chain-PEG grafting. Acetylation was performed at constant temperature (30°C) for 5 h in acetic anhydride using sulphuric acid (0.4 vol.%) as catalyst, whereas grafting of monomethylated poly(ethylene glycol) (PEG) (average molar mass 350 g mol^{-1}) on the flax fibres was carried out according to a patented procedure [92]. The SEM results confirmed that surface acetylation increased adhesion between flax fibres and P(3HB-*co*-3HH) compared to unmodified fibres and provided the best results (Fig. 4.2).

CNFs and CNWs have proved to be useful reinforcement also in the case of PHA matrices. Jiang et al. [80,81] compared the thermal and mechanical properties of PHBV/CNW composites fabricated by solution casting using *N*,*N*-dimethylformamide as solvent with those of nanocomposites manufactured through melt processing (extrusion and injection moulding). Solution casting allowed an homogeneous dispersion of CNW which resulted in increased tensile strength (from 14.1 MPa for neat PHBV to 26.1 MPa at 5% CNWs) and Young's modulus (from 0.82 GPa for neat polymer to 1.76 GPa for PHBV/5% CNW). On the contrary, melt processing was found not to be able to disperse the fillers and therefore the properties did not show any increase compared to the neat polymer. Yu et al. [93] produced green nanocomposites containing biodegradable PHBV and cellulose nanocrystals/silver (CNC–Ag) nanohybrids. It was found that homogeneously dispersed CNC–Ag could act as bifunctional reinforcements to improve the thermal, mechanical, and antibacterial properties of PHBV. Compared to neat PHBV, the tensile strength and the maximum decomposition temperature of the nanocomposite with 10 wt% CNC–Ag were enhanced by 140% and 24.2°C, respectively. In addition, the nanocomposites displayed reduced water uptake and water vapour permeability.

Frollini et al. [94] prepared biocomposites based on PBS and several lignocellulosic fibres, namely coconut, sugarcane bagasse, curaua, and sisal. The relatively low processing temperature of PBS allowed the manufacture of composites without incurring the thermal degradation of natural fibres. The results showed that sisal and curaua fibres have a huge potential as reinforcing agents of PBS due to their superior chemical compatibility with the aliphatic matrix as well as to their surface morphology. Sisal/PBS and curaua/PBS composites also exhibited greater resistance against water absorption if compared to coconut/PBS and sugarcane bagasse/PBS composites. In addition to natural fibres [95–98], PBS proved to be a suitable matrix also for natural fibres of

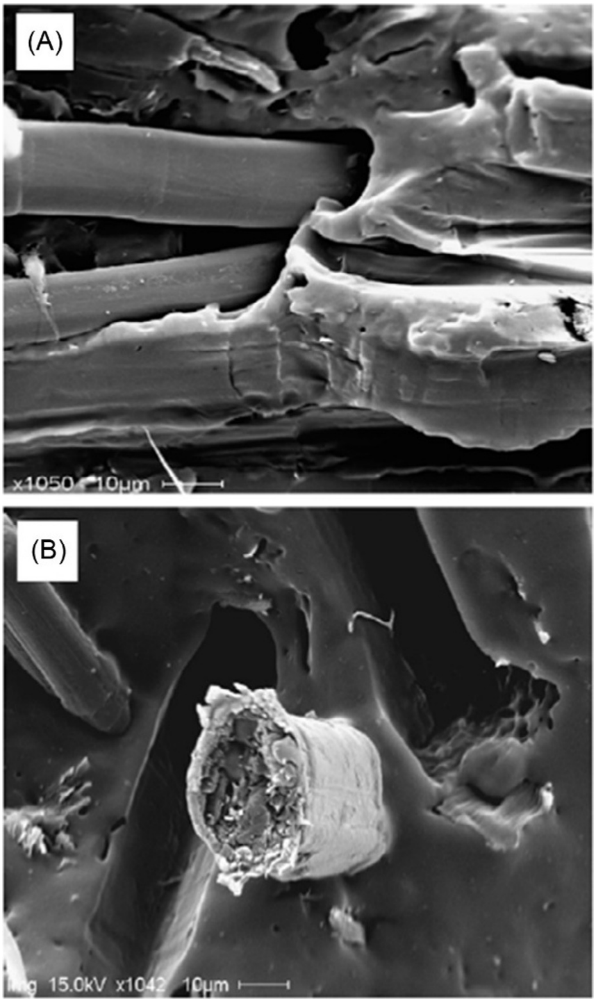

Fig. 4.2 SEM micrographs of the fractured surface after tensile test containing fibres: (A) unmodified and (B) acetylated.
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mineral origin, namely basalt fibres [99,100]. The basalt fibres enhanced the tensile strength of composites from 31 to 46 MPa as the basalt fibre loading increased from 3 to 15 vol.%, and this effect was even higher for Young's modulus, for which a fibre loading of only 3 vol.% caused an increase in the modulus of PBS by about 100%. Basalt fibres had a positive effect also on the thermal properties of PBS, as the heat deflection temperature of the composites increased from 82°C to 114°C whilst the Vicat softening temperature increased from 96°C to 109.1°C with increasing fibre content.

The large-scale application of PCL is still limited because of its relatively high price along with some intrinsic inferior properties [18]. Properties and cost of biopolymers can be tailored and improved through several approaches, including blending [101] or through the use of natural fibres that can reduce the cost of the material without affecting their biodegradability. As regards PCL, different types of cellulose-based natural fibres have been successfully incorporated as fillers to obtain biodegradable composites with improved properties [102]. Cellulosic fibres are generally incompatible with polymers due to their hydrophilic nature and therefore their reinforcing effects can be improved if the adhesion is promoted by fibre surface treatments or modification of the polymer matrix. As an example of the former, Arbelaiz et al. [103] investigated the mechanical properties of PCL/flax fibre bundle composites with different amounts of synthesized PCL-*g*-maleic anhydride (MA) coupling agent and fibre content. Mechanical properties and crystallinity of composites decreased with the addition of small amounts of PCL-*g*-MA coupling agent (5 wt%, respect to fibre bundle content). The decrease in mechanical properties was ascribed to the reduction in crystallinity of the composites. The increase of coupling agent amount resulted in a higher crystallinity with a corresponding increase in mechanical properties. The highest crystallinity and the best mechanical properties were obtained for flax/PCL-*g*-MA composites, with improvements for tensile and flexural strength of 54% and 44%, respectively. Siqueira et al. [104] have investigated PCL-based composites reinforced with CNWs and microfibrillated cellulose (MFC) both extracted from sisal fibres. In addition, they evaluated the effect of nanofiller surface modification (by *N*-octadecyl isocyanate) on the properties of the resulting composites. As a first result, the chemical grafting resulted in increased dispersion of nanofillers in organic solvents. Sisal whiskers were found to impart a limited reinforcing effect because of their aggregation during film formation. However, the presence of the filler increased the glass transition, crystallization, and melting temperatures, as well as the degree of crystallinity of the neat matrix. The chemical grafting improved both stiffness and ductility of the composites. When comparing sisal whiskers and MFC (both chemically modified), the authors found that the modulus was higher for MFC-reinforced composites, whereas the elongation at break was lower at a given filler amount. The addition of MFC did not cause an increase in the degree of crystallinity of the matrix and in the melting point.

4.2.2 Processing properties

As a general introduction, the processing through extrusion of biopolymers such as PHAs and PLA is limited by their high sensitivity to moisture and high temperature. The extrusion of PLA-based materials is generally coupled with other processing steps such as thermoforming, injection moulding, fibre drawing, film blowing, bottle blowing, and the final properties of the polymer will be a function of the specific conditions during the processing steps. The main problem associated with the manufacturing of PLA-based products is the limited thermal stability during the melt processing. In particular PLA has generally a low melt viscosity, inadequate temperature stability, slow crystallization rate coupled with long moulding cycles [3]. PLA has a melting temperature in the range of 165–185°C and is generally processed at temperatures of 185–190°C where chain scission reactions and thermal degradation are likely to occur. Moreover, a prolonged exposure at high temperatures allows the formation of lactide that results in the reduction of melt viscosity and elasticity. This confirms that PLA has a very limited processing window. A strategy to increase melt elasticity whilst keeping the viscosity at low levels, involves the broadening of the molecular weight distribution through branching by peroxide modification. Processing at lower temperatures can be achieved by the addition of plasticizers and in this regard low-molecular-weight PEG, polypropylene glycol, and fatty acid can be used as plasticizers. The processing of PHAs depends very much on the grade of the polymer used but traditional processing techniques can be used, such as injection moulding and extrusion. Two main problems with PHA are the low melt viscosity and low melt elasticity. Along with these two drawbacks, thermal stability is also low that results in a significant decrease in molecular weight leading to a further decrease in melt viscosity and nonoptimal mechanical properties. The use of copolymers with a view to improving the flexibility for potential packaging applications leads also to a decrease in the glass transition and melting temperatures. In addition, the HV broadens the processing window since there is improved melt stability at lower processing temperatures. Another strategy involves the use of plasticizers like glycerol, tributyrin, triacetin, acetyltriethylcitrate, and acetyltributylcitrate. In addition, lubricants like glycerolmonostearate, glyceroltristearate, 12-hydroxystearate, and 12-hydroxystearic acid can also be used [70].

Fabrication of natural fibre-reinforced composites is challenging especially because of the low stability during processing of natural fibres. Generally, manufacturing techniques originally designed for conventional fibre-reinforced polymer composites and thermoplastics, such as compression moulding, injection moulding, or vacuum infusion (for thermoset-based composites), are under consideration for the fabrication of NFCs. In addition to the problems related to the processing of biopolymers, several important issues in processing the related composites can be ascribed to the structure and properties of the fibres themselves. In fact, unlike many synthetic fibres, lignocellulosic fibres are inherently thermally unstable and thermal degradation occurs at temperatures in the range of 150–220°C. Therefore it is advisable to maintain the processing temperatures below 150°C. In this regard, some authors have found a beneficial effect on the thermal stability of plant fibres by treating them with alkali [105] or by grafting functional monomers on the fibre surface [106]. It is well known that the dispersion of natural fibres determines the mechanical performances of the ensuing composites. Although the dispersion is a fibre size dependent phenomenon, it is not easy to achieve good dispersion of natural fibres in biopolymers and several physical and chemical treatments of fibres can be used to enhance the fibre dispersion in the matrix. Different coupling agents, such as maleic anhydride [64,107,108], mineral oil, or stearic acid, have been reported to improve the dispersion. Stearic acid improves the dispersion by reducing the fibre-to-fibre interaction [99,100], whereas mineral oil acts as a lubricant that induces disentanglement of fibres thus improving the dispersion [109]. Processing of green composites differs from traditional polymer composites also due to changes in rheological behaviour, thermal instability, tendency to water absorption, and morphological differences within natural fibre types and species. Natural fibres and biopolymers exhibit viscoelastic behaviour causing a change in the flow characteristics. Few studies on the flow behaviour of natural fibre-reinforced composites highlighted the increase in viscosity of the composites with fibre content and reduced processability [110]. For instance, in [111], the authors reported a decrease of the melt flow index (MFI) as a function of fibre content and also with MA-*g*-PP addition in a Curaua fibers-Ecovio (BASF) system due to the presence of fibres that hindered the mobility of the polymer matrix thus increasing the apparent viscosity [112]. The decrease in MFI value for the composites with MA-*g*-PP was likely due to the ester linkages formed by chemical reactions of the MA-*g*-PP coupling agent and fibres as well as the physical entanglement from the MA-*g*-PP coupling agent and the polymeric matrix [113]. On the other hand, biopolymers like PLA show poor flow properties [114]. Moreover, hydrophilic nature of natural fibres reduces fibre–matrix adhesion and fibre dispersion which are important parameters for processing [115]. Depending on the types of biopolymers used and their application, modification is necessary to achieve the desired processability and performance properties. Biopolymers have poor processability due to lower melt strength and sensitivity to moisture [116]. For instance, PLA and PHA have relatively lower molecular weight and are brittle, factors that have been proved to limit their rheological properties during compression moulding and thermoforming [116]. Some studies used chain extenders (Joncryl from BASF) for PLA, PHA, and PHB or copolymerization showing that enhanced fibre/matrix entanglement can be achieved thus leading to higher melt strength and larger processing window [117]. As for the reinforcement form (length and orientation), the effect of the manufacturing route is particularly important, especially in the case of injection moulding, where at each stage the fibre length reduces. During the compounding step, fibres are submitted to intensive thermal and mechanical stresses, leading to their rupture and thus to a partial loss of reinforcing action. The aspect ratio of the fibre is an important parameter for composite mechanical properties. Contrary to synthetic fibres, natural ones can also be reduced in their diameter due to the separation of bundles into elementary fibres [118–120]. Quantitative relationships between the processing conditions and fibre breakage have been reported for glass fibres [121] but for natural fibres the rupture mechanisms are less understood [122]. Natural fibres will not experience breakage in the same way due to their flexibility and therefore they are likely more inclined to entangle. Another issue that needs more in-depth investigations is the complex relationship between different processing routes of the composites with regard to their mechanical properties that has recently been highlighted by Graupner et al. [118,119]. The authors found significant differences as a function of the processing technique (compression moulding vs injection moulding), the fibre loading, and the fibre orientation in a lyocell fibre/PLA system, with higher tensile and impact strength for compression moulded composites compared to injection moulded ones.

4.3 Polymer blends

When dealing with biopolymers, one can recognize two stark differences compared to traditional products derived from petrochemical feedstock: (i) their sometimes not-so-satisfactory inherent properties and (ii) their lower processability. A way to tackle and overcome these issues is to blend a biopolymer with another polymer that is not necessarily a biopolymer. This route has been followed by many researchers as supported by the extensive literature and patents available on the subject, even though, as a general rule, polymer blends with enhanced properties usually show lower biodegradability especially in the case of miscible blends with non-biodegradable polymers.

As already highlighted in Section 4.2, PLA suffers from three main limitations, namely low ductility, low melt viscosity, and low thermal stability. Ikada et al. [123] and Tsuji and Ikada [124] produced via solvent casting films of 1:1 blend and non-blends from poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA). The blended films exhibited higher (~50°C) melting temperature (in the range of 220–230°C) compared to neat PLLA or PDLA along with improved mechanical properties in terms of tensile strength, Young's modulus and strain-at-break. The authors ascribed this behaviour to the microphase structure difference generated as a result of formation of many stereocomplex crystallites [125] which acted as intermolecular cross-links during solvent evaporation of blend solution, thus limiting large-sized spherulites which are known to decrease the mechanical properties. This enantiomeric polymer blending was confirmed to show enhanced thermal stability compared to neat polymers in Tsuji and Fukui [126] where equimolar enantiomeric blend (PLLA/PDLA) films were prepared again by solvent casting. With a view to increasing the degradation rate of PLA, poly(aspartic acid-*co*-lactide) (PAL) represents a suitable additive, as confirmed by Shinoda et al. [127]. The mechanical properties of the produced melt-blended films were not significantly affected by the addition of PAL and also the PLA transparency was preserved. The degradation rate of PLA was indeed enhanced in water, soil, and compost. PLA was also found to be an effective additive to increase the nonenzymatic hydrolysis rates of both PBS and PCL. Blends of PLA with several biodegradable polyesters such as PBS [128], PCL [129], PHB [130–133], PHBV [134–136], PBAT [137] have been reported in the literature. Zhang et al. [138] prepared blends of PLA and PHB by dissolving the polymeric binary mixtures in chloroform and casting films and were found to be immiscible whilst the melt-blended samples prepared at high temperature showed some evidence of greater miscibility. Compared to plain PHB, the blends exhibited improved mechanical properties. Ma et al. [135] investigated PLA/poly(β-hydroxybutyrate-*co*-β-hydroxyvalerate) (PHBV) blends prepared by melt compounding. The blends showed two separate glass transition temperatures, indicating that the PLA and PHBV are not miscible. The ductility and toughness of the PLA was effectively improved by 10–30 wt% of the PHBV coupled with a significant increase in the elongation at break and the impact toughness. The toughness mechanism was ascribed to extensive fibrillation, partial interfacial debonding, PHBV domain cavitation, and matrix yielding. Jiang et al. [137] prepared PLA/PBAT blends using a twin screw extruder. The authors found that both melt elasticity and viscosity of the blends increased with the concentration of PBAT and in addition to toughen the PLA, PBAT increased the processability of PLA in extrusion by acting as a lubricant at low extrusion temperature. This blend is an immiscible two-phase system with a significant toughening mechanism ascribed to debonding-initiated shear yielding.

The blending of P3HB or PHBV with other polymers has attracted much interest to improve the inherent brittleness as well as to reduce high production cost of the microbial polyesters. Recent advances in the field have been reviewed by Ha and Cho [139]. PLA and P3HB and/or PHBV are immiscible and the mechanical properties of the resulting blends are usually intermediate between those of the individual constituents. P3HB has been reported to show a limited miscibility at low concentrations (up to 20 wt%) with PBS [140] whilst PHBV showed no miscibility with PBS at all concentrations [3]. The inherent low ductility of PHB is still an issue not easily solved through blending without tolerating a significant decrease of mechanical properties. In this regard, Yoon et al. [141] blended poly(*cis*-1,4-isoprene) (PIP) with (PHB) via solvent casting in an attempt to improve the mechanical properties of PHB. The two species were found to be immiscible, therefore poly(vinyl acetate) (PVAc) was grafted onto PIP and the resulting blends were characterized. As the amount of the PIP-*g*-PVAc copolymer increased, tensile strength of the PHB/PIP-*g*-PVAc blend decreased but to a lesser extent compared to the PHB/PIP blend. However, toughness and strain at break were markedly enhanced by the addition of the graft copolymer, contrary to the PHB/PIP blend. The same conclusions can be drawn from the work of Parulekar and Mohanty [142] who prepared through reactive extrusion and subsequent injection moulding blends of PHB and functionalized natural rubber. A maleated polybutadiene with high grafting and low-molecular weight was used as compatibilizer for the PHB–rubber blend system that showed an increased toughness compared to PHB by 440%. Also in this case there was a significant decrease in tensile strength and modulus.

PBS have been blended with many other biopolymers such as PLA [143–146], PHB [140,147], and its copolymers [147]. PLA and PBS are immiscible in melt but when the blending ratio is 80/20 and 20/80 the dispersed phase is finely distributed and this results in good mechanical properties. Blending PBS with PLA enhances both the tensile strength and modulus without impairing in a significant way the ductility [148].

Another family of blends that has been exploited in literature is the one obtained mixing hydrophobic and hydrophilic polymers, in particular starch. Blending starch with PLA is a promising effort to combine the great availability and low cost of starch with the good mechanical properties offered by PLA. Starch is able to increase the crystallization rate of PLA even at low contents (1%), with increasing trend as the starch content increases from 1% to 40% [149]. In starch-based blend systems, one of the most important factors affecting final mechanical properties is the interfacial affinity with the polymer matrix. In this regard gelatinization of starch is an effective strategy because it causes the disintegration of the granules thus overcoming the strong crystalline intramolecular forces prior to mixing with other polymers. It is necessary to remove the water present in the gelatinized starch prior to blending with easily hydrolyzed polymers such as aliphatic polyesters. The problem is that during water removal, starch tends to reform the strong crystallinity due to hydrogen bonding. Glycerol can be used as a plasticizer to hinder this reformation of the strong crystallinity in starch. Park et al. [150] prepared gelatinized starches with different amounts of glycerol that were melt blended with PLA. They found that starch lowered the crystallization temperature and increased the degree of crystallinity in PLA/starch blends. The starch acted as a nucleating agent whilst glycerol was a plasticizer that improved crystallinity in the PLA blends. The adhesion between hydrophilic starch and hydrophobic PLA can be also enhanced by addition of methylenediphenyl diisocyanate [151,152], dioctyl maleate [153], maleic anhydride (MA), and poly(vinyl alcohol) [154].

Several attempts have been made to produce PHA/starch blends with improved physical properties. Innocentini-Mei et al. [155] investigated blends of PHB with natural starch, starch-adipate, and grafted starch-urethane derivatives. They reported that blends containing natural starches resulted in brittle materials and that for all PHB blends a decrease of the Young's modulus compared to the neat PHB occurred. In addition, a marked decrease of both glass transition and melting temperatures was observed for all formulations. Reis et al. [156] prepared PHB-hydroxyvalerate and maize starch blend films by a casting technique. The Young's modulus, strength, strain at break were all found to decrease with an increase in starch content in the blend with PHBV as no intermolecular interactions existed between the two polymers with a low crystallinity (<4%). Zhang and Thomas [157] examined the properties of PHB when blended with two types of maize starch, one containing 70% amylose and the other one containing 72% amylopectin. The authors reported a nucleating effect of starch particles for PHB crystallite formation even though the mechanical properties were not satisfactory. They also highlighted the better role play by the high amylose content.

In an attempt to improve the properties of biopolymers, blending with non-biodegradable polymers based on petrochemical feedstock has also been explored. Many of these blends are immiscible with coarse phase morphologies that result in poor mechanical properties and concerns about the full biodegradability of the resulting material. Blends of PLA and PHB with several synthetic polymers such as poly(methyl methacrylate), polyethylene, poly(ethylene oxide), and polypropylene have been reported to improve the toughness, impact strength, and thermal stability, compared to the neat polymer but usually at the expense of general mechanical performance [158–165]. Choudhary et al. [166] successfully prepared by melt-blending PLA/PP blends with improved tensile modulus, tensile strength, flexural strength, and impact properties. In particular, MAH-*g*-PP proved to be suitable compatibilizer helping the dispersion of the PP phase and enhancing the overall properties in the system. Sadi et al. [167] blended polypropylene with PHB and because of the immiscibility between PP and PHB, they investigated several copolymers as possible compatibilizers: poly(propylene-*g*-maleic anhydride) (PP–MAH), poly (ethylene-*co*-methyl acrylate) [P(E–MA)], poly(ethylene-*co*-glycidyl methacrylate) [P(E–GMA)], and poly(ethylene-*co*-methyl acrylate-*co*-glycidyl methacrylate) [P(E–MA–GMA)]. They reported the following order of compatibilizer efficiency: P(E–MA–GMA) > P(E–MA) > P(E–GMA) > PP–MAH.

Despite the increased properties, these blends still cannot be used for a wide range of applications on their own because they cannot meet some of the product requirements [168]. In this regard the introduction of natural fibres represents a suitable alternative and solution to overcome the intrinsic limitations of biopolymers and related blends. Nagarajan et al. analyzed the performance of five different lignocellulosic fibre (miscanthus, switchgrass, wheat straw, soy stalk, and corn stalk) reinforced poly(hydroxybutyrate-*co*-valerate) PHBV/poly(butylene adipate-*co*-terephthalate) PBAT (45/55 wt%) composites. Comparing the effects of all the fibre types, miscanthus-based composites showed slightly higher tensile strength, Young's modulus improved by 104%, and the heat deflection temperature was found to be 110°C. Similar observations were found in miscanthus fibre-reinforced PHBV/polylactide (PLA) (60/40 wt%) composites [169], a blend that showed a comparable strength and modulus to that of polypropylene [136,170]. Recently Zhang et al. [171] reported that toughened multiphase green composite can be obtained from miscanthus fibre-reinforced PHBV/PBAT/epoxidized natural rubber matrix with enhanced stiffness and thermal resistance without compromising the toughness of the blend matrix. In another study by Muthuraj et al. [172] miscanthus fibres were added to a 40:60 wt% blend of poly(butylene adipate-*co*-terephthalate), PBAT and poly(butylene succinate), PBS. This is motivated for instance by the fact that the impact toughness/strength of PBS is insufficient for a wide range of applications and by blending PBS with PBAT can enhance the impact and toughness of the PBS. The authors found that the stiffness and flexural strength of the PBS/PBAT (60/40 wt%) blends is improved with addition of miscanthus fibres. Same positive effects due to the incorporation of natural fibres in blends were reported also in Ref. [173] in system made of curaua fibres and Ecovio matrix, which is a blend composed by a compound of poly(butylene adipate)-*co*-poly(butylene terephtalate) (P(BA-*co*-BT)) and PLA. In this case incorporation of 20 wt% of curaua fibres and 2 wt% MA-*g*-PP provided a 23% increase in hardness, a 75% increase in the tensile strength, and a 56% increase in flexural strength, as well as a Charpy impact strength improvement with respect to neat blend. These results are promising in view of a much more in depth exploitation of biopolymer blends as matrices for NFCs [73].

4.4 Biodegradation of biodegradable polymers; from renewable resources, petrochemical sources, and related blends

4.4.1 Definition of terms

The word ‘biodegradable’ is abused in the literature and is definitely a misleading one, as it does not provide any information about the specific environment where the biodegradation is envisaged to happen, the rate at which the process will proceed and the extent of biodegradation (for instance partial or total conversion into CO_2). This preliminary specification is necessary because in theory any organic compound can be defined as biodegradable in the sense that the organic carbon of any substance after a series of degradation processes can be oxidized into carbon dioxide through microbial respiration and, in the absence of oxygen, methane and CO_2 (mineralization). Nevertheless it is difficult to give a unique and precise definition of biodegradation. In this regard it is found to be suitable the definition given by Albertsson and Karlsson according to which biodegradation is an event that takes place through the action of enzymes and/or chemical decomposition associated with living organisms (bacteria, fungi, etc.) or their secretion products [174]. However, abiotic reactions such as photodegradation, oxidation, and hydrolysis need to be taken into account as they can also alter the polymer before or during the biodegradation due to environmental factors. Several different definitions of a biodegradable plastic or biodegradation have been published by national and international standardization organizations over the years and some inhomogeneities can be recognized. The evaluation of biodegradable plastics should always be based on definitions and tested according to relevant test procedures. Interested readers are referred to Amass et al. [175], Funabashi et al. [176], Pagga [177], and Steinbüchel [178]. Before concluding this brief preface, a further distinction between biodegradable and compostable polymer seems to be appropriate. Compostability indicates an additional property of plastic materials and its definition given by CEN (European Committee of Standardisation) is as follows: (i) compostability is a property of a packaging to be biodegraded in a composting process; (ii) to claim compostability it must have been demonstrated that a packaging can be biodegraded and disintegrated in a composting system (as can be shown by standard test methods) and completes its biodegradation during the end-use of the compost; (iii) the compost must meet the relevant quality criteria. Quality criteria are, for example, heavy metal content, no ecotoxicity, and no obviously distinguishable residues [179]. Based on this definition a biodegradable material is not necessarily compostable, because it must also disintegrate during the composting cycle and it must cause no problem either to the process or to the final product (the compost).

4.4.2 Biodegradation mechanisms of selected biodegradable polymers

As a general mechanism of biodegradation, it is worth mentioning that the size of polymer macromolecules and the lack of water solubility usually hinder the transport of the polymeric materials directly into the cells by the microorganisms. This implies that microorganisms must first excrete extracellular enzymes that depolymerize the polymers outside the cells and act mainly on the polymer surface and as a consequence the biodegradation of plastics can be described as a surface erosion process. During this surface process, if the molar mass of the polymers is sufficiently reduced to generate water-soluble intermediates, these can be easily assimilated into the cells and fed into the appropriate metabolic pathways with final products in terms of water, carbon dioxide, and methane (in the case of anaerobic degradation), along with a new biomass. This enzyme-based mechanism is generally the main process leading to biodegradation, other non-biotic chemical and physical processes can also act on the polymer including chemical hydrolysis, thermal degradation, and photodegradation. The scenario is even more complicated because the rate of biodegradation is markedly influenced by many other factors, notably those related to the environment (temperature, moisture level, pH, and nutrient supply) and those related to the polymers themselves (composition, crystallinity, additives).

The most important type of biodegradable biopolymer degradation is represented by hydrolysis. In particular PLA hydrolysis is an important phenomenon as it leads to chain fragmentation [4], and can be associated with thermal or biotic degradation. In general poly(α-ester)s (PLA, PGA, etc.) exhibit hydrolytic rates higher than those of PHAs with an abiotic bulk mechanism ascribed to their more hydrophilic character. Whilst the rate of abiotic hydrolysis is mainly controlled by the molecular weight, the rate of enzymatic hydrolysis is markedly influenced by the degree of crystallinity. The hydrolysis of aliphatic polyesters starts with a water uptake phase, followed by hydrolytic scission of the ester linkages. This process is known to start in the amorphous parts of the polymer with associated increased crystallinity [180] followed by hydrolytic degradation of the crystalline regions that leads to increased rate of mass loss and finally to complete resorbtion. Temperature plays a significant role in accelerating this type of degradation. The biodegradation of PCL using soil burial, activated sludge tests and composting is reported to generate loss of mechanical properties and rapid weight loss and a bulk random chain scission mechanism has been proposed. Abiotic hydrolysis occurs more slowly because of the hydrophobicity of the polymer and in this way it is similar to PHB [175]. PHAs undergo quite rapid enzymatic hydrolysis in soil, sewage sludge, and seawater especially in the presence of extracellular P(3HB) depolymerases [181–183], but being the polymers hydrophobic, abiotic hydrolysis is generally relatively slow. The major factor controlling the microbial hydrolysis rate of the PHB or PHBV is the degree of crystallinity. The rates of enzymatic degradation for melt-crystallized films of PHA copolymers (3-hydroxybutyric acid with different hydroxyalkanoic acids such as (*R*)-3-hydroxypentanoic acid, (*R*)-3-hydroxyhexanoic acid, 4-hydroxybutyric acid, 6-hydroxyhexanoic acid) with different crystallinities and different lamellar thicknesses were studied. The rates of enzymatic erosion for melt-crystallized copolyester films significantly decreased with increasing degree of crystallinity and it was proposed that the PHB depolymerase at first hydrolyzes polymer chains in the amorphous phase and then erodes the crystalline phase. The enzymatic erosion rate of crystalline region in polyester films decreased with an increase in the lamellar thickness. PBS and its copolymers are found to be biodegradable in lipase solution, soil burial, water, activated sludge, and compost [184]. Cho et al. [185] investigated the effect of crystalline morphology on the hydrolytic degradation behaviour of poly(butylene succinate) in an alkaline solution. It was found that an isothermally crystallized sample at 60°C, which had spherulites composed of less densely packed fibrils, showed a higher degradation rate compared to a melt-quenched sample with similar crystallinity, thus highlighting the important role played by the internal structure of the spherulites.

From a practical perspective, biodegradability is one of the most important properties of natural fibre-reinforced biocomposites and it is therefore quite surprising the relatively low coverage of the subject in the literature. Durability of natural fibre reinforced polymer composites in a dry environment does not seem to be an issue. Biodegradation of fibres causes further reduction in properties and protection against biodecay is generally obtained (i) by making the fibres less accessible to enzymes, (ii) by removing the components most sensitive to biodegradation, and (iii) by making fibres less hydrophilic. Treatments that can be used to make natural fibres more durable are for instance those essentially derived from the wood industry, such as furfurylation, acetylation, and heat treatment. Peterson et al. [186] investigated the biodegradability of Pinus radiata fibres in a Biopol matrix. Composites of varying fibre mass fraction (0%, 15%, 20%, 25%) were incubated in activated sludge soil for 5 weeks at 40±2°C. The authors found that the composites degraded faster than the neat matrix specimens and this behaviour was ascribed to the presence of wood fibres which acted as conduits for the bacteria, thus allowing greater access and therefore faster degradation rates. A higher degradation rate for biocomposites was found also by Mohanty et al. [187] in jute-fabric/Biopol composites. Composites were buried in a compost mixture for 150 days and the effect of different fibre surface treatments (dewaxing, alkali, graft copolymerization with AN and also with MMA, cyanoethylation) was addressed. About 34% weight loss was observed for neat Biopol, whilst dewaxed, alkali-treated, 19% AN-grafted and 30% AN-grafted jute/Biopol composites decreased their weights by about 56%, 42%, 37%, and 34% after this period. Fortunati et al. confirmed even in the case of nanocomposites the higher [68] disintegration rate of PLA due to the addition of silver nanoparticles and cellulose nanocrystals obtained from microcrystalline cellulose, as can be seen in Fig. 4.3.

Avella et al. [77] reported that steam-exploded wheat straw–PHBV composites degraded at the same rate in liquid environment and in long-term soil burial tests. In the composting simulation test the rate of biodegradation was reduced for composites with more than 10% of fibre content. The service life of biocomposites is not adversely affected by their biodegradability. In this regard Kumar et al. [188] showed that the biodegradability of PLA reinforced with flax fibres can be tailored through a judicious selection of amphiphilic additives. In particular the higher loss in weight was obtained in the presence of mandelic acid whilst dicumyl peroxide comparatively delayed the biodegradability of the composites. Harnnecker et al. [173] studied the biodegradability of Ecovio/curaua composites by compost-soil burial test and highlighted that the presence of 20 wt% of curaua fibre increased the retained mass more than twice compared to neat matrix after 210 days of exposure to the soil. Moreover, MA-*g*-PP presence led to higher contents of retained mass in composites as supported also by the work of Liu et al. [97] on PBS/jute composites. Even fewer studies have been performed on the behaviour of biocomposites under anaerobic conditions [189,190]. Recently Iwańczuk et al. [191] investigated the behaviour of two biodegradable polymers (PLA and PHB–PHV) and polyethylene as reference material and their composites with flax fibres in anaerobic digestion trials. The digestion tests were performed by means of wet fermentation at temperature of 37°C and lasted for

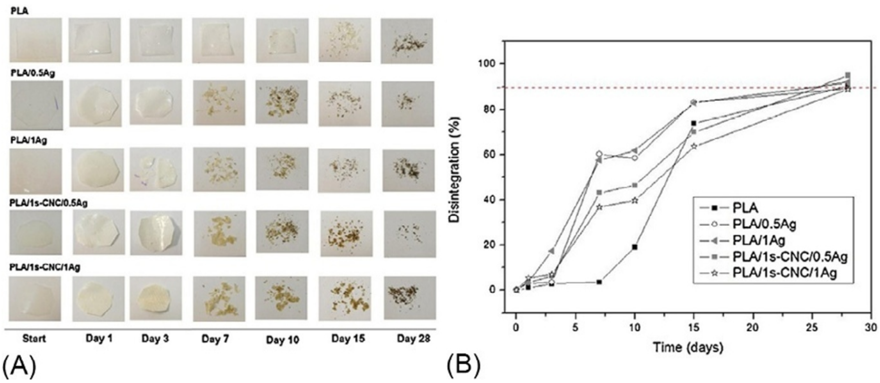

Fig. 4.3 (A) PLA and PLA nano-biocomposites before (0 days) and after different stages of disintegration in composting at 58°C. (B) Disintegrability percentage values of PLA and PLA nano-biocomposites at different stages of incubation in composting.
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72 days. Anaerobic sludge from a sewage plant was used as an inoculum. Extensive anaerobic biodegradation of PHB–PHV and PHB–PHV composites with flax fibres was observed whilst PLA exhibited a little change in properties after immersion in the anaerobic sludge. Polymer composites underwent biodegradation faster than the neat matrix but the extent of degradation is lower if the fibers are more resistant to biodegradation than the polymer.

4.5 Present application areas/commercial products

According to European Bioplastics [192], bioplastics represent about 1% of the about 300 million tonnes of plastic produced annually, but the market is already growing by about 20%–100% per year. Global production capacity of bioplastics is predicted to quadruple in the medium term, from around 1.7 million tonnes in 2014 to approximately 7.8 million tonnes in 2019. Biobased, non-biodegradable plastics, such as biobased PE and biobased PET, are the main drivers of this growth even if production capacities of biodegradable plastics, such as PLA, PHA, and starch blends, are also growing steadily, nearly doubling from 0.7 million tonnes in 2014 to well over 1.2 million tonnes in 2019. Bioplastics are currently used in several markets, from packaging, catering products, consumer electronics, automotive, agriculture/horticulture, and toys to textiles. Among these sectors, packaging confirms to be the largest field of application for bioplastics with almost 70% (1.2 million tonnes) of the total bioplastics market [192], a number that is expected to increase to more than 80% (6.5 million tonnes) in 2019. One of the main market drivers is undoubtedly represented by the adoption of bioplastics performed by big industrial companies such as Procter & Gamble, Coca-Cola, Danone, Puma, Samsung, IKEA, Tetra Pak, Heinz, or Toyota, which have already introduced first large-scale products in Europe. At present, due to the increasing number of applications, it is possible to find a host of industries producing biopolymers of several commercial grades which are summarized in Table 4.3, which is not intended to be a complete and exhaustive list.

The packaging sector represents the most important market in volume for biodegradable packaging. PLA is one of the most popular and commercially available materials for packaging film applications. Other biobased polymers such as PHAs, and particularly P3HB, are also of high interest and are becoming commercially available. At present, PLA-based materials are mainly found in three different markets, namely, the biomedical, the textile and the packaging (mainly food). PLA is transparent and is approved for food contact applications, therefore it is suitable for packaging and is currently used in transparent thermoformed trays and films, mostly for fresh organic products. Several companies are producing biodegradable films including NatureWorks (Ingeo), Novamont (Mater-Bi, Origo-Bi) and BASF (Ecoflex, Ecovio) to be used as organic waste bags, dual-use bags (first for shopping, then for organic waste) or agricultural films. These biopolymeric films have also found applications as shrink films, cling films. Biofoam by Synbra Group is a new PLA-based foam that can replace EPS (polystyrene foam) packaging. In fact the thermal properties are very similar, which has led to an interest in the cooled transport for supplies of medical substances.

Table 4.3 List of commercial grades of biopolymers

Biopolymer	Commercial name	Manufacturer	Application
PLA	Ingeo 2000 series 2003D 2500HP Ingeo 3000 series 3001D 3052D 3100HP 3251D 3260HP Ingeo 4000 series 4032D 4032D (film) 4043D 4044D 4060D Ingeo 6000 series 6060D 6100D 6201D 6202D 6252D 6260D 6302D 6362D 6400D 6752D Ingeo 7000 series 7001D 7032D Ingeo 8000 series 8052D Ingeo 10000 series 10361D Ingeo 3D series 3D850 3D860 4043D	NatureWorks LLC	2300D: fresh food packaging and food service ware applications 2500HP: crystalline sheet for cards, graphic arts, and signage 3001D, 3052D, 3251D: cutlery, cups, plates, cosmetics 3100HP, 3260HP: disposables such as cutlery, cups, plates, cosmetic packaging, and durables such as electronics housings and semidurable building materials 4032D: Signage, gift card, profiles 4032D, 4060D: can be converted into a biaxially oriented film for laminations and other packaging applications 6060D, 6302D: Thermal bonded nonwovens 6100D, 6201D, 6202D: Staple fibre, nonwovens, agricultural woven and nonwoven fabrics, articles for household disposal, textiles, continuous filament 6252D, 6260D: wipes, geotextiles, hospital garments, absorbent pad liners, personal hygiene products, agriculture/horticultural products 6362D: low melt binder fibres/sheath, low melt coatings, dissolvable/sacrificial fibre 6400D: tufted carpet-loop pile, tufted carpet–cut pile, broad loom carpet, carpet mats 6752D: nonwoven (spunlace wipes), multifilament twine 7001D, 7032D: injection stretch blow moulded bottle applications 8052D: expanded foam sheet 10361D: binder for inorganic pigments, dyes, or colorant products for plastics, paints, and coatings or printing applications 3D850, 3D860, 4043D: 3D printer monofilament

Table 4.3 Continued

Biopolymer	Commercial name	Manufacturer	Application
PLA	Lacea H-100 Lacea H-280 Lacea H-400 Lacea H-440	Mitsui Chemicals	Bags, containers, films, nonwovens, packaging
PLA	Lacty 5000 series Lacty 9000 series	Shimadzu Corp	Injection moulding, fibres, films, and sheets
PLA	Terramac TE-2000 Terramac TE-1030 Terramac TE-1070 Terramac TE-7000 Terramac TE-7307 Terramac TE-7300 Terramac TE-8210 Terramac TE-8300 Terramac TP-4000 Terramac TP-4030 Terramac HV-6250H	Unitika Ltd.	TE-2000, TE-1030, TE-1070—injection moulding grade: smaller goods, containers, various plastic parts TE-7000, TE-7307, TE-7300, TE-8210, TE-8300—injection moulding grade: containers, table wear, chassis, etc.; TP-4000, TP-4030, HV-6250H-Extrusion, blow, and foam: containers, bottles, pipes, foam sheet, etc.
PLA/Copolyester	Bio-Flex A4100 CL Bio-Flex F1130 Bio-Flex F1137 Bio-Flex F1138 Bio-Flex F2110 Bio-Flex F2201 CL Bio-Flex F5710 Bio-Flex F6510 Bio-Flex F6513 Bio-Flex F6611 Bio-Flex S5630 Bio-Flex F9533	FKuR Kunststoff GmbH	A 4100 CL: blown film extrusion, flower wrapping, clam shell packaging F1130: air pillow, carrier bag, waste bag F1137, F1138: shopping bags F2110: deep freeze packaging, fruit netting, waste bag F2201 CL: Multilayer films F5710: straws F6510: ball pens, mugs, straws F6513: injection moulding F6611: thermoforming S5630: thermoformed inlay F9533: injection moulding applications
PGA	Kuredux Kuresurge	Kureha	Kuredux: Barrier layer in multilayer PET bottles and/or rigid packaging. Can be extruded or moulded by itself or in combination with PET, PP, PE, PLA Unique material combinations for bottles, sheet, film, and fibres are possible via multilayer coextrusion and polymer blending

Continued

Table 4.3 Continued

Biopolymer	Commercial name	Manufacturer	Application
PLA	PURAPOL L175 PURAPOL LX175 PURAPOL L130 PURAPOL L105 PURAPOL D070	Corbion	L175, LX175: film extrusion, thermoforming or fibre spinning L130: injection moulding and fibre spinning L105: thin wall injection moulding and fibre spinning D070: extrusion, injection moulding
P3HB	Mirel P1003 Mirel P1004 Mirel P4001	Metabolix	P1003, P1004: injection moulded food service and packaging applications including caps and closures, and disposable items such as forks, spoons, knives, tubs, trays, jars, and consumer product applications P4001: cast sheet extrusion designed for a wide range of sheet applications including: gift cards, promotional materials, indoor/outdoor signage, plant pots and plant tags;
P3HB	Biocycle B1000 Biocycle B18BC-1 Biocycle B189C-1 Biocycle B189D-1	PHB Industrial S/A	Films, disposables, medical applications
P3HB	Biomer P300F Biomer P226F Biomer P304 Biomer P209F Biomer P316E	Biomer	Extrusion and injection moulding
PHBV	Enmat Y1000 Enmat Y1000P Enmat Y3000 Enmat Y3000P	TianAn Biologic Materials Co., Ltd.	Injection moulding, extrusion, thermoforming, blown films
Polyhydroxy butyrate-hexanoate (PHBHHx)	Nodax	P&G Chemicals	Packaging, laminates, coatings, nonwoven fibres
PCL	Capa 6000 series	Perstorp	Medical applications: alternative to plaster, orthopedic splints, dental impressions. Blown films, laminates and packaging
PBS	Bionolle 1000 series	Showa Denko	1001MD: Blown film extrusion (compost bags and mulching film) 1903MD: Foam extrusion 1020MD: injection moulding

Table 4.3 **Continued**

Biopolymer	Commercial name	Manufacturer	Application
PBSA	Bionolle 3000 series	Showa Denko	3001MD: Blown film extrusion (compost bags and mulching film) 3020MD: injection moulding
PBAT	Ecoflex F Blend C1200	BASF	Flexible films using a blown film or cast film process. Typical applications are packaging films, agricultural films, and compost bags

BioFoam is also claimed to be resistant to liquid nitrogen and CO_2 granules or dry ice, the latter being often used in the cooled transport chain. In the container field, the most frequently used material for making bottles is PET due to its excellent properties but biopolymers are envisaged as a sustainable alternative even though their full potential has not been fully realized so far. The development of biobased non-biodegradable polymers such as bio-PET is becoming more and more frequent, as supported by several commercial products such as the ones manufactured by Coca-Cola (PlantBottle), Heinz (ketchup), or Dasani (water). There are in the market some examples of bottles made of PLA used to contain water (Clare Spring Water Ltd.), where PLA is obtained from corn or sugar beet. When dealing with the manufacture of PLA beverage bottles compared to PET, several issues and concerns need to be taken into account, such as the significant risk of inadvertent thermal crystallization in PLA, the lower mechanical strength of PLA, lower melting temperature of PLA, and the inferior gas barrier properties. In addition, there is also a well-known problem in PLA bottles for water called ‘paneling,’ that is basically an inward deformation of the bottle sidewall in response to vacuum created within the bottle due to the escape of water vapor through the PLA bottle wall [3]. PHAs are currently mainly applied in films for carrier bags and in applications where biodegradability is crucial (e.g. mulch films). PHAs are relatively expensive and the processing of pure PHAs is still subject to technical limitations. A main disadvantage of PHAs in packaging applications is that they are not transparent but isotropic PHB foils exhibit excellent barrier properties against gas permeation. Another option is the modification of paper as paper/poly(HB-*co*-HV) foils that are completely biodegradable, unlike paper coated with conventional polymer foils. In this regard, Bio-on and the University of Tampere have recently announced that they produced for the very first time tetrapak type containers made of a combination of paper and bioplastic, namely the special grade extrusion coating (EC) of the Minerv PHA biopolymer developed by Bio-on. The Minerv PHA EC industrial research and development project produces polylaminate via extrusion of the molten PHA polymer directly onto the paper or cardboard substrate, with subsequent cooling and consolidation of the plastic film by passing through cooled rollers (an overall process called EC). Another active field for biopolymers is the agricultural one, in particular the agricultural coverings which include mulch films, protective films, silo films, nets, nonwovens, geotextiles (landscape fabrics), mats, and wrapping. Most biodegradable mulch films that are currently available are made from starch but the poor mechanical properties of starch, including its brittleness, make the blending with other polymers or plasticizers necessary. Products currently available on the market include BioTelo and Bio360 mulch films (Dubois Agrinovation) both based on MaterBi (Novamont), Ecovio F mulch film (BASF), Bio-Flex (FKuR Kunststoff GmbH), antiweed sheets (Toyo Heisei Polymer Co., Ltd.) made of PBS (Bionolle 1001, Showa Highpolymer Co., Ltd.).

In the field of medical and pharmaceutical applications, the applications of PHAs appear to be much more realistic, due to the combination of biodegradability, hydrophobicity, and biocompatibility, along with other interesting specific properties [193]. PHB composites with apatite can be used as biodegradable bone fracture fixations or even as bone repair materials [194,195]. Other potential areas include controlled drug release [196–198] and tissue engineering [199,200]. PLA has been widely studied for applications in the medical sector due to its bioresorbability and biocompatible properties in the human body. The main reported examples on medical or biomedical products are fracture fixation devices like screws, sutures, delivery systems [201–206]. Bio-on S.p.A has recently developed a new formulation, called Minerv PHA Bio Cosmetics (type C1), which is designed to make 100% bio-based and biodegradable microbeads suitable for the cosmetics industry currently used as thickeners or stabilisers in lip gloss, creams, shampoo, shower gel, and toothpaste. Bio-on has developed microbeads that are bio-based and biodegradable based on their material Minerv PHA Bio Cosmetics. More importantly, the biopolymer is capable of binding active molecules and antioxidants in a given cosmetic product, such as Coenzyme Q10, vitamins, proteins, and active substances in general, transporting them naturally to parts of the body where cosmetics products are normally applied.

The automotive industry is an important sector of plastic users with about 12–17 wt% of a vehicle made up of plastics. During the last years there has been an increasing use of materials that are more sustainable from a total life cycle perspective, including recycled, renewable, and recyclable materials. For instance the average Ford vehicle uses 20–40 pounds of renewable materials. Currently the most important polymers in automotives are polypropylene, polyamide (nylon), polyurethane, and acrylonitrile-butadiene-styrene. This ‘green strategy’ started in 1930s when Henry Ford used bio-based materials in the production of vehicle parts and components and in 1941 he presented a prototype car that had plastic body panels made of hemp fibres and phenolic resin. The use of biobased materials in vehicle components started again in the 1990s due to Toyota which was the first to develop biopolymers and in 2003 it started selling car accessories made from these materials, employing biopolymers in the cover (cap) for the spare tire in the 2003 model Toyota Raum. Toyota plans to replace 20 wt% of the polymers used in automobiles with biobased polymers. This resurgent interest in biobased materials has also been supported by the introduction of natural fibres as reinforcement of both traditional and biobased polymers. The use of NFCs in the automotive sector has been recently reviewed in Ref. [207] and nowadays they represent a material of choice in the automotive sector, as recently stated by Ford Motor Company in their sustainability report [208]. In fact, cellulose-reinforced plastic, using fibres from sustainably grown trees, has been used to replace the fibreglass in the centre console of the 2014 Lincoln MKX; wheat-straw-reinforced plastic used in the storage bins of the Ford Flex has cut petroleum use and CO_2 emissions. Kenaf, a tropical plant, is used in compression-moulded plastic door parts in the Ford Escape; a material containing 50% flax fibre is used in the armrest of the Ford B-MAX in Europe; rice hulls, a byproduct of rice grains, reinforce the composite plastic in the wire harness of the 2014 Ford F-150; whilst coconut coir, from coconut husks, is used in the trunk mats of the Ford Focus Electric battery electric vehicle. Biobased and biodegradable polymers have problems in fulfilling the high-performance specifications of the automotive industry due to lower physical properties when compared to other general-use polymers. For instance PLA, which is the most advanced biopolymer, is not completely considered suitable for use in automobile parts because of its poor heat and impact resistance whilst other biobased non-biodegradable polymers such as bio-based polyamides, poly(ethylene terephthalate) (bio-PET), and polyurethanes are already successfully used by major automobile manufacturers. A potential solution to the limitations of biopolymers is represented by their use as matrices for NFCs. Biocomposites made of aliphatic polyesters and natural fibres have shown potentials and can be prepared using a lot of different and conventional methods such as melt blending, extrusion, hot pressing, compression moulding, injection moulding, and solution casting, being kenaf, flax, hemp, and jute the most used fibres as reinforcing agents [209]. Several vehicle manufacturers are already using such biocomposites in interior and exterior parts and many others have been patented. For instance, Toyota's Lexus models (e.g. CT200h, ES 300, HS) use biobased polymers reinforced with kenaf and bamboo fibres for interior components such as the luggage compartment, package shelves, and floor mats, the PLA/kenaf and ramie biocomposites used in the translucent roof on Toyota 1/X plug-in hybrid concept vehicle, Mitsubishi Motors Corporation uses a PBS/bamboo composite for headliner/ceiling material. For a detailed review of patents available and commercial applications the interested reader is referred to Niaounakis [210]). Nowadays natural fibres have reached a level of industrial maturity that allows them to be manufactured and commercialized in products completely similar to the ones available for traditional synthetic counterparts such as carbon, glass, and aramid fibres. In this regard an increasing number of companies are marketing semifinished products reinforced with natural fibres to be used in conventional equipments such as extrusion and injection moulding. Most of these injection moldable compounds, which are designed to solve the difficulties inherent in the dispensing and homogenizing of natural fibres in the melted polymer, are based on conventional polymers such as polyolefins, but some industries are already offering compounds based on biopolymers. Some commercial products include: WoodForce, which is an engineered diced pellet based on polyolefin compounds, NCell (by GreenCore Composites Inc.) which is a polypropylene (PP) or polyethylene (PE) matrix reinforced with up to 40% natural cellulosic microfibres (with possibility to be extended also to biobased resins), Bast Fibers LLC which commercializes injection mouldable natural fibre-reinforced plastics (jute, kenaf, flax, and hemp fibres), LINCORE (by Groupe Depestele) which is a compound based on PP, ABS, PVC, and PLA reinforced with flax fibres, NetComposites has developed injection mouldable long fibre thermoplastic (LFT) Flax/PP and Jute/PP pellets made using pultrusion technology and commingled yarns. It is worth mentioning that some companies are already marketing fabrics made of commingled flax and PLA filaments to be used in stamp forming or compression moulding processes, such as Biotex Flax/PLA–Commingled (by Composites Evolution) and LINCORE PLA FF (commingled flax and PLA filaments by Groupe Depestele). These examples of products where the matrix is already incorporated in the reinforcement can definitely suit the existing industrial processing reality that has represented a major barrier to mass-market applications of biocomposites.

4.6 Conclusions and further research areas

Recent increasing economic and ecological concerns are triggering the replacement of traditional polymer materials derived from fossil feedstocks with more environmentally friendly materials from renewable resources, for a wide range of applications. Today, PLA represents the most commercialized biopolymer but some improvements are still necessary as far as its limited toughness, heat resistance, barrier properties, and durability issues are concerned, in order to meet market expectations and broaden its applications. PLA grades commercially available are difficult to be used in applications requiring long-term durability when exposed to elevated temperature and humidity. As a general comment, the reviewed literature highlights PHAs as a very promising class of polymers for a wide range of applications showing, for example better barrier properties compared to the more popular PLA. However, PHAs still suffer from intrinsic brittleness despite the recent progress through the formulation of PHAs with tailored additives and related blends leading to greatly improved mechanical behaviour, as well as suitable processability via conventional extrusion or injection moulding. One of the main limitations in the application of PHAs is the relatively high cost along with the scant world production. These polymers are for instance rather too expensive for the automotive sector that represents one of the key driving forces for developing biopolymers and biocomposites for durable applications. In this regard, a potentially viable strategy, already well exploited, is the use of biopolymers as matrices for composites reinforced with natural fibres. In this case additional technical challenges need to be taken into account, such as the fibre/matrix adhesion, the increased viscosity for high fibre loadings that involves shear heating/degradation, appearance problems (limited colorability and opacity) along with durability issues, flame retardant properties, and emission issues (i.e. fogging, odour) [211]. From the relevant data presented in the chapter, it is evident that current biopolymers are already positioned in the space from commodity thermoplastics up to engineering materials and even though their present properties need to be optimized according to the challenges highlighted, their growth and developments will definitively offer suitable alternatives for petrochemical-based plastics in the next future. However, the success in the production of NFCs based on biopolymer matrices requires a proper understanding of the correlation among the selection of materials, processing methods and the final properties of the composites.

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Forensic identification of bast fibres

5

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5.1 Introduction

The use of natural fibres as the reinforcement in composites is the subject of a number of books [1–8]. The use of bast (stem) fibres in composites is the subject of a number of reviews by the author [9–13] and others (e.g. Refs. [14–17]). Bast fibres are grown in the temperate zone (e.g. flax, hemp, white ramie/China grass) or the tropical zone (e.g. kenaf, green ramie/rhea, roselle).

There is increasing interest in the use of natural fibres as the reinforcement for polymer matrix composites. The most common synthetic reinforcement fibres can be clearly distinguished, within a manufacturing facility or the component, by colour (carbon, aramid, or glass are seen as black, gold, or transparent, respectively) and they are normally supplied as continuous fibre tows. However, plant fibres are generally coloured from white through to brown (except where dyed for clothing/furniture uses) dependent on the species and fibre treatments and are inevitably fibres of finite length. Bast fibres generally have the best mechanical performance amongst the plant fibres, at relatively high cost, and are also inherently discontinuous (albeit often long) fibres. This opens up the opportunity for unscrupulous activity within the supply chain, especially where the high value fibre may be adulterated by partial replacement with lower value fibres. A rigorous sampling method would be required within quality assurance procedures to detect the presence of cheaper substitutes within the raw materials.

Bast fibres find, or are being proposed for, use in numerous composites applications including marine vessels (e.g. *Araldite* which has raced across the Atlantic Ocean), aircraft interiors (including luggage lockers), and automotive applications. The inadvertent use of compromised raw materials could lead to catastrophic failure of the composite below the design stresses. Any consequent litigation could require forensic investigation.

There is an extensive literature on the forensic discrimination of textile fibres, e.g. ASTM D276-12 [18] and Houck [19]. Textile fibres in forensic science are a form of trace evidence which is part of the broad category called physical evidence. Physical evidence can be any material but, in a legal context it refers to materials which may be bought into court and are formally entered as exhibits. The significance of fibres evidence, and other physical evidence, is based upon Locard's Exchange Principle. The Exchange Principle can be summarized as 'whenever two objects come into contact, a transfer of material will occur' [20]. The type of contact which occurs and the

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material transferred are dependent upon the circumstances of the crime. For example fibres may be transferred from a suspect's jumper to a car seat whilst driving. Any fibres evidence found at a major crime scene is initially treated as relevant, as it may have come from the offender and therefore link that person with the scene. Further analysis and comparison of fibres evidence to suspect samples can help to provide information about events leading up to the crime, at the crime scene and events after the crime scene. This is known as reconstruction of the crime scene. Trace evidence has also proven in the past to be very useful for two other reasons. These are their use as an investigative aid and their use as associative evidence. Fibres, amongst other trace evidence types, can provide very good investigative leads as their characterization may provide information about the source of the fibre and the object that it was shed from. As associative evidence, fibres can provide links or relationships between people or between people and objects after suspects have been identified. For example fibres from a balaclava can be found in the head hair of the wearer [21].

To provide this information in a criminal case, information about the fibre evidence is required, such as its microscopical and chemical characteristics. It is also common for forensic analysts to identify the fibre type, which helps inform the analysis methods to be used, the possible source of the fibre and its potential evidential value. Forensic determination of fibre type may also be necessary to detect counterfeiting or in policing fair trade programmes, trade embargos, protection of biodiversity by detection of Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES) and/or for other reasons.

Although there is a large amount of literature surrounding the identification of synthetic fibre types, for example [22–28], there is very little literature directly devoted to the ability to distinguish between the different bast fibres which may find application as reinforcement fibres within the composites sector. The principal sources include Menzi and Bigler [29], Marshall [30], Greaves and Saville [31], and Robertson and Grieve [32], all published in the previous century. The latter authors present data for typical dimensions and chemical composition of the key bast fibres (Table 5.1) but the data does not indicate growth stage and plant maturity.

Gordon [34] states that cotton fibres, after scouring and bleaching, contain nearly 99% cellulose, whereas the bast fibres (specifically those in Table 5.1) are typically three-quarters cellulose, wood fibres have 40%–55% cellulose and other plant species and parts have even lower cellulose contents. As the main chemical entity in bast (and other vegetable) fibres is cellulose; techniques that would be used to distinguish between synthetic fibre types are not useful for these natural types [31]. In forensic examinations of these fibres, the main forms of analysis method are microscopy based; these are discussed later in this chapter.

Natural fibres from a single plant species can be considerably more variable than synthetic fibre types, especially given the range of growth stages, processing, and consequent features (e.g. dimensions, thermal, and mechanical properties). In forensic analysis, this variation, along with limited characteristics to identify, means that natural fibres are generally less evidentially useful than synthetic fibres. This is due to the possibility of a target fibre having differing characteristics to a control fibre, even if it has come from the same source. To reach a conclusion, great knowledge of

Table 5.1 Characteristics of dry natural unprocessed bast fibres

Fibre	Ultimates (dia. × length)	Cellulose	Hemi-cellulose	Pectin	Lignin	Wax, etc.
Flax[b]	15–20 μm × 3 mm	75%	15%	2.5%	2%	1-1.5%
Flax[a]	Length: 1.6–24 mm	~	~	~	~	~
Hemp[b]	15–50 μm × 0.5–5.0 mm	75%	17%	1%	3.6%	2.8%
Hemp[a]	Length: 1.0–34 mm					
Jute[b]	15–25 μm × 1–6 mm	71%	13%	0.2%	13%	2.8%
Jute[a]	Length: 0.6–5.3 mm	~	~	~	~	~
Kenaf[c] (raw)	~	63.5 ± 0.5%	17.6 ± 1.4%	~	12.7 ± 1.5%	6.2 ± 1.8%
Kenaf[c] (bleached)	~	92.0 ± 1.4%	5.2 ± 0.6%	~	0.5 ± 0.4%	0.5 ± 0.3%
Ramie[b]	40–75 μm × 2.5–3 mm	75%	16%	2%	1%	6%
Ramie[a]	13.0–82.7 mm	~	~	~	~	~

After Catling and Grayson[a], 1982 via Robertson and Grieve[b] [32] or Jonoobi et al.[c] [33]

the breadth of this variation is required; something which is generally unknown in natural fibre sources and as such leads to weak evidence in court. Due to the variation in the morphological and mechanical properties of natural fibres, the focus in forensic analysis is regularly placed upon the presence and quantification of any colourants in the natural fibre [35], something which may not be a priority when testing fibres in composite manufacturing.

5.2 Analysis methods

5.2.1 The forensic approach to analysing fibres

Analysis of textile fibres has been carried out by manufacturers for many years to allow the desired qualities of fibres to be identified and monitored. Characteristics such as fibre extensibility, softness, density, shrinkage, and affinity for dyes are tested [36]. Though these properties are important in the textile industry, they are not often analysed when fibres are characterized for forensic purposes.

Currently, forensic examination of fibres is mainly a comparative analysis between control fibres (known fibres) and target fibres (unknown fibres, a.k.a. questioned fibres), where controls may be taken from a victim or suspect of a crime and target fibres are retrieved from a scene(s) of crime. This form of analysis requires layers of information (from simple observations to detailed composition) to be obtained about both the target and control fibres so as to make a conclusion about whether these fibres have originated from the same source. Alternatively, when ‘gathering intelligence information’, a fibre analyst may be requested to identify the source or possible end-use of the fibre which has been collected as evidence [32]. For example in the Atlanta child murders, it was helpful to establish which manufacturer produced a green trilobal carpet fibre found on many of the bodies [37,38]. In fibre comparisons and in intelligence gathering, fibre *type* is commonly determined and can form the foundation upon which screening for target fibres is carried out, for example cotton fibres are easily identifiable from their morphology and can be searched for or screened out from bulk samples quickly. In addition to fibre type, other observations are crucial for forensic comparisons, including; colour quantification (commonly using microspectrophotometry), morphological features (e.g. thickness (μm), cross-sectional shape, presence or absence of inclusions), optical properties (e.g. birefringence, sign of elongation, and dichroism), any fluorescent properties, and chemical composition (using Fourier Transform Infrared Spectroscopy, Raman Spectroscopy, and/or Pyrolysis-Gas Chromatography). The analysis methods used in forensic casework is dependent upon the fibre type (as synthetic fibre types generally lend themselves to greater characterization than natural fibres) and whether intelligence information is sought about the fibres, as generally greater information is required to identify the manufacturer of a sample. The gathering of intelligence information from fibres is generally employed in major crimes when there is no control sample for comparison and as much information as possible is sought about the fibres in order to try and identify a potential source and therefore suspect. Cost effectiveness of the analysis methods is a key consideration in forensic science as it is in the composite manufacturing industry. The budget to be spent on a case depends on many factors, including whether the crime is a volume crime (e.g. theft, or in composites manufacturing supply of adulterated material) or a major crime (e.g. murder). Due to the reduction in Police budgets over the years, greater focus has been placed upon creating cost-effective forensic strategies and reducing the cost of existing techniques and methods. This is particularly true for fibres investigations, where the costs of analysis is high and in the perceived value low compared to other evidence types. Work is ongoing in forensic fibres work to decrease cost by speeding up sampling and screening processes [39] and to increase the evidential value of fibres evidence by creating better discriminating techniques and generating large reference data sets for sample comparisons.

Commonly, the forensic identification of natural fibres relies upon microscopy techniques and the use of reference collections which contain authentic samples which can be compared to unknowns. Preliminary observations may be conducted upon the sample under a low-powered microscope to determine the fibres colour and texture, this is often conducted on the fibre bundle (i.e. a collection of ultimates along with other cells/components that were part of the stem, sometimes called the technical fibre) [32]. A series of tests may be applied to the technical fibre such as scraping the fibre (to observe the epidermal tissue and the calcium oxalate crystals), ashing (an alternative to scraping), preparing cross-sections, and testing for lignification using phloroglucinol. In addition to these tests, observations of the individual fibre ultimates under a high-powered microscope may be carried out, including the average length and width of the ultimates, the presence of transverse lines (a.k.a. cross marks) and parallel striations, the presence, shape, number and average distance between any nodes/dislocations, the Herzog test and the morphology and thickness of the lumen compared to the overall thickness of the ultimate [31,32].

The process for the analysis of natural fibres in forensic investigations currently differs to the approaches used by the composite industry in the following ways:

1. Focus is placed upon the quantification of any colourants in forensic analysis, not the fibres affinity to dyes, as this characteristic has the potential to better discriminate between natural textile fibres of the same type.
2. Characteristics that are fundamentally stable to the environment are chosen as any properties that could readily change between the time of deposition at a crime scene and the apprehension of a suspect would not enable any links to be made.
3. Tensile strength and related characteristics are not analysed in forensic science as these may not be consistent to a particular source, unless a fabric was being analysed for textile damage which may have occurred during an incident. In this latter situation, the tensile strength of the fabric may be investigated within the context of a case, e.g. the force required to tear a fabric during an assault.
4. Initial techniques in forensic analysis should be quick and effective in screening for relevant target samples so as to reduce the overall cost of analysis. Subsequent more detailed analysis techniques may be more expensive in terms of time and equipment but would be employed on fewer samples.

5.2.1.1 Sampling of textiles

Sampling for fibres in forensic investigations includes two areas; obtaining target fibres which have been transferred to surfaces of interest, e.g. the outer surface of a victim's clothes and gathering control samples from textile items for comparison. The latter of these is the most in line with testing of samples for the composite industry with the following ideas being an important consideration in both forensic science and industrial testing:

1. Obtaining a representative sample so as to account for any variation seen in the textile. For the biocomposite industry this is to identify the uniformity of the sample in terms of its mechanical properties and surface characteristics.
2. Using a retrieval method that does not damage or contaminate the fibres.
3. Using a robust labelling system so as to prevent sample mix-up.
4. Sampling and storing samples in an appropriate environment; although fibres are relatively stable, fibrous materials can be sensitive to temperature and humidity so testing should therefore normally be undertaken under appropriate internationally agreed standard conditions (e.g. 20 ± 2°C and 65 ± 2% relative humidity).
5. Preparing samples appropriate for the technique being used; as much of forensic testing of bast fibres involves microscopy techniques, this involves creating microscope slides using an appropriate mounting medium.

Booth [40] and Saville [41] present a deeper discussion of issues relating to sampling of textile materials.

5.2.1.2 *Optical techniques*

Microscopy within forensic science has almost limitless applications. This is due to the microscope's ability to detect, resolve, and image very small items of evidence. This ability is very important when analysing trace evidence such as textile fibres [42]. It has been noted on numerous occasions that microscopy is the essential core for fibre identification and comparisons and is normally the first choice for fibre identification [32,42–47]. Microscopy is dominant in this field primarily because it:

1. is non-destructive,
2. allows visualization of fibres due to fibres small size,
3. is a relatively quick means of sample analysis (important for timeliness of analysis, case throughput, and if repeat measurements are needed) [45],
4. is inexpensive after the initial outlay (very few consumables),
5. has the ability to identify microscopic characteristics and polymer type (for synthetic fibres),
6. allows point-to-point, side-by-side microscopic comparison which is the most discriminating method of determining if two or more fibres are consistent with originating from the same source,
7. has the ability to distinguish between fibres of the same type but from different sources, for example different manufacturers.

The popularity of microscopy techniques in forensic fibre analysis was highlighted in Wiggins review of fibre examination [43]. As previously mentioned, brightfield and polarized light microscopy are used by the majority of US and European laboratories but also fluorescence and comparison microscopy are routinely employed. Microscopy is the only area where ASTM D276-12 [18] offers comments specific to natural fibres: Section 4.3 'For plant (native) cellulose and animal hair fibers microscopical examination of longitudinal and cross-sections is used to distinguish species' and Section 9.1 'Examine and observe fibre characteristics as directed in the AATCC Test method 20'.

There is an arsenal of microscopes available for fibre analysts. Table 5.2 outlines the different types available and their main uses.

Table 5.2 Microscope types and the uses for fibre examinations.

Microscope type	Uses	Comments
Stereomicroscope	Primarily used to search, recover, and manipulate individual fibres from tapings. Also used for the examination of textile damage and textile construction. It is not suitable for accurate identification of fibre type	Usually low power, for example a typical range of magnification is between ×0.5 and ×10. Stereomicroscopes should be equipped for observation with both transmitted and reflected light [46]
Polarizing Light Microscope	Arguably, the most useful and versatile of all the microscope types available to fibre analysts. This microscope allows the same observations as a compound microscope but also permits observations and measurements using plane polarized light and between crossed polars (the arrangement of two polars in sequence so that the vibration directions are at 90 degrees to each other). The polarized light microscope allows qualitative information such as sign of elongation to be gained and also quantitative information such as birefringence	Although this information can lead to preliminary identification of the generic type of man-made fibres, it must be noted that polarizing microscopy cannot be used to identify exact chemical composition
Comparison Microscope	Provides a side-by-side microscopic comparison between multiple fibres in a single field of view	A discriminating method for determining if two or more fibres are consistent with originating from the same source
Fluorescence Microscope	Used to search for and observe fluorescence in fibres originating from some dyes, optical brighteners, or contaminants	The microscope is set up in incident light with a selection of filters that cover the excitation range of ultraviolet through violet, blue, and green [46]
Hot-Stage Microscope	Melting point determination of fibres [46]	Technically an accessory which fits upon the stage of a light microscope. The hot stage should reach to above 300°C and should allow the user to increase the temperature by 4°C min^{-1} or less [32]

Continued

Table 5.2 Continued

Microscope type	Uses	Comments
Scanning Electron Microscope (SEM)	As an imaging tool, it provides high resolution, three-dimensional images at very high magnifications, particularly useful for visualizing fibre surface characteristics. SEM can also yield additional physical and analytical information	SEM utilizes high-energy electrons to scan the surface of the fibre. Images of surface topography are either derived from backscattered electrons or secondary electrons
Interference Microscopy	To determine the refractive indices of fibres and combined with a Standort diagram can determine sign of elongation	This utilizes an interferometer to split polarized light. An interferogram is produced of the recombined light beams to enable the refractive indices of the fibre to be determined. By plotting the refractive indices on a Standort diagram the sign of elongation can be determined [24]

5.2.1.3 Microscopical observations of bast fibres

Natural fibres can be distinguished from each other by observing the fibres' microscopical morphological characteristics, e.g. cross-sectional shape, length of ultimates, presence of nodes, and thickness of lumen [32]. In addition to these morphological features, the optical properties of natural fibres may be useful for identifying fibre type.

By definition, fibres have a high-aspect ratio and it is appropriate to examine the fibre both longitudinally (side on) and transversely (cross-section). For longitudinal examination, the fibre may be mounted between a glass slide and a cover slip with a few drops of mounting liquid to enhance optical contrast. Cook and Norton [48] have evaluated a wide range of media against ideal properties but analysts still must be aware that interaction between the fibre and the mounting liquid may result in dimensional changes. Appendices 5.1 and 5.2 summarize key features which might be observed under the microscope. A comprehensive selection of bast fibre plan view and sections is presented by Kicińksa-Jakubowska et al. [49], including eight different bast fibres (flax, hemp, kenak, jute, ramie, isora, nettle, and Spanish broom).

Figs. 5.1–5.3 show jute, flax, and hemp fibres, respectively, in DPX mounting medium (RI = 1.52) under plane polarized light taken using a Nikon Optiphot2 polarizing light microscope at ×400 magnification. At this magnification it is possible to see the internal features of the fibres and key characteristics such as cross marks and striations. Length of ultimates can be particularly useful for differentiating between certain bast fibre types, for example flax and ramie ultimates can be very long (can reach 25 mm in length) [32].

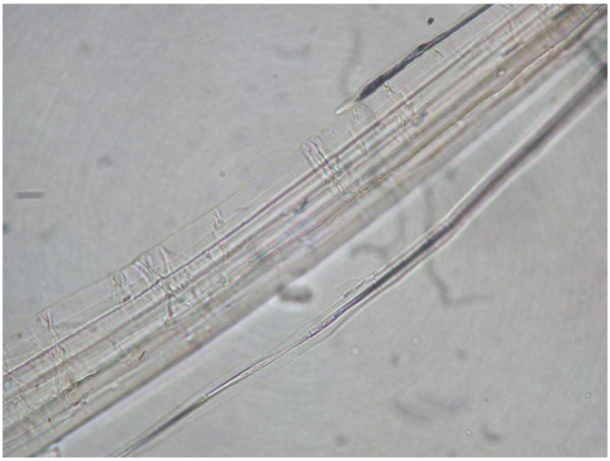

Fig. 5.1 Jute fibre at showing cross marks and longitudinal striations (image width ~144 μm).

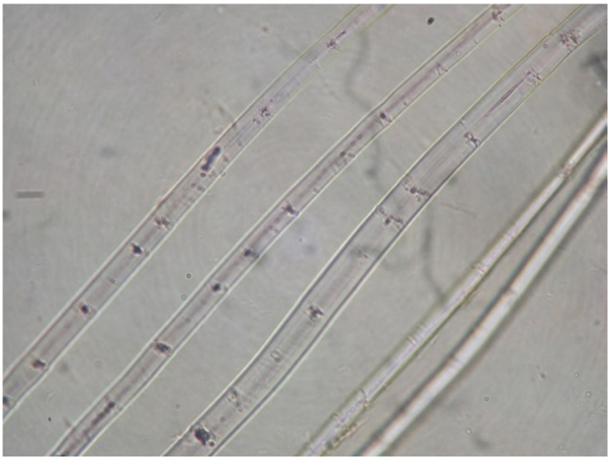

Fig. 5.2 Flax fibre ultimates (image width ~144 μm).

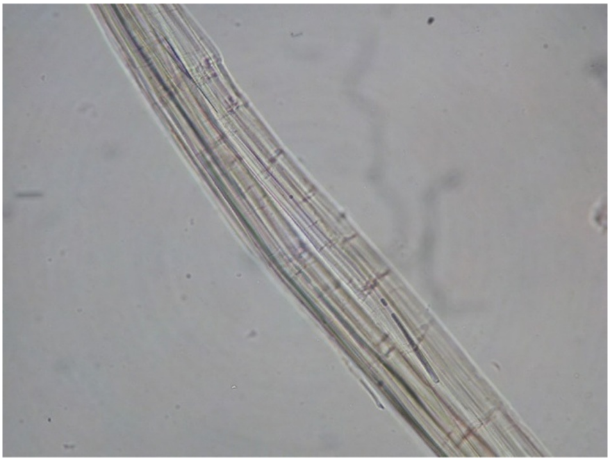

Fig. 5.3 Hemp technical fibre bundle (image width ~144 μm).

The cross-sectional shape can be a simple but effective characteristic to observe to distinguish bast fibres from leaf fibre substitutes as bast fibres have a polygonal shape whilst leaf fibres are more round in appearance [32]. Goodway [50] has suggested that 'optical sectioning' can be a quicker and much less tedious procedure than cutting cross-sections for *initial* screening. This is achieved by focussing on the fibre at 'fairly high powers' (i.e. high magnification) whilst moving the focal plane slowly through the fibre. Although the approximate cross-section can be identified by viewing the fibre longitudinally, it is more accurate to make a transverse cross-sectional cut and view the actual cross-section mounted in a section under a microscope [32,51,52]. There are a variety of different methods for preparing a fibre for cross-sectional determination depending upon the number of fibres and the experience of the analyst. The classic method for creating sections is utilization of a microtome. Two other common methods utilized by fibre analysts to create fibre sections are the use of polyethylene film 'sandwich' technique developed by Palenik and Fitzsimons [52] or the Joliff Plate method developed by Joliff [52,53].

The anisotropic nature of fibres with oriented molecules results in birefringence (the longitudinal $\eta_{\|}$ and transverse $\eta_{\perp}$ refractive indices differ) which is defined as $\Delta\eta = \eta_{\|} - \eta_{\perp}$. When the fibre is viewed at 45 degrees to the cross-hairs, under a polarizing light microscope, the intensity of the image will change as the analyser filter is rotated, exhibiting colours within the fibres. The specific colours (called interference colours) will differ between fibre types, and represent the retardation (also called Optical Path Difference (OPD)) of the fibre. The OPD along with the thickness of the fibres can be used to determine the birefringence. Fig. 5.4 shows flax fibre ultimates under cross-polar conditions exhibiting interference colours.

A common forensic science approach for measuring the OPD (and therefore birefringence) is the use of compensators, e.g. quartz wedge or tilting compensator. Compensators consist of thin sections of birefringent minerals such as quartz, gypsum, mica, and calcite. Compensators have controlled thicknesses and optical orientation

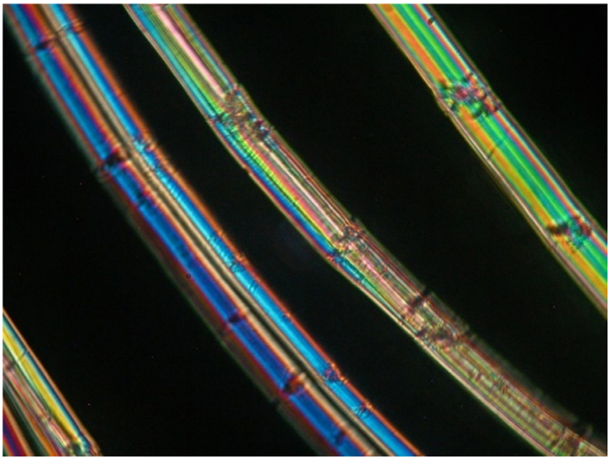

Fig. 5.4 Flax fibre ultimates under cross-polars (image width ~144 μm).

Table 5.3 **Refractive indices and birefringence of bast fibres**

Fibre	η longitudinal	η transverse	Birefringence	Source
Flax	1.58–1.60	1.52–1.53	<0.06	[56]
Hemp	1.58–1.59	1.53–1.54	<0.05	[57]
Ramie	1.59–1.60	1.53–1.54	<0.07	[58]

so as to provide known values of retardation and direction of high and low refractive indices [54]. Each compensator type may be utilized for specific fibre types depending on its range of retardation. The Berek compensator, which is a tilting compensator, is utilized regularly for fibres with retardation values between 0 and 20λ, where λ is wavelength [54,55].

In addition to compensators, the immersion method can be utilized to identify the longitudinal $\eta_{\|}$ and transverse $\eta_{\perp}$ refractive indices separately. If there is a perfect match between the refractive indices of the fibre and the mounting liquid then the sample will become invisible, whilst the definition and contrast will increase with the difference in these refractive indices (Table 5.3). Use of a range of liquids will permit the identification of the refractive index of the fibre (the closest match may be taken as that of the fibre). For better precision, interpolation can be used or the Becke test in which a bright line appears as the objective lens is moved away from the subject causing the bright Becke line in the out-of-focus image to move towards the medium with the higher refractive index. Accuracy can be improved using monochromatic light and an interference microscope. However, immersion refractometry is rarely used in forensic science to prevent cross-contamination and evidence loss. This method is also very time-consuming which increases the cost of analysis; therefore, compensators are the preferred method and could be employed within the biocomposite industry more readily.

Herzog [59] and Luniak [60] noted that flax and hemp fibres could be differentiated by their opposite behaviour in polarized light under crossed polars when a selenite Red I plate was inserted in the 45 degrees position. Flax fibres show addition colours when parallel to the plane of the polarizer and subtraction colours when normal to the plane of the polarizer, whilst the hemp fibres have the opposite response and the differences may be less pronounced. The use of known comparison samples is recommended with emphasis on dimensions, shape, colour, and texture. Every fibres analyst must have access to a comprehensive reference collection in order to make more confident identifications. The use of a comparison microscope that allows side-by-side analysis of reference samples and unknowns is an effective method. A current reference collection, available to analysts from Microtrace LLC, is the Arbidar collection of natural fibres, fur and hair which contains 145 different samples.

The helical orientation of the cellulose molecules in plant cell walls is specific to the species. In flax, nettle and ramie, the fibrillar orientation corresponds to S-twist, whilst in hemp and jute the orientation corresponds to Z-twist as illustrated in Fig. 5.5 [61]. Bergfjord and Holst [61] have presented a simple procedure based on measurement of the fibrillar orientation of textile bast fibres using polarized light microscopy and on detection of the presence of calcium oxalate CaC_2O_4 crystals (COX). Star-like

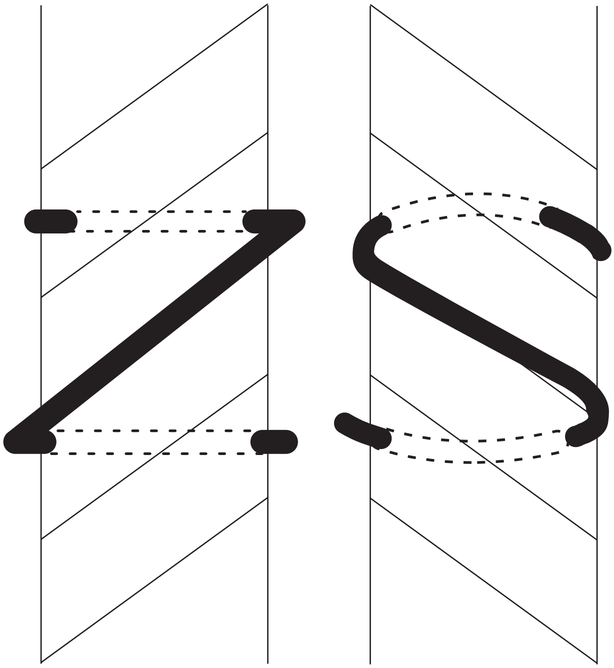

Fig. 5.5 A diagram of Z-twist (*left*) and S-twist (*right*).
After Bergfjord C, Holst B. A procedure for identifying textile bast fibres using microscopy: flax, nettle/ramie, hemp and jute. Ultramicroscopy 2010, 110(9), 1192–1197, doi:10.1016/j.ultramic.2010.04.014.

cluster COX with many facets protruding from a small central volume (named druses by botanists) occur in nettle, ramie, hemp, and jute with single COX in hemp and jute but no COX in flax. The retting process will significantly reduce the presence of oxalate crystals as they are found in the associated tissue around the fibre. Single crystals have anisotropic optical properties and can be identified under polarizing light whilst cluster crystals will be visible independent of orientation. The crystal test is complemented by focussing the polarized light into the upper fibre surface to determine the fibrillar orientation (Table 5.4).

Dai and Fan [63] treated hemp fibres with copper nitrate or cobalt chloride solutions in an ultrasonic bath at 80°C. Optical photomicrographs and image analysis were used to measure the microfibril angle (MFA). It was found that the S1 layer had an S-helical orientation with an average MFA of 80.35 degrees and the S2 layer had a Z-helical orientation with average MFA of 23–30 degrees (outer part) and 2.65 degrees (inner layer).

Müller et al. [64,65] used X-ray micro-diffraction to distinguish between archaeological samples and claimed to unambiguously identify cotton, flax, ramie, and wool. However, the technique uses a synchrotron and hence may not be cost-effective for numerous samples.

Table 5.4 Identifying features for bast fibres

Fibre	Fibrillar orientation	Oxalate crystals[a]	Features[b]
Flax	S-twist[a] (clockwise[b])	Absent	Polygonal ultimates, thick walls, small lumina, dark dislocations normal to fibre axis
Hemp	Z-twist[a] (counter-clockwise[b])	Cluster (and rarely single)	Wider lumen and fewer nodes than flax, cross-section rounder and more flattened than jute
Jute	Z-twist[a] (counter-clockwise[b])	Single (and rarely cluster)	Polygonal ultimates, medium-sized lumina, angular X- or Y-shaped dislocations
Nettle	S-twist[a]	Cluster	
Ramie	S-twist[a]	Cluster	Very long and very wide ultimates, thick walls, flattened cross-section, frequent short dislocations and longer transverse striations, radial cracks in cross-section

After Bergfjord and Holst[a] [61] or Houck Ch.2[b] [62].
NB: absence of crystals does not imply that the fibre is flax.

Scanning electron microscopy (SEM) is used in forensic fibre investigations when the surface of the fibre needs to be viewed. The biggest advantage of SEM is its ability to produce high-resolution images enabling analysts to identify surface features that otherwise would not be seen under normal microscopy conditions. The excellent depth of field has allowed textile scientists to identify fibre fatigue, abrasion, and deterioration caused by mechanical damage for many years; this is also particularly useful for forensic scientists examining textile damage [66]. Samples are bombarded with a fine beam of electrons and an image created from the resultant radiation; these may be secondary electron emission or backscattered electrons [31]. Fibres are generally non-conducting which can cause a build-up of charge and create a distorted image. Samples are often coated with a conductive coating to prevent charging but this coating is permanent thus meaning that SEM should be completed after light microscopy. Figs. 5.6–5.8 show SEM micrographs of the same fibres seen in Figs. 5.1–5.3, namely jute, flax, and hemp at between ×500 and ×750 magnification.

Using microscopy techniques is a fundamental part of the forensic analysis of fibres and by utilizing a range of microscopical techniques and characteristics it is possible to identify a large range of bast fibres. Practically, light microscopy is the easiest method to introduce at industrial levels due to the possibility for fast screening and relatively low-cost equipment. SEM would be a very useful technique in composite manufacturing but access to, and the expense of, the equipment combined with time consuming sample preparation mean that this is likely not to be used on an industrial scale.

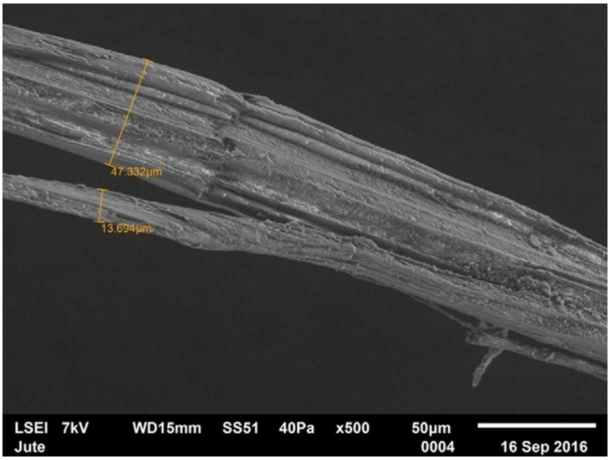

Fig. 5.6 SEM micrograph of jute fibre showing thickness measurements.

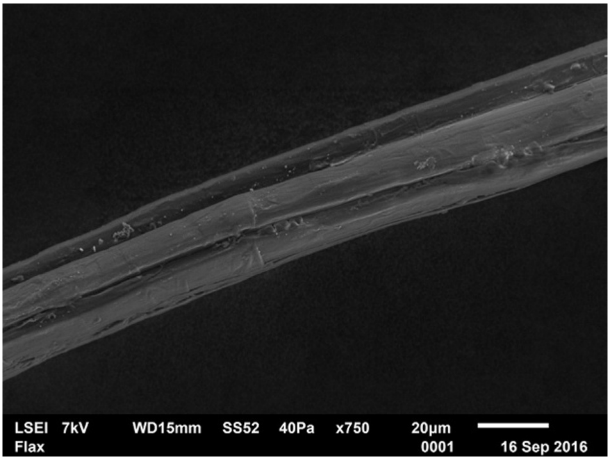

Fig. 5.7 SEM micrograph of flax fibre.

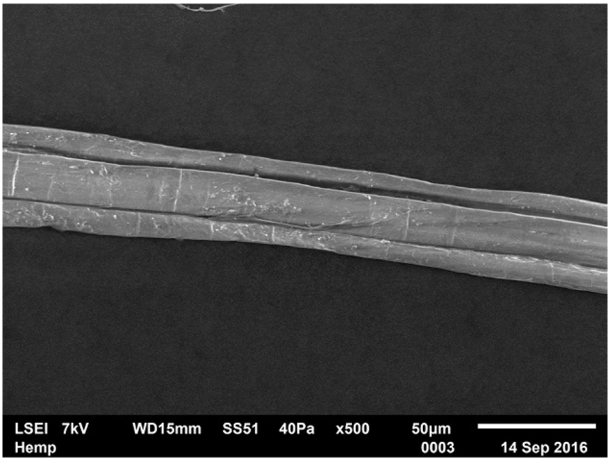

Fig. 5.8 SEM micrograph of hemp fibre.

5.2.1.4 Chemical tests

Solubility tests will not distinguish chemically similar materials such as cellulosic plant fibres [67], however, a wide range of chemical tests do exist for the identification of undamaged plant fibres [67]:

- Cuprammonium hydroxide (Schweitzer's reagent) causes swelling and dissolution of cellulose: the pattern and rate of this process can characterize different species.
- Phloroglucinol: selectively stains lignin.
- Zinc chloroiodide (Herzberg reagent): highlights structures within cell walls and differentially stains cellulose, lignified cellulose and lignin.

And for damaged fibres [67]:

- Congo red: dyes the inner fibre more strongly than the exterior indicating swollen or slip cell walls.
- Fehling's solution: precipitates red copper I oxide in regions of acid damage.
- Turnbull blue: dark blue stains in regions of acidic or oxidative damage.

The most commonly used chemical test in forensic examinations is the phloroglucinol test which can be added onto cross-section cuts and observed for a colour change which ranges from pink to deep red. No colour change indicates fibres that are practically pure cellulose, e.g. hemp and flax, a bright red colour for jute fibres and pink for semi-lignified fibres, such as manila [32]. Marshall [30] proposed a test protocol for the identification of flax, hemp, jute, or ramie fibres using multiple chemical tests, which is summarized in Appendix 5.3.

Chemical tests are quick and easy to carry out and are therefore beneficial for screening samples on a large scale. These tests are not able to identify bast fibres solely by themselves and therefore should be used in conjunction with other tests, such as microscopy techniques. The nature of the tests subsequently changes the colour of the fibres and/or causes damage to the fibres; due to this these tests should be used after initial microscopical characterization and thought should be given as to the effect of these tests upon other analytical techniques. In addition to this, some of the chemicals, e.g. the phloroglucinol reagent requires an equal quantity of concentrated hydrochloric acid, which needs specialist storage and handling and therefore may not be suitable for some industrial environments.

5.2.1.5 Physical/mechanical tests

If individual fibre samples are wetted with distilled water, then a clamped sample will show a specific rotational twist on drying [67–69]. The sample is normally oriented with the fibre principal axis in the horizontal plane and viewed from above. However as with viewing a transparent clockface from the front (obverse) or back (reverse), the motion may be described as clockwise or counter-clockwise, respectively. There is general (but not universal) agreement in the literature that flax and ramie turn in one direction whilst hemp and jute have the opposite rotation. Throughout this chapter, all reported responses have been referenced to the counter-clockwise rotation reported by, e.g. Hock [68] and Marshall [30] for flax and ramie, rather than the rarer clockwise response reported on occasions. Wiener et al. [70] used an 80°C hot-plate with the sample behind an air convection current screen and a specimen protrusion length of ~20 mm (10 mm minimum and 30 mm maximum).

5.2.1.6 Thermal techniques

The interaction of heat with fibres will result in changes due to glass transition, desorption of water, crystallization, fusion (melting), chemical reactions, and irreversible decomposition. Differential thermal analysis (DTA) monitors changes in temperature of a sample and an inert reference material to determine the temperatures at which changes occur but can only provide limited quantitative information. Differential scanning calorimetry (DSC) uses a similar configuration to monitor the relative heat flows and can provide the magnitude of enthalpy and entropy changes at each transition.

Thermogravimetric analysis (TGA) monitors the sample mass on a thermal balance during a linear temperature ramp. Changes in the recorded mass may indicate drying, loss of volatiles, chemical reactions, or chemical degradation. For control hemp fibres, Özmen [71] reported three regions of thermal decomposition: I (25–250°C, related to the release of moisture), II (150–420°C, related to the degradation of cellulose, hemicelluloses, and lignin), and III (425–670°C, related to degradation of the char) with complete decomposition of the fibre at 670°C. There was a clear shift in the active temperature of decomposition from 376°C for control samples to 392°C after acetylation. Acetylation was also found to reduce char formation from 33% of total weight for the control fibres to 14%–22% dependent on the modifying agent. Kaith et al. [72] found that grafting flax fibres with MMA reduced the thermal stability of the fibre (Table 5.5).

Singha and coworkers [73–78] have reported combined TGA/differential thermal analysis (DTA) and derivative thermogravimetry (DTG) measurements on buel (*Grewia optiva*: GO) and roselle (*Hibiscus sabdariffa*: HS) fibres (Table 5.6). The differences between untreated GO and HS fibres are minimal, but changes between untreated and silane-treated fibres were larger.

A bomb-calorimeter measures the heat created by a sample burned in an oxygen atmosphere in a closed vessel under controlled conditions. A similar technique is pyrolysis gas chromatography (Pyr-GC) where flash pyrolysis of a fibre in an inert atmosphere produces volatile components that can be analysed by gas chromatography. Smith [79] has reported preliminary calorific values for natural fibres measured in a Parr 1356 Bomb calorimeter (Table 5.7).

Thermal analysis of fibres is not a common approach used in forensic investigations due to the destructive nature of the test and the overlap in thermal characteristics, e.g. melting points of fibres. Pyrolysis gas chromatography holds additional benefits for synthetic fibres as it has the ability to effectively classify fibres to subtypes, but this is not true for bast fibres. In order for thermal analysis to be more reliably used in bast fibre identification, a comprehensive collection of thermal data of true bast fibres and other fibres, commonly used as inexpensive alternatives, is required. This would allow the full extent of variation in thermal characteristics between bast fibres to be known.

Table 5.5 Thermal behaviour of ungrafted (UG) or methyl methacrylate-grafted (MMAG) mercerized flax fibres (FF) [72]

Material	Thermogravimetric data					DTA peaks (°C)	
	Temp (°C)	Weight loss (%)	Residue (%)	IDT (°C)	FDT (°C)	Exo	Endo
UG-FF	307.2–345.4	31.5	29.17	307.2	559.3	309.5	360
-ditto-	345.4–559.3	39.33				465.6	
MMAG-FF	277–331.6	59.5	3.83	277	446.6	346.8	370
-ditto-	331.6–446.6	36.67				415.1	

Table 5.6 Combined TGA/DTA and DTG measurements on buel (GO: *Grewia optiva*) and roselle (HS: *Hibiscus sabdariffa*) fibres

Parameter	Technique	Units	GO [73–76] untreated	GO [76] silane	HS [77,78] untreated	HS [78] silane
Initial decomposition temperature (IDT)	TGA/DTA	°C	200	199	199	197
Weight loss at IDT	TGA/DTA	%	7.25	9.1	7.65	8.3
Final decomposition temperature (FDT)	TGA/DTA	°C	501	510	500	512
Weight loss at FDT	TGA/DTA	%	87.44	60.57	85.71	55.50
Residue wt. at FDT	TGA/DTA	%	12.66 (sic)	39.43	14.29	44.50
Exothermic peak 1	TGA/DTA	µV	−2.0 at 61°C	~	−0.9 at 63°C	−0.7 at 51°C
Exothermic peak 1	DTG	µg/min	98 at 61°C	~	98 at 56°C	62.3 at 49°C
Exothermic peak 2	DTG	µg/min	237 at 293°C	~	237 at 293°C	342.8 at 304°C
Exothermic peak 3	DTG	µg/min	1126 at 355°C	~	1126 at 355°C	
Exothermic peak 4	TGA/DTA	µV	−3.3 at 361°C	~	−1.5 at 361°C	

Table 5.7 **Calorific values for various natural fibres obtained using a bomb calorimeter**

	Flax (Top-F)	Hemp (Strick H)	Jute (Wingham)	Jute (Virk)
Calorific value (GJ/tonne)	16.36 ± 0.05	17.20 ± 0.24	17.46 ± 0.14	17.75 ± 0.17

5.2.1.7 Chemical spectroscopy

Infrared (IR) spectroscopy interrogates the stretching and bending vibrations in adjacent atoms of a polar molecule. The transition from near-(NIR) to mid-(MIR) IR occurs at 2000 nm (4000 cm^{-1} wave number: wavelength (nm) = 10^7/wavenumber (cm^{-1})). Infrared microscopes may operate in either transmission or reflectance modes: IR normally penetrates between 6 and 15 μm dependent upon the refractive index of the material [80]. Fourier transform IR (FTIR) spectroscopy simultaneously collects a wide spectral range of data with high resolution, whereas the older dispersive IR instruments scan through a range of wavelengths over a longer time period.

Special techniques in IR spectroscopy include attenuated total reflection (ATR), diffuse reflectance IR FT-spectroscopy (DRIFT), and photo-acoustic spectroscopy (PAS) [80]. In ATR, the infrared beam enters an optically dense crystal with a high-refractive index. At a certain angle, the internal reflectance creates an evanescent wave that extends into the sample close to the surface of the crystal. ATR requires pressure to be applied to achieve close contact between the crystal and the sample. The evanescent wave interrogates only a few micrometres (0.5–5.0 μm) into the sample. ATR can be an excellent identification technique for many fibres revealing useful differences between the bulk and the surface material.

In DRIFT, the infrared radiation reflected from roughened surfaces is collected and analysed. The incident radiation is divided between regular reflection (specular reflection), diffuse scattering, and penetration into the sample. The Kubelka–Munk function, developed for radiation transport in scattering media, is used to correct for peak shifts so that absorbances remain true.

The photoacoustic technique (PAS) can yield excellent quality FTIR spectra from highly absorbent samples, e.g. dark coloured fibres [80]. The PAS spectrum has different physical characteristics to an optical technique with a tendency to give higher intensity at the lower frequencies (1600–400 cm^{-1}). PAS does require an in-house library of authenticated samples for online spectral searching and comparison.

Raman spectroscopy is a complementary technique that considers the change in bond polarizability during bond vibration and the effect on inelastic scattering of visible light. Fan et al. [81] and Kavkler and Demšar [82] have reviewed the use of spectroscopy for the determination of the structure, morphology, and chemical composition of natural fibres.

Appendix 5.4 presents pairs (different positions from the same batch of fibres) of typical IR spectra for hemp, ramie, and two separate batches of jute. Differences between these samples include:

- split peaks at 2917/2849 (hemp) which are less pronounced in the other fibres,
- no peak at 1731 in ramie (present in the other three fibres),
- a single peak at 1636/1638 in ramie/hemp but a double peak at 1638/1594 in both jute fibres,
- four clear peaks at 1423/1364/1316/1237 in jute but not in hemp or ramie.

The fibres had minimal information on pre-delivery processing (otherwise considered as raw fibres), but were conditioned together for an extended period. A compilation of the assignments of FTIR spectral bands for natural fibres can be found in Appendix 5.5. More comprehensive sampling than this limited set of eight indicative tests would be necessary to confirm these features as appropriate for the confirmation of fibre identity or stage of processing. The compilation of an Atlas of Spectra mapping changes according to the stage of processing and surface treatment of the fibre would be a useful addition to resources.

Garside and Wyeth [83] used ATR-FTIR to distinguish between flax, hemp, jute, ramie (bast), sisal (leaf), and cotton (seed) fibres. Two ratios were calculated from the respective spectral intensities: $R_1 = I_{1595}/I_{1105}$ and $R_2 = I_{1595}/I_{2900}$, where the numerical subscript corresponds to the specific absorbance wave number (band). Each fibre occupied a unique region in a plot of R_1 against R_2.

Garside and Wyeth [83] defined a crystallinity index, X, as the ratio of the two band intensities, I_{1160}/I_{1060} for ATR FTIR spectra of hemp and flax fibres progressively rotated from 0° to 180° in 7.5° steps. The minimum X-value for flax occurred at a negative angle (roughly corresponding to the 6.5° S-twist) whilst the X-value for hemp occurred at positive angle (corresponding to the 7.5° Z-twist).

Garside and Wyeth [84] have used surface-sampling-polarized ATR-IR spectroscopy (Pol-ATR) and transmission-polarized infrared microspectroscopy (Pol-μIR) to study ramie (bast), sisal (leaf), and two viscose (regenerated) fibres. Pol-ATR was able to derive the principal alignment of the cellulose molecule with respect to the fibre axis and an indication of the degree of crystallinity. The S-direction twist ramie fibres were identified as having a 7.5 degrees winding angle.

Sohn et al. [85] used near infrared (NIR) spectra to distinguish between flax fibres subjected to successive cycles of cleaning in a Shirley Analyser. Systematic changes were observed in the absorbance bands at 1730, 1766, 2312, and 2350 nm. An index was calculated from the second derivative of the absorption at the four wavelengths and was found to decrease with increasingly pure fibre. The absorbances were ascribed to the epidermal layer which is progressively removed with each cleaning cycle. Further to this, the band absorption around 1724 nm was present in the spectra for dew-retted Natashja flax, but absent from the spectra of enzyme-retted Jordan flax.

Edwards et al. [86] used FT-Raman spectroscopy with laser excitation at 1064 nm. They provided tabulated wave numbers and vibrational assignments for seven natural plant fibres: flax, jute and ramie (bast), sisal (leaf) and coir, cotton and kapok (seed). To discriminate between the fibres they define two ratios of band intensities: $R = I_{1096}/I_{2900}$ (i.e. glycosidic C–O–C link ring stretch/unresolved C–H bond) and $R' = I_{1121}/I_{1096}$ (i.e. doublet of glycosodic C–O–C link stretching modes). R' shows remarkable consistency (except for coir and kapok fibres) whilst R may provide a suitable method for non-destructive characterization of the fibres (Table 5.8).

Table 5.8 **Relative FT-Raman band intensities for natural fibres (after Edwards et al.: typical deviation is ±0.03 [86])**

Sample	R' (I_{1121}/I_{1096})	R (I_{1096}/I_{2900})
Bast: flax	0.72	0.85
Bast: ancient linen	0.75	1.08
Bast: modern linen	0.76	1.12
Bast: jute	0.77	0.92
Bast: ramie	0.70	1.63
Leaf: sisal	0.73	0.91
Seed: coir	0.96	0.32
Seed: cotton	0.79	0.75
Seed: kapok	0.89	0.35

Ho and Bismarck [87] used electro kinetic analysis (EKA) to determine the zeta (ζ) potential at surfaces in natural fibres. The ζ-potential correlates well with maximum moisture uptake of natural fibres with typical values for 100% RH given in Table 5.9. Adhesion in fibre-reinforced polymers can be correlated to ζ-potential measurements.

Spectroscopic techniques are fundamental techniques in forensic fibre analysis and are commonly employed after microscopy methods, particularly IR spectroscopy in the form of Fourier transform infrared spectroscopy (FTIR). Like many techniques, these are used primarily for synthetic fibres, but research from the textile industry could be employed for natural fibres in forensic examinations. An important aspect of fibre identification is the generation of data collections of spectra to allow for fast and reliable interpretation.

Table 5.9 **Zeta (ζ) potential measurements determined at 100% RH ($\zeta_0 - \zeta_\infty$)/ζ_0 and dissociations of functional groups (ζ_{plateau}) properties for some common natural fibres**

Fibre	$(\zeta_0 - \zeta_\infty)/\zeta_0$	ζ_{plateau} (mV)
Abaca bold[a] (Philippines/leaf fibre)	0.82	0
Abaca fine[a] (Philippines/leaf fibre)	0.76	−0.6
Coir[a] (India/fruit fibre)	0.22	−3.8
Flax[a] (Belgium)	0.95	−1.1
Green flax fibre[b]	0.88	$\zeta_\infty = -1.7$
Dew-retted flax fibre[b]	0.85	$\zeta_\infty = -2.7$
Duralin flax fibre[b]	0.55	$\zeta_\infty = -5.3$
Hemp[a] (Central Asia)	0.91	−0.1
Henequen[a] (Mexico/leaf fibre)	0.76	−0.6
Lechuguilla[a] (Mexico/leaf fibres)	0.62	−2.5
Lyocell[a] (regenerated wood cellulose)	0.55	−3.2
Jute[a] (India)	0.18	−2.6
Sisal[a] (India/leaf fibre)	0.76	−1.7
Sisal[a] (Mexico/leaf fibre)	0.88	−0.4

After Ho and Bismarck[a] [87] and Stamboulis et al.[b] [88].

5.2.1.8 Molecular probes

Blake et al. [89] used a series of monoclonal antibodies (protein responses to antigens or foreign/toxic substances) and carbohydrate-binding modules (CBM) as molecular probes in conjunction with optical microscopy to assess the occurrence of cell wall epitope (the portion of a molecule to which an antibody binds) in hemp and flax stems. The LM5 galactan epitope was found to be abundant in flax fibre secondary cell walls but absent from hemp fibre cells whereas the LM11 xylan epitope was present only at the cell periphery and not in the cell walls (as seen in hemp). The LM6 arabinan epitope was present in flax fibre secondary cell walls but only weakly present in early development fibres and at the inner region of cell walls of mature secondary fibres in hemp. The LM10 xylan epitope was not detected in flax fibre cell walls.

5.2.1.9 DNA analysis

Enzymes are proteins which catalyse specific biochemical reactions. They are named using the target species followed by –ase (e.g. cellulase and pectinase break down cellulose and pectin, respectively).

Techniques exist to extract and purify DNA (deoxyribonucleic acid) from animal fibres in sufficient quantity for DNA fingerprinting. The quantities can then be increased by in vitro DNA amplification using the polymerase chain reaction (PCR). The extraction of identifiable DNA from plant materials is possible but relies on having undamaged associated tissue [90], i.e. raw (no wet processing) fibres [34]. Rogers and Bendlich [91] used cetyl trimethyl ammonium bromide (CTAB) with subsequent DNA precipitation of cotton fibres with seed material present.

In 2008 [92], Applied DNA Sciences Incorporated announced fiberTyping textile genotyping using DNA isolation from cotton fibre cell nuclear and chloroplast genes [92,93]. The assay can discriminate between Pima (*G. barbadense*) and Upland (*G. hirsutum*) cotton. Gordon states that:

> *It remains to be seen whether the genetic variation between varieties of the same species is large enough to be a measurable point of differentiation. Determining the point of origin or place of production will remain unlikely without the application of a DNA-based, electro- or nano-based labelling procedure.*

Dunbar and Murphy [90] used DNA analysis to distinguish between different fibres used to manufacture rope. The crude procedures used to extract fibres from plant materials generally produce dead fibre cells (with no nucleus or other cytoplasmic organelles containing DNA) with associated parenchymal, collenchymal, and epidermal cells (with nuclei or other cytoplasmic organelles) attached. The ribulose biphosphate carboxylase/oxygenase large protein sub-unit (rbcL) was chosen for analysis as it is present in all plant species, is plant specific (hence animal or fungal contamination will not distort results) and present in multiple copies. Different enzymes were used to cut the 771 bp amplicon (the base pair small replicating fragment of DNA synthesis using amplification techniques) into two or three fragments. For pure samples of each fibre type, clear differences were found in the results (Table 5.10).

Table 5.10 **DNA fragment sizes from restriction analysis of rope fibres**

		Bast (stem) fibres			Leaf fibres	
Enzyme	**Sequence**	**Flax**	**Hemp**	**Jute**	**Abaca**	**Sisal**
Acc I	GT’(A/C)(G/T)AC	578 + 193	518 + 60 + 193	230 + 288 + 253	230 + 541	230 + 541
Bam HI	G’GATCC	Uncut	115 + 656	115 + 656	Uncut	Uncut
Dra I	TTT’AAA	35 + 736	Uncut	332 + 439	Uncut	Uncut
Pst I	CTGCA’G	Uncut	386 + 385	Uncut	Uncut	386 + 385
Sac II	CCGC’GG	385 + 386	Uncut	734 + 37	Uncut	Uncut

NB: the sum for each cell is either zero or 771.
After Dunbar and Murphy [90].

The whole genome sequencing of the chromosome sets for flax [94,95] and hemp [96] should facilitate DNA analysis for the bast fibres. CoGePedia [95] states that flax has a small total genome size (estimated to be ~350 megabases). The current assembly v1.0 was produced entirely by Illumina sequencing and consists of a huge number of scaffolds (>88,000). However 290 megabases of the flax genome are present in only 664 scaffolds. The National Center for Biotechnology Information (NCBI) [97] provides access to a comprehensive database of biomedical and genomic information (Appendix 5.6).

Both molecular probes and DNA analysis are not conducted on natural fibres in forensic investigations as the cost of the analysis cannot be justified for the limited additional information gathered about the sample. DNA analysis is a powerful but expensive tool, is utilized for identification of individuals not plant materials in forensic analysis, as the additional cost of using this technique would have to allow for greater discrimination so as to increase the evidential value of the fibres. With this in mind, it is unlikely ever to be a commonly employed technique for the analysis of fibres.

5.3 Discussion

This chapter has identified a range of techniques that have potential for the forensic identification of, or discrimination between, natural fibres. Some of these techniques are already prolifically used in forensic casework and others have only been addressed within textile research. However, there is considerable scope for research to extend knowledge in the effectiveness of some of these techniques, including their ability to differentiate between bast fibres and fibres commonly used to replace these fibre types. There is also a need for extensive databases of known natural fibres to help address these gaps in knowledge. Development, standardization, and validation of the various procedures currently not being used in a forensic context would assist in their acceptance within the legal system although cost of the techniques would ultimately be the deciding factor as to whether these were used. Many of the forensic techniques to fibres analysis may find a place within the analysis of fibres for the composite industry as both industries have similar drivers, including the need for fast, reliable, and cost-effective techniques. A compilation of readily accessible fibre micrographs at various magnifications, and representing each stage of fibre treatment, would be indispensable for fibres analysts, particularly those working in the composite industry.

A more problematic issue is that composite failure analysis could require the removal of fibres from the composite before examination with the chosen analytical technique. The interaction between the matrix and the fibre during manufacture and/or the extraction of fibres from the cured matrix could change the nature of the fibre and hence compromise analysis. The development of a procedure for separation of the undamaged natural fibres from the matrix would find wider application given the potential for the determination of fibre weight (and hence volume) fractions within the composite.

It is essential that any analysis undertaken is accompanied by adequate sampling of the source materials and ideally using materials where the statistical ranges of a parameter do not significantly overlap.

5.4 Conclusions

A variety of techniques exist to discriminate between the bast-reinforcement fibres, including optical and electron microscopy, chemical reactions, mechanical twist, thermal properties, chemical spectroscopy, and genetic probes. Some of these techniques are already well established in forensic analysis but others have limitations for forensic science. The nature of the questions asked in a forensic investigation compared to those asked in the composite industry differ to the degree that many techniques employed in textile science are not fit-for-purpose in forensic analysis. In addition to this, the generally low evidential value of natural fibres and variation means that the emphasis is placed more heavily on discrimination of natural fibres samples by colour. Having stated this, some analysis methods overlap, notably those which allow for the quick identification of fibre type. There are a number of discernible differences between species and/or fibre treatment. However, in many cases the analytical data set is limited and there is scope for the development of more comprehensive databases. No single technique in isolation can give definitive characterization for a specific fibre but combinations of techniques can be used to identify the respective species. There is considerable scope for research to refine the above techniques leading to the development of internationally accepted standard procedures for the identification of bast fibres.

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Appendix 5.1 Identification of bast fibres (extracted from Robertson and Grieve [32])

Fibre	Colour	Lumen	Cross marks	Miscellaneous	Pits on maceration	Crystals on ashing
Flax	Usually white	Narrow regular	Few, Faint	–	Very fine, difficult to see	None
Hemp	Brown	Variable in width	Frequent	Hairs	Parallel to long axis (slit-like)	Clusters in short chains and singularly, Occasionally rhombic/cubic crystals
Jute	Brown	Constricted	Few, Faint	Few spirals	Bordered	Mainly rhombic and cubic in chains, single-cluster crystals
Kenaf/Roselle	Brown	Constricted	Few, Faint	–	Bordered	Cluster crystals in chains and singularly, very occasionally cubic/rhombic crystals

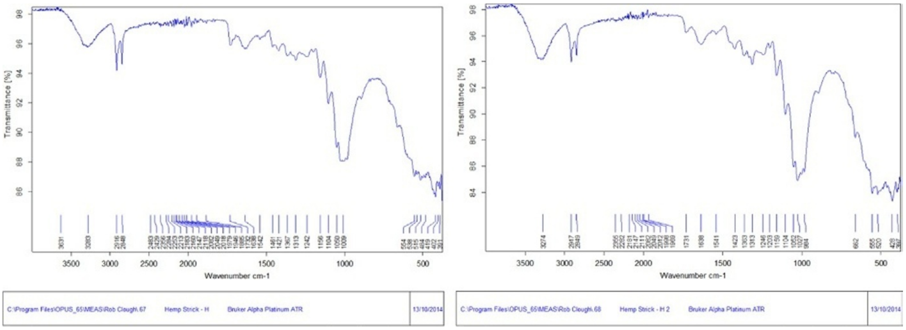
Appendix 5.2 Features of common bast fibres (data from Catling and Grayson via Robertson and Grieve [32])

Species	Extraneous material	Cross-markings	Lumen and cell wall	Pits	Crystals/silica ash
Flax	Epidermis with paracytic stomata Parenchyma Xylem elements	Rare. When seen, often very regular along whole length of fibre cell	Cell wall occasionally striated. Cell wall thick. Lumen narrow, regular	Very fine. Not obvious. Can be seen in polarized light	No crystals reported or seen
Hemp	Laticiferous elements in unmacerated fibre Parenchyma of various types Cluster crystals free or in cells Hairs. Epidermis More rarely, blocks of tissue and xylem elements	Variable. Some cells with fine regularly spaced marks in every specimen. Marks from chambered cells. Several series on one fibre cell. More frequent than in flax. Occasional remains of cells attached to marks	Cell wall striated Lumen most commonly 3–5× width of cell wall	Slit-like, parallel to long axis of cell, sometimes coalescing	Cluster crystal in short chains, often 3–4 together. Single-cluster crystals. *Very* occasional cubic or rhombic crystal in some specimens
Jute	Few. Mostly parenchyma, sometimes with cubic or cluster crystals. Very occasional vessels	Few, faint. Occasional marks from chambered cells Scalloped edges to fibre cells	Lumen of varying width, often varying regularly along the whole length of cell	Bordered, funnel-shaped inside view	Cubic crystals in chains sometimes mixed with occasional cluster crystals. Single-cluster crystals
Ramie	Parenchyma. Cluster crystals free or in parenchyma Cluster crystals in chambered cells Few hairs and vessel elements	Common, fine, nearly always with attached remains of parenchyma cells. Several series on one fibre cell. Occasional marks of chambered cells	Lumen difficult to see because (a) it varies, (b) cell wall is striated, (c) fibres tangle. Lumen commonly 2–3× width of cell wall	Elongated, slit-like parallel to long axis of cell, sometimes coalescing	Cluster crystals in chains Single-cluster crystal

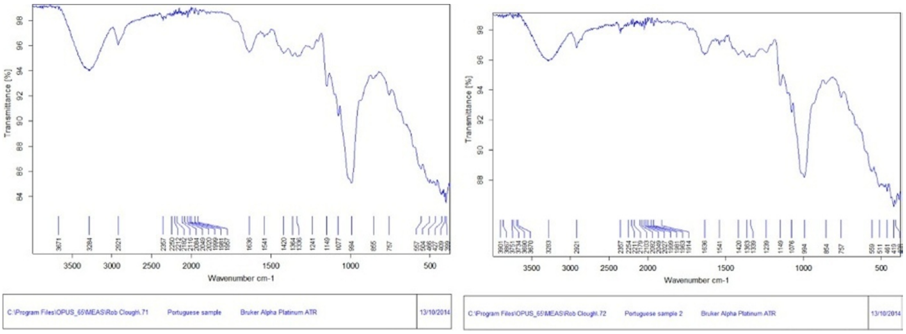
Appendix 5.3 Test protocol for the identification of flax, hemp, jute, or ramie fibres (after Marshall [30])

Test	Flax	Ramie	Hemp	Jute
Optical microscopy and electron microscopy	Single fibres Bamboo-like appearance caused by frequent swollen nodes	Single fibres Flat twisting ribbon-like cells	Bundles Fewer nodes but appearing across several fibre cells	Bundles Fewest and unswollen nodes
Twist test (looking down on the fibre after Hock, 1942)	Counter-clockwise	Counter-clockwise	Clockwise	Clockwise
Phloroglucinol and HCl	Normally no magenta colour change when processed	Normally no magenta colour change when processed	Pink or magenta	Deeper magenta than hemp
Herzberg's reagent: Zinc chloroiodide	Turns violet Highlights cellular structures Lumina more easily visible Yellow staining of extraneous tissue	Turns violet Highlights cellular structures	Turns violet Highlights cellular structures Cross-markings	Turns greenish brown Highlights cellular structures Dark streaked lumen, nodes, and cell ends
Schweitzer's reagent: Cuprammonium hydroxide	Swells Dissolves quickly Leaves threads of protoplasm	Swells Dissolves quicker than flax Islands of cells, then no residue	Swells Dissolves slower than flax Ruffling and pleating of middle lamella	Swells Dissolves very slowly Cell ends break away from the bundle and twist Pale blue transparent residue
Fibre diameter and range	14.7 ± 5.3 μm 5.1–25 μm	21.6 ± 9.5 μm 10–40 μm	58.7 ± 69.7 μm 1–100 μm	54.7 ± 27.7 μm 20–100 μm

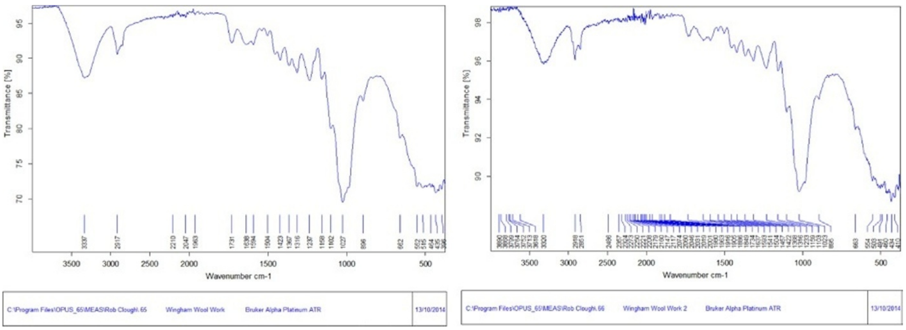
Appendix 5.4 FTIR spectra from the Bruker Alpha Platinum ATR FTIR (courtesy of Rob Clough and Michael Foulkes)



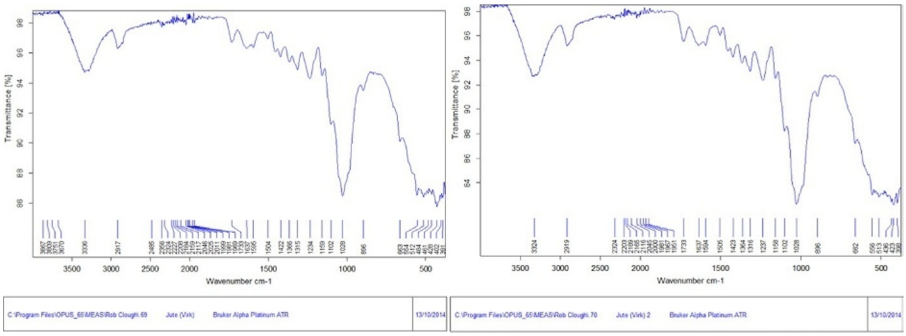
Hemp.
Wingham Wool Work, Rotherham, UK.



Ramie.
Courtesy of Georgios Koronis at MIT Portugal.



Jute.
Wingham Wool Work, Rotherham, UK.



Jute.
IJIRA/IJSG—India via AS Virk doctoral studies.

Appendix 5.5 FTIR spectral lines of natural fibres

Wavenumber (cm^{-1})	Vibration	Sources
3350	OH stretching (H bonded)	Jute [98]
3336	OH stretching	Cellulose, hemicellulose [63]
~3335 {3300}	ν (OH) free ‖	[83,99]
3327 (3332)	OH stretching	Hemp [81]
3300	OH linked shearing	Hemp polysaccharides [100]
3200–3600	OH stretching	Jute [101]
2922	C-H vibration (doublet with 2854) replacing single band at 2900 on depolymerization	Flax [82]
2900	C-H stretching in methyl and methylene	Jute [98,101]
~2900	ν (C−H) ⊥	[83,99]
2887	C−H symmetrical stretching	Cellulose, hemicellulose [63,101]
2885	C−H symmetrical stretching	Hemp polysaccharides [100]
2883 (2882)	C−H symmetrical stretching	Hemp [81]
2854	C−H vibration (doublet with 2922) replacing single band at 2900 on depolymerization	Flax [82]
2850	CH_2 symmetrical stretching	Hemp wax [100]
~2850	$\nu(CH_2)$ symmetrical stretching (non-dichroic °)	[83,99]
1750	Shifted carbonyl band	Flax aged with *Penicillium corylophilum* [82]
1740	C=O stretching vibration (disappears after treatment)	Jute hemicelluloses [101]
1735	C−O stretching in carbonyl and unconjugated β-ketone	Jute [98]

Continued

Wavenumber (cm^{-1})	Vibration	Sources
~1735	ν(C=O) ester	[99]
1732	C=O unconjugated	Hemp xylan hemicellulose [100]
1730–1733	Present in untreated fibre, not in NaOH treated fibres, reappears with MPP treatment	Jute [102]
1729	C=O stretching vibration	Pectin, waxes [63]
1724 (1724)	C=O stretching vibration	Hemp [81]
~1635	Adsorbed water	[99]
1630–1650	OH in water	Water [100]
1623	OH bending of absorbed water	Water [63]
1623 (1624)	OH bending of absorbed water	Hemp [81]
~1595	ν(C=C) aromatic in-plane	[99]
1506	C=C aromatic symmetrical stretching	Lignin [63]
1506 (disappear)	C=C aromatic symmetrical stretching	Hemp [81]
1505	C=C aromatic symetrical stretching	Hemp lignin [100]
~1505	ν(C=C) aromatic in-plane	[99]
~1475	$\delta(CH_2)$ scissoring	[99]
1455	C–H deformation and CH_2 bending	Jute [98]
~1455	δ(C–H); δ(C–OH) primary and secondary alcohol	[99]
1432	CH_3 asymmetric deformation	Jute lignin [101]
1425	CH_2 symetrical bending C=C stretching in aromatic groups	Hemp (pectin. lignin, hemicelluloses, calcium pectates) [100]
1423	HCH and OCH in-plane bending vibration	Cellulose [63]
1423 (1423)	HCH and OCH in-plane bending vibration	Hemp [81]
~1420 {1425}	δ(C–H) $\parallel$	[99]
1376	C–H symmetric deformation	Jute lignin [101]
1370	C–H deforming (asymmetric)	Jute [98]
1370	In-the-plane CH bending	Hemp polysaccharides [100]
1368	In-the-plane CH bending	Cellulose, hemicellulose [63]
1368 (1367)	In-the-plane CH bending	Hemp [81]
1363 (1363)	In-the-plane CH bending	Hemp [81]
~1365 {1370}	δ(C–H) $\parallel$	[83,99]
1362	In-the-plane CH bending	Cellulose, hemicellulose [63]
1335	C-O aromatic ring	Hemp cellulose [100]
~1335 {1355}	$\delta(CH_2)$ wagging $\parallel$	[83,99]
1325 (1325)	S ring stretching	Hemp [81]
1320	Overlapping of 1335 and 1315 bands due to hydrolysis	Flax inoculated with *Fomes fomentarius* [82]

Wavenumber (cm^{-1})	**Vibration**	**Sources**
1317	CH_2 rocking vibration	Cellulose [63]
~1315	δ(C-H)	[99]
1314 (1313)	CH_2 rocking vibration at C6	Hemp [81]
~1280	δ(CH2) twisting ||	[83,99]
1259 (1261)	G ring stretching	Hemp [81]
1250	C–O stretching in acetyl groups (disappears after treatment)	Jute hemicelluloses [101]
1246	C=O and G ring stretching	Lignin [63]
1245 (1244)	C–C plus C–O plus C=O stretch; G condensed > G etherified	Hemp [81]
1240–1241	Present in untreated fibre, not in NaOH treated fibres, reappears with MPP treatment	Jute [102]
1240	C–O aryl group	Hemp lignin [100]
~1235	δ(C–OH) out-of-plane	[99]
1232 (1231)	C–O–H bending at C6	Hemp [81]
1230–1240	C–O stretching in acetyl group	Jute [98]
1204 (1199)	C–O–C symmetric stretching, OH plane deformation	Hemp [81]
1202	C–O–C symmetric stretching	Cellulose, hemicellulose [63]
~1200	δ(C–OH); δ(C–CH)	[99]
1162	C–O–C asymmetrical stretching	Hemp cellulose and hemicellulose [100]
1155	C–O–C asymmetrical stretching	Cellulose, hemicellulose [63]
~1155 {1160}	ν(C–C) ring breathing, asymmetric ||	[83,99]
1152 (1156)	C–O–C asymmetrical stretching	Hemp [81]
~1105	ν(C–O–C) glycosidic	[99]
~1050 {1060}	ν(C–OH) secondary alcohol (non-dichroic °)	[83,99]
1048	C–C, C–OH, C–H ring and side group vibrations	Cellulose, hemicellulose [63]
1046 (1043)	C–C, C–OH, C–H ring and side group vibrations	Hemp [81]
1030	Aromatic C-H in plane deformation	Jute [98]
~1025	ν(C–OH) primary alcohol	[99]
1020 (1018)	C–C, C–OH, C–H ring and side group vibrations	Hemp [81]
1019	C–C, C–OH, C–H ring and side group vibrations	Cellulose and hemicellulose [63]
~1005	ρ(–CH–)	[99]
995	C–C, C–OH, C–H ring and side group vibrations	Cellulose and hemicellulose [63]
994 (996)	C–C, C–OH, C–H ring and side group vibrations	Hemp [81]

Continued

Wavenumber (cm^{-1})	Vibration	Sources
~985	ρ(−CH−)	[99]
900	Decreased intensity with increased crystallinity	Cotton, flax, hemp [82]
896	C−O−C, C−C−O, C−C−H deformation and stretching	Cellulose [63]
895 (894)	C−O−C, C−C−O, C−C−H deformation and stretching	Hemp [81]
895	Glycosidic bonds	Hemp polysaccharides [100]
~895	ν(C−O−C) in plane, symmetric	[99]
830	Aromatic C−H out-of-plane vibration	Jute [98]
670	C−OH out-of-plane bending	Bast [100]
662 (663)	C−OH out-of-plane bending	Hemp [81]
662	C−OH out-of-plane bending	Cellulose [63]

For dichroic bands, the notation is ° (non-dichroic), || (parallel) or ⊥ (perpendicular).
For fibres without/with dislocations, the wavenumbers are outside/within brackets respectively.
For the various motions of atoms within the normal modes, the notation is δ bending; ν stretching; ρ rocking; τ torsion; ω wagging.

Appendix 5.6 NCBI genome nucleotide dataset samples for flax and dataset numbers for bast fibres (surveyed at 13 March 2014)

		Genome/Gene						
	Accession	Flax (Linum usitatissimum)	GI					
1	AFSQ00000000.1	Whole genome shotgun sequence	344029616	48,397 rc linear DNA	GenBank			
2	HM991839.1	SP2047 fatty acid desaturase 3C (FAD3C)	319999847	3739 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
3	HM991837.1	M5791 fatty acid desaturase 3C (FAD3C)	319999843	3874 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
4	HM991838.1	UGG5-5 fatty acid desaturase 3C (FAD3C)	319999845	3737 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
5	HM991836.1	Fatty acid desaturase 3C (FAD3C)	319999841	3732 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
6	HM991835.1	SP2047 fatty acid desaturase 3B (FAD3B)	319999839	4573 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
7	HM991834.1	UGG5-5 fatty acid desaturase 3B (FAD3B)	319999837	4569 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
8	HM991833.1	M5791 fatty acid desaturase 3B (FAD3B)	319999835	4626 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
9	HM991832.1	Fatty acid desaturase 3B (FAD3B)	319999833	4570 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
10	HM991831.1	SP2047 truncated fatty acid desaturase 3A (FAD3A)	319999831	5332 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences

Continued

		Genome/Gene						
	Accession	**Flax (Linum usitatissimum)**	**GI**					
11	HM991830.1	UGG5-5 fatty acid desaturase 3A (FAD3A)	319999829	5385 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
12	HM991829.1	M5791 fatty acid desaturase 3A (FAD3A)	319999827	5500 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
13	HM991828.1	Fatty acid desaturase 3A (FAD3A)	319999825	5383 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
14	L24120.1	Peroxidase precursor (FLXPER2) mRNA, 3’end	1854580	1153 bp linear mRNA	GenBank	FASTA	Graphics	Related Sequences
15	JX174449.1	Clone LuBAC346C18, complete sequence	395146555	130,251 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
16	JX174448.1	Clone LuBAC395P20, complete sequence	395146541	184,896 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
17	JX174447.1	Clone LuBAC375N24, complete sequence	395146526	180,098 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
18	JX174446.1	Clone LuBAC375M9, complete sequence	395146501	214,610 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
19	JX174445.1	Clone LuBAC364K11, complete sequence	395146479	179,112 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
20	JX174444.1	Clone LuBAC317I7, complete sequence	395146470	172,458 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
21	JN133301.1	Cultivar CDC Bethune clone FLA-fosmid sequence	355430106	26,231 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences

		Genome/Gene						
	Accession	Flax (Linum usitatissimum)	GI					
22	JN133300.1	Cultivar CDC Bethune clone LTP-fosmid sequence	355430066	31,478 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences
23	JN133299.1	Cultivar CDC Bethune clone SAH-fosmid sequence	355429955	34,640 bp linear DNA	GenBank	FASTA	Graphics	Related Sequences

Flax (*Linum usitatissimum*)	10,890 nucleotide records	Five transcriptome or gene expressions	Reference genome
Hemp (*Cannabis sativa*)	93,653 nucleotide records	Three transcriptome or gene expressions	Reference genome
White Jute (*Corchorus capsularis*)	83 nucleotide records	<none>	<none>
Dark Jute (*Corchorus olitorius*)	2036 nucleotide records	<none>	<none>
Kenaf (*Hibiscus cannabinus*)	194 nucleotide records	Two transcriptome or gene expressions	<none>
Nettle (*Urtica dioica*)	268 nucleotide records	<none>	<none>
Ramie (*Boehmeria nivea*)	159 nucleotide records	Six transcriptome or gene expressions	<none>

Note. Online version of this table has additional information and links to resources on the internet.

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Fibre/matrix interface

6

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6.1 Introduction

Composite materials are, by design, made of different materials. One of the main focuses in those materials is to ensure the bonding between constituents to allow stress transmission between reinforcements and matrix. The bonding between reinforcements and matrix can result from covalent bonds or physico-chemical interactions. The strongest bonds result from covalent bonding and a modification of the chemistry of the reinforcement surface is often used in petro-sourced composites to induce covalent bonds with reactive resin such as epoxy. These kinds of surface treatments imply an increase of the carbon dioxide footprint of the overall process of composite manufacturing. Focusing on minimizing this footprint by the use of bio-based reinforcement, adding a chemical treatment can counterbalance the gain from the environmental point of view. Several ways have been explored to improve wettability and bonding of bio-based reinforcements by polymer resins. Basalt fibres, with chemistry quite similar to glass, can be sized with organosilanes or coated with thermoplastic sizing for example. The approach must be different when it comes to natural fibres such as flax or hemp. Chemical treatments developed for petro-sourced reinforcements are no longer applicable. Surface modification by selective dissolution or thermal cracking has been tested but is not yet brought to the industrial level. The most common treatment that has been tested on a large amount of fibres is an alkaline treatment to solve some surface components of the natural reinforcement. Surface treatments that have a lower environmental effect have also been tested, for example, the use of formic acid or thermal treatments in neutral atmosphere. All those treatments have an effect on both wettability of the reinforcement and on bonding properties after processing. More importantly, it can also affect the dimensional stability of natural fibres that are, by nature, sensitive to water sorption. The stability and durability of these treatments is still an issue and is not well known yet. One of the main issues will also be to investigate the durability of bonding properties in a humid environment.

6.2 Adhesion and bonding

6.2.1 Wetting properties

In a first approach, permeability and particularly unsaturated permeability have been investigated on biobased reinforcements. Liotier et al. [1] have shown that even considering fabrics with the same weaving and the same tow count, unsaturated permeabilities in the main directions of the fabric are different in a biobased reinforcement (in this

Biocomposites for High-Performance Applications. http://dx.doi.org/10.1016/B978-0-08-100793-8.00006-5

case flax fabric reinforcement) from those measured in a similar glass reinforcement. This study [1] tends to prove that capillary effect has to be considered during unsaturated permeability measurements. This effect is even more important considering natural fibres since they tend to be more hydrophilic than the synthetic ones [2].

The wetting behaviour can be analysed using a tensiometric method, which is, for now, the most reliable method. A tensiometer is an electronic microbalance (resolution down to 0.1 μm) to which the tested solid is clamped. A test liquid vessel can move up and down via a piezo-actuated support. To determine apparent static contact angles, the Wilhelmy's force balance equation can then be used:

$$mg = p\gamma_{\mathrm{L}} \cos\theta_{\mathrm{e}} \tag{6.1}$$

where p is the wetting perimeter of the solid (probe), γ_{L} is the liquid–gas surface tension of the liquid, θ_{e} is the contact angle between the fluid and the solid probe, g is the gravitational constant, and m is the mass of the wetting meniscus evaluated, thanks to the microbalance. This basic relationship simply describes the weight of the meniscus formed due to surface tension effects at a fluid–solid interface, both in terms of gravitational force and through the equivalent contribution calculated from the wetting characteristics of the fluid–solid contact. Operating a measurement consists in moving the liquid vessel upward, until the balance detects a weight drop corresponding to the contact established between the solid and the liquid surface that tends to creep up the solid surface. From the measurements of the meniscus weight, according to Wilhelmy's equation (Eq. 6.1), if the liquid tension surface (γ_{L}) and solid geometry (wetting perimeter p) are known, the static contact angle can be determined (Eq. 6.2)

$$\cos\theta_{\mathrm{e}} = \frac{mg}{p\gamma_{\mathrm{L}}} \tag{6.2}$$

The surface free energy of a solid (γ_{S}) consists of two components: a dispersive component of nonpolar interactions ($\gamma_{\mathrm{S}}^{\mathrm{d}}$) and a polar component ($\gamma_{\mathrm{S}}^{\mathrm{p}}$) that incorporates the rest of interactions. The polar component contains the Coulomb's interactions between permanent dipoles and the interactions between permanent and induced dipoles. The interactions resulting from the time fluctuations of the charge distribution within the molecules are called disperse interaction. The surface energy of a solid and the surface tension of a liquid are the sum of both polar and dispersive contributions (Eq. 6.3):

$$\gamma_{\mathrm{S}} = \gamma_{\mathrm{S}}^{\mathrm{d}} + \gamma_{\mathrm{S}}^{\mathrm{p}} \tag{6.3}$$

There are several methods in literature available to calculate these components of surface energy. The most common methods are those using the results of contact angle measurements [3], that can be characterized through the Wilhelmy equation (Eq. 6.1). Using two wetting liquids with known surface tension, the dispersive and polar components can easily be determined by solving the Owens and Wendt equation that is a geometrical mean approach (Eq. 6.4) [4].

$$\gamma_{\mathrm{S}} + \gamma_{\mathrm{L}} - \gamma_{\mathrm{SL}} = 2\left(\gamma_{\mathrm{S}}^{\mathrm{d}}\gamma_{\mathrm{L}}^{\mathrm{d}}\right)^{1/2} + 2\left(\gamma_{\mathrm{S}}^{\mathrm{p}}\gamma_{\mathrm{L}}^{\mathrm{p}}\right)^{1/2} \tag{6.4}$$

Considering the Young–Laplace's equilibrium equation:

$$\cos\theta_\mathrm{e} = \frac{\gamma_\mathrm{S} - \gamma_\mathrm{SL}}{\gamma_\mathrm{L}} \tag{6.5}$$

and inserting this equation into Eq. (6.4), it is possible to obtain the following equation:

$$\gamma_\mathrm{L}\left(1+\cos\theta_\mathrm{e}\right) = 2\left(\gamma_\mathrm{S}^\mathrm{d}\gamma_\mathrm{L}^\mathrm{d}\right)^{1/2} + 2\left(\gamma_\mathrm{S}^\mathrm{p}\gamma_\mathrm{L}^\mathrm{p}\right)^{1/2} \tag{6.6}$$

This equation relates measurable physical values (cos θ_e; γ_L) to polar and dispersive components of liquid and solid. In order to determine the solid surface energy components, it is necessary to determine first the components of surface tension for two liquids, one of which is totally dispersive, i.e., with the polar component equal to zero ($\gamma_\mathrm{S}^\mathrm{p}=0$ in Eq. 6.6). After determining the equilibrium contact angle of the two liquids with the solid, it is possible to calculate the polar and dispersive components of the solid surface energy since one of the test liquids has no polar component.

In dynamic conditions, the Washburn's approximation describes the capillary rise of a liquid in a tube and by extension into a porous medium [2,5]. It can be used to determine the dynamic advancing angle during wetting. Washburn's equation defines the flow of a liquid through a capillary tube:

$$h^2\left(t\right) = \frac{r}{2}\frac{\gamma_\mathrm{L}\cos\theta_\mathrm{a}}{\mu}t \tag{6.7}$$

where h is the distance travelled by the liquid front, r is the radius of the capillary tube arrangement, θ_a is the advancing contact angle, μ is the viscosity of the liquid, and t is the time of flow. The corresponding mass change over time can be deduced, it is written as:

$$m^2\left(t\right) = \frac{\pi^2 r^5}{2}\frac{\rho^2\gamma_\mathrm{L}\cos\theta_\mathrm{a}}{\mu}t \tag{6.8}$$

Following Washburn's modified approach; a porous material packed in a column can be described as a bundle of capillary tubes. Assuming that a mean capillary radius exists, referred to as $\vec{r}$, one can derive a modified Washburn's equation for porous media:

$$h^2\left(t\right) = \frac{c\bar{r}}{2}\frac{\gamma_\mathrm{L}\cos\theta_\mathrm{a}}{\mu}t \tag{6.9}$$

where c is a constant accounting for the tortuous path of the liquid in the equivalent capillary tubes arrangement. Then a tensiometer can be used to track the rise of the liquid by recording the weight of liquid penetrating the cylindrical porous medium.

$$\begin{aligned} m^2\left(t\right) &= \frac{c\bar{r}\epsilon^2\left(\pi R^2\right)^2}{2}\frac{\rho^2\gamma_\mathrm{L}\cos\theta_\mathrm{a}}{\mu}t \\ &= C\frac{\rho^2\gamma_\mathrm{L}\cos\theta_\mathrm{a}}{\mu}t \end{aligned} \tag{6.10}$$

Where ε is the relative porosity and R is the inner radius of the sample holder.

Knowing the mass variation over time $m(t)$, the apparent wetting properties of the porous medium are easily derived from Eq. (6.10). More precisely, the so-called geometric porous medium factor C (cm^5) is derived [5].

The dynamic contact angle measurement, according to the modified Washburn's equation, consists of two tests: the first one to set constant C, and the second one for the contact angle calculation with a test liquid. For the first test, in order to get rid of the contact angle in the modified Washburn's equation (Eq. 6.10), it is necessary to use a totally wetting liquid (such as *n*-hexane) which has an apparent contact angle of 0 degrees with the porous medium, thanks to its low surface tension. Then, by plotting the square of the mass gain $m^2(t)$ as a function of time, and through a linear fit of the liquid intake stage, the geometric porous medium constant C can be determined knowing liquid density, surface tension, and viscosity.

6.2.2 Interfacial behaviour

To analyse interfacial behaviour of fibres, micromechanical tests of resin droplets debonding on fibres can be used [2]. This is the most simple and widely used approach for analysing failure in microbond specimens. The sample preparation requires the deposit of a 50 μL droplet of the studied resin on each fibre. To do this they have to be bonded to a thin piece of paper with a central longitudinal slot. After the deposit of the droplet, embedded length must be verified by optical observation and included between 100 and 300 μm [2]. An example of the microdroplet from a publication of Baley et al. [2] is shown in Fig. 6.1.

This method requires assuming that the droplet shears off the fibre when the average shear stress at the interface, i.e., when the experimentally observable applied force, F_d, becomes large enough to break the interface [6,7]. The force, F_d, at the instant of debonding is predicted to be directly proportional to the joining surface between fibre and matrix. The fibre-droplet debonding load, F_d, was plotted against

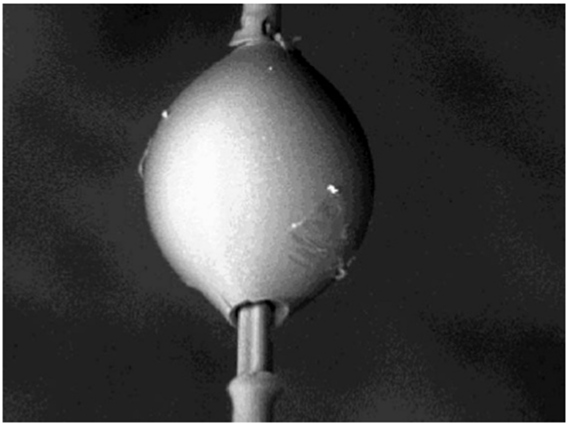

Fig. 6.1 Example of a microdroplet after debonding [2].

embedded surface, and a linear regression is used to determine τ_i (apparent interfacial shear strength IFSS). The problem with such an analysis lies in the assumption that only the average shear stress determines failure. This is unrealistic and a finite element analysis [8] shows that the shear stress is nonuniform along the fibre/matrix interface and there is a significant radial tensile stress concentration at the point where the fibre enters the droplet. A more complex model has been proposed by Scheer and Nairn [4,9,10], in which the state of stress in the microbond specimen is derived by a recently developed variational mechanics analysis. F_D, the debonding load can then be expressed as follow:

$$F_D = \pi r_f \left(\sqrt{\frac{2G_{ic}}{r_f C_{33S}}} - \frac{D_{3S}\Delta T}{C_{33S}} \right) \tag{6.11}$$

where G_{ic} is the critical energy release rate for the interface, r_f is the fibre radius, and ΔT is the temperature difference between the temperature during the test and the stress free temperature.

C33S and D3S are constants:

$$D_{3S} = \frac{1}{2}(\alpha_f - \alpha_m) \tag{6.12}$$

$$C_{33S} = \frac{1}{2}\left(\frac{1}{E_f} - \frac{V_f}{V_m E_m} \right) \tag{6.13}$$

The axisymmetric stress tensor is determined for the fibre as well as for the matrix, and the solution also includes the thermal residual stresses resulting from specimen preparation. Debonding is predicted from the energy release rate for initiation of an interfacial crack at an edge of the droplet. This is a logical assumption since this is the point where the interfacial stresses reach the highest values [11]. The energy release rate for initiation of an interfacial crack, *Gi*, is calculated by assuming that specimen failure occurs when *Gi* reaches the critical energy release rate for the interface, or interfacial toughness, Gic.

6.2.3 Multilayered fibres and interphase

It is well known that botanic natural fibres such as flax are multilayered (Fig. 6.2, [9]). The study of their surface properties can be affected by this structure. During micromechanical tests, the bonding between the fibre layers can be weaker than the bonding between the fibre and the polymer matrix. This could result in debonding like it is shown in Fig. 6.2. This complexifies the analysis of bonding properties. Rupture has to be located at the interface between the fibre and the matrix to allow calculation of the critical shear strength and the critical energy release which are a relevant indicator of the bonding properties.

It can be even more complicated to consider natural fibres since the surface layer of the fibres itself can be porous. The interface can then be more described like an interphase than an interface. Le Duigou et al. [10] have proved that with some polymer matrices, there is a diffused interphase between natural fibres (flax in their study) and

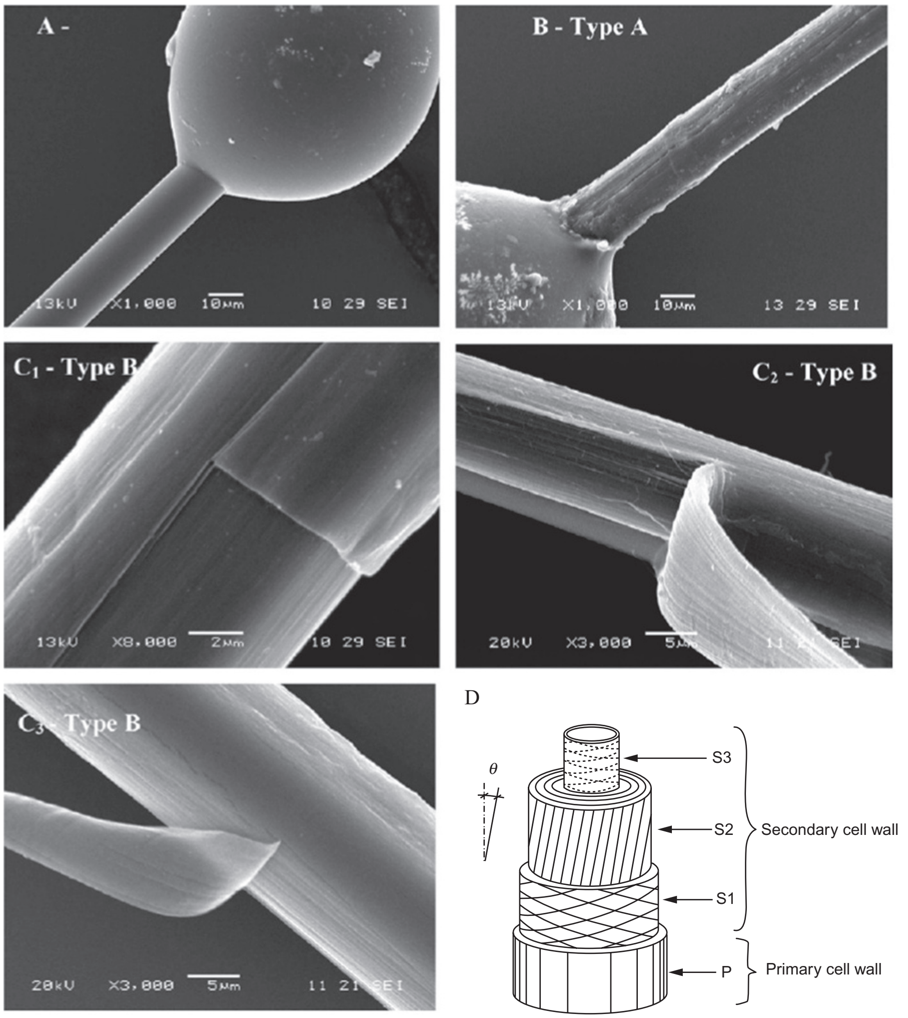

Fig. 6.2 (A) Droplet on a synthetic fibre; (B) droplet on a flax fibre; (C) peeling of layers during micromechanical tests; (D) shema of a multilayered natural fibre [9].

polymer matrix. This has been proved by the analysis of specific markers by laser confocal microscopic observation on fibres and resin that have been labelled by different fluorescent dye before composite manufacturing (Acriflavine for fibres and Rhodamine B for the matrix). Fig. 6.3 shows that markers from resin and fibres are both detected by laser confocal spectroscopy in fibres outer layers. This is even more obvious plotting the fluorescence intensity on the line in yellow on Fig. 6.3F. It is clear that the transition in fluorescence intensity at the interface between fibres and matrix is not sharp (even considering the resolution of laser confocal microscopy) proving the existence of an interphase. This proves that a specific attention has to be given to the rupture feature after a micromechanical test to check that the values are really relevant to bonding properties.

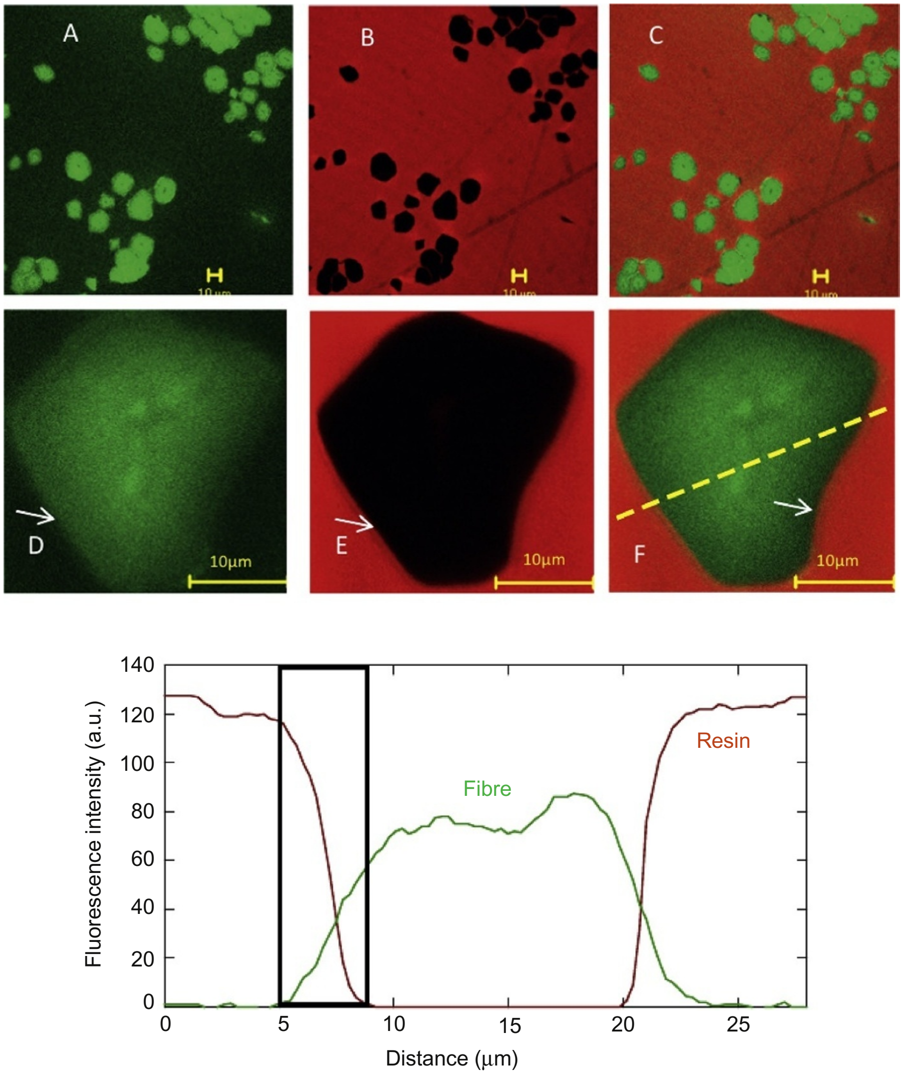

Fig. 6.3 *Up*: (A, D) Fibres signature; (B, E) resin signature; (C, F) composite signal for both resin and fibres. *Down*: Signal along the yellow line presented in F [10].

6.3 Fibre treatments and surface modifications

6.3.1 Characteristics of natural fibres surface

Natural fibres are constituted of several bio-polymers and polysaccharides making the fibre itself a composite. Cellulose is the main constituent of the fibre itself and ensures the mechanical properties. Some studies on reconstructed cellulose have been undertaken, especially in measuring surface energy of those fibres in order to compare it later to natural fibre ones [12]. This kind of fibres will not be included in this chapter since a part of the literature is considering them as man-made fibres. Hemicellulose is a branched polymer that is embedded in the plant cell walls. They have a significant contribution to the surface energy of fibres since the cell wall is part of the fibre surface. The other polysaccharides that can be found in natural fibres are lignin and pectin. The ratio between these components can vary largely depending on the species. For example, there is a significant amount of lignin in wood (up to 20%) but this polysaccharide is very rare in flax (about 2%).

6.3.2 Chemical and thermal treatments of fibres and fabrics

Several treatments have been tested on natural fibres in order to modify their chemical composition. In particular, the main aim of these treatments is to modify the ratio between cellulose, hemicellulose, pectin, and lignin. It is known that pectin, lignin, and hemicellulose can be degraded or solved by acid and alkaline treatments [2,13,14]. This can be used to measure the relative content of these components in any kind of natural fibres, but also to modify their chemical structure and surface properties. Numerous studies have focused on the effect of an alkaline treatment on natural fibres. Some of them have associated an acid treatment to the alkaline one. In order to limit the environmental impact of these treatments, bio-based acids, such as formic acid have been tested. Sizing inspired from those used for petro-sourced reinforcements have also been used. For example thermoplastic sizing on natural fibres have been explored. These are significantly increasing the environmental impact of reinforcements preparation but allow, theoretically, a better control and reproducibility of the surface properties. The following examples will focus on flax fibres since the treatments have been largely documented on those fibres. The textiloplastic sizing is not used for botanic fibres. It still can be used for basalt fibres for example. A last example of treatment that can modify the bonding properties of natural fibres with polymer matrix is plasma treatment under air or argon. Both atmospheric conditions and the plasma power appear to have an influence on natural fibres surface modification.

6.3.2.1 Alkaline treatment

Alkaline treatments have the purpose to partially solve the noncellulosic polymers, such as pectin and hemicellulose. Since the mechanical properties are supposed to be mainly due to cellulose, this kind of treatment should remove components that are complexifying the understanding of the wetting properties of natural fibres. Typical alkaline treatments can be an immersion in a sodium hydroxide (10 g/L) ethanol solution for 2 h at 78°C [2] or in a 1.5 M sodium hydroxide solution for 1 h at 100°C [14,15] (Fig. 6.4C).

This kind of treatments, even if they have been largely used in literature, have been found to have a very minor effect on surface energy modification (the change is lower than 5% on the overall surface energy [2]). The polar component of the surface energy is slightly weakened, so is the total surface tension. Microbonding tests have shown that the shear strength and the critical rupture energy are lowered by more than half

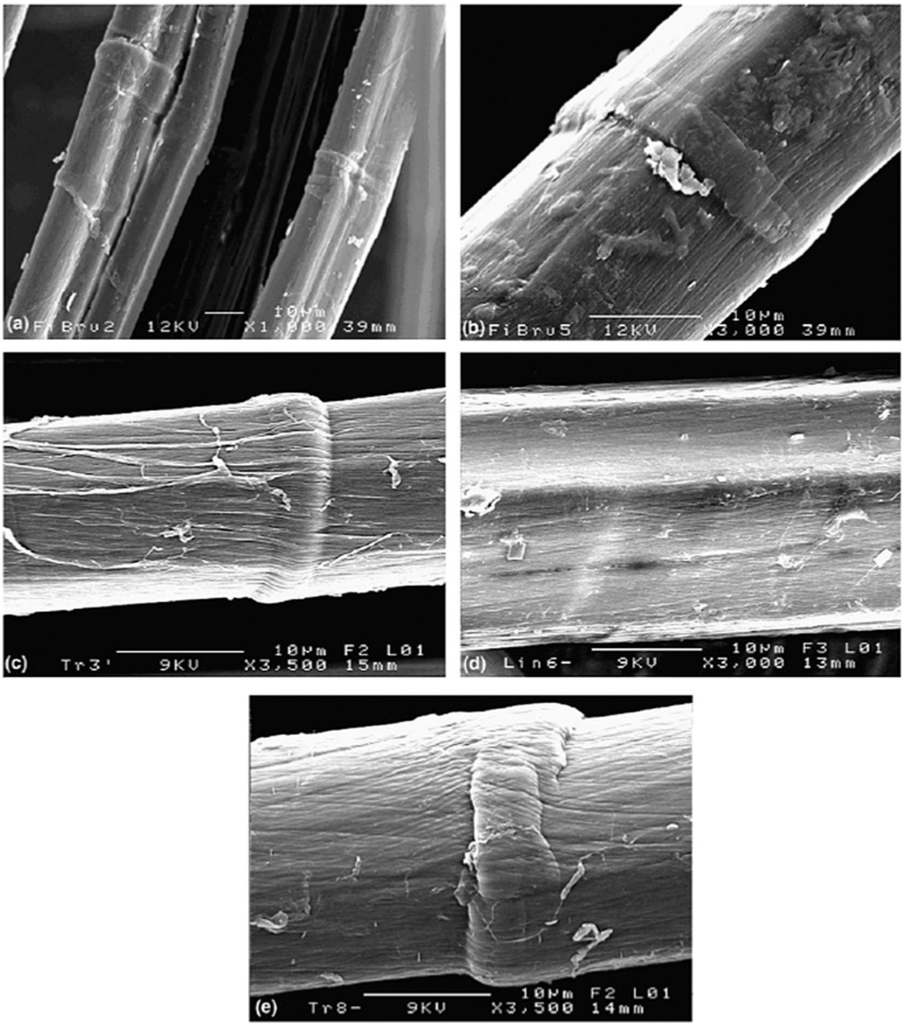

Fig. 6.4 SEM micrographs of flax fibres: (A, B) Untreated; (C) after alkaline treatment; (D) after alkaline treatment *followed by an acid treatment*; (E) after formic acid (biobased) treatment [4].

after this treatment. In order to improve interfacial properties, immersion in an acid solution can be added to completely remove the noncellulosic polymers.

6.3.2.2 Alkaline treatment followed by an acid treatment

The precedent treatment can be coupled with an immersion in acid solutions. Typical example of treatments can be an immersion for 1 h in pure acetic anhydride at room temperature [9] or for a total solvation of the noncellulosic polymers for 1 h in a 0.015 M of HCl solution at 100°C [14,15] (Fig. 6.4D).

The immersion in acetic anhydride, coupled with the alkaline extraction, has been proved to enhance slightly the shear strength measured by microbonding tests even if the modification of surface energy is not significant. There is also a significant effect on the critical rupture energy measured during this test (roughly multiplicated by 1.5). This tends to prove that, even the alkaline treatment can be harmful; its coupling with an acid solvation can improve the interfacial properties.

6.3.2.3 Formic acid (bio-based) treatment

This treatment is of particular interest since formic acid can be bio-based and the treatment duration is shorter. Indeed an immersion for 40 min at room temperature in 99% formic acid has proved to have the same effect as that of the previous treatment (NaOH + acetic anhydride) [2] (Fig. 6.4E). The environmental impact is then lower and the process is much easier since no heating is required.

6.3.2.4 Textiloplastic sizing

Standard sizings, such as organosilane covalent bonding or thermoplastic coating, are also used for bio-based fibres such as basalt fibres. Those, such as glass, have a mainly polar surface energy that makes them difficult to wet with mostly dispersive resins or polymer. The same sizing than for glass have been used to make those fibres surface more dispersive. For example, oragnosilanes can be used and also thermoplastic coating. Organosilane treatment is now well known and allows having a very good surface regularity. The process for thermoplastic coating can be nonhomogeneous along the fibre (Fig. 6.5), as proved by Pucci et al. [16]. This kind of sizing is only applied on basalt fibres and, for now, is rarely used on other natural fibres.

6.3.2.5 Thermal treatment under neutral atmosphere

Flax reinforcements can be subjected to a thermal treatment in order to degrade the hemicelluloses that are partly responsible for the hydrophilic character of the flax fibres. It has been shown on wood products [17,18] that the hemicelluloses start to crack at ~200°C producing free radicals that are susceptible to create reticulation in the lignins or pectins. The treated flax fibres have thus been subjected, after drying, to a temperature of 220°C for 2 h under circulation of nitrogen to prevent oxidation and fire [15,19].

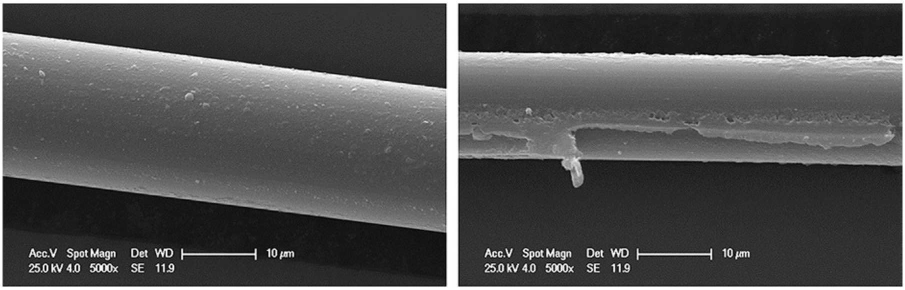

Fig. 6.5 Basalt fibres with organisolane based sizing *(left)* and thermoplastic coating *(right)* [16].

Previous research on wood [17,18] has shown that the thermal treatment induces a degradation of hemicellulose. This degradation tends to produce free radicals that are by definition very unstable. These free radicals tend to create cross-linking in lignins when they are generated in wood. Flax fibres contain a very low amount of lignin [20] and the measured amount of lignin can depend on the extraction method [21]. The process of free radicals stabilization could thus be different. The difference in mass loss during selective dissolution [15] shows an effect of these free radicals on the pectin. This may indicate an increase of the amount of structural pectins (the overall pectins are classified into structural and matrix pectins, and this implies that a part of the matrix pectins have been converted into effective structural pectins that are more strongly bonded).

6.3.2.6 Plasma treatment

Usually, atmospheric plasma is generated between two electrodes through which runs an alternative current that makes the selected operating gas into plasma. Gases used can be argon, air, or ethylene [22,23]. The plasma power can be modulated and varies in the literature from 100 to 400 W [22,23]. The main effect of this treatment appears to be the surface roughness modification on flax fibres. A rougher surface can induce a better mechanical coupling between fibres and matrix. Bozaci et al. [22] have shown that even if the tensile strength of elementary fibres decreases when the plasma power increase, the IFSS is significantly improved. Bonding properties being determinant for composites, a light decrease of tensile strength of fibres along with a significant increase in the IFSS can result in a stronger composite. Data on composites after treatment of fibres are rare in the literature since a perfect control of manufacturing is yet to be achieved.

6.3.3 Effect of treatments on fibres wetting

Dynamic tests of capillary wicking on fabrics have been performed [19,24]. The sample holder in which fibres were placed consists of a hollow cylinder with an inner radius R of 6 mm and a height H of 20 mm. A piston at the upper end and a screw cap at the lower end of the cylinder ensure compaction of fabrics and no change in the sample volume. It is thus possible to control the global volume fibre ratio V_f from which the relative porosity $\varepsilon = 1 - V_f$ can be calculated. A vessel filled with test liquid moves up to the detection of the sample holder and the mass gain over time is recorded. More details of sample preparation to perform wicking in x-direction and sample holder design were given in literature [24].The conventional Washburn equation (Eq. 6.10) can be adopted to fit experimental data of wicking if the square of mass gain recorded during tests has a linear trend. Knowing the linear square mass variation over time $m^2(t)$, the apparent wetting properties of the porous medium are easily derived from Eq. (6.10). More precisely, the geometric porous medium factor $C(\mathrm{m}^5)$ and the geometric product $c\vec{r}(\mathrm{m}^5)$ are determined using n-Hexane, a totally dispersive liquid for which the apparent advancing contact angle is supposed to be 0 degree. Then the apparent advancing contact angle θ_a is determined with another liquid.

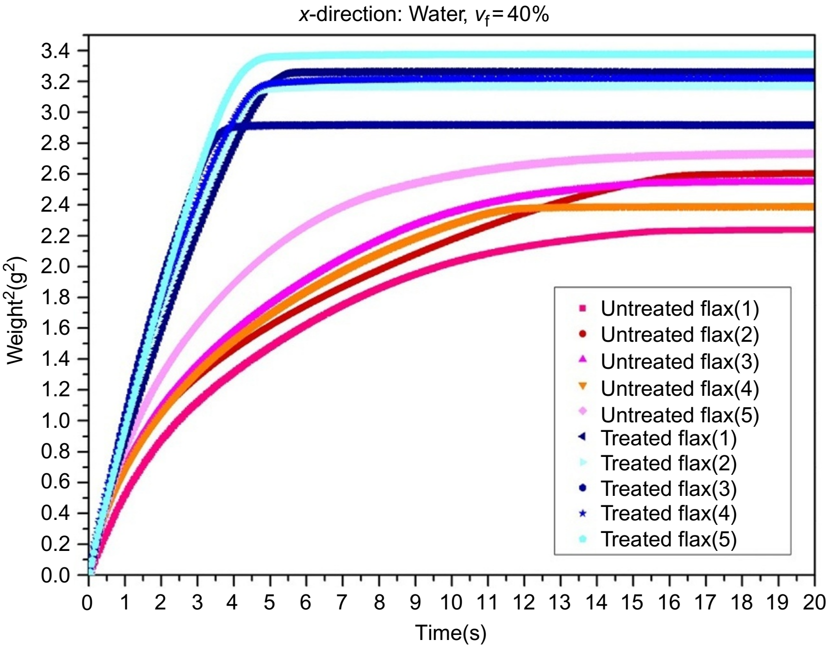

Fig. 6.6 Squared mass gain in samples of both thermal treated and untreated flax fabrics during wicking.

Fig. 6.6 presents tests on untreated and thermal treated flax fabrics, five for each type of fabrics, carried out with water for a fibre volume ratio of 40%, in order to determine an apparent advancing contact angle θ_a. This parameter is required to estimate the capillary pressure P_{cap} described in literature [19,24]. In this case, a relevant influence of treatment on flax reinforcements was observed on wicking (Fig. 6.6). It is clear that the linear fit of curves with the conventional Washburn equation is possible only for treated fabrics. Untreated reinforcements show a different trend. Differences in wicking are due to sensitivity to water that induces swelling in untreated flax fibres, while this effect is not relevant for treated fabrics that were found to be less hydrophilic [15,19]. Swelling of flax fibres causes an increase of fibre volume ratio (i.e. a decrease of porosity ε and of the mean pore radius $\vec{r}$) during wicking [19]. This modification is not considered in conventional Washburn equation. Moreover, the swelling effect is higher when the fibre volume ratio increases [19] and the equilibrium weight is lower than for treated flax. Untreated flax fabrics do not show a linear trend and achieve the equilibrium weight more slowly, that is due to the decrease of pore radius as a result of swelling and the capillary rise rate, according to Washburn theory [5,24]. Those curves, and especially the equilibrium weight, prove that the mass gain due to water in fibres themselves (including both mass absorbed by fibres and liquid that is eventually in lumens) can be neglected compared to the pore radius modification, implying a diminution of the equilibrium weight [19]. It is obvious that treated fibres lead to higher equilibrium weight. Since the morphology is the same and the fibre volume ratio is unchanged, it is reasonable to neglect the mass of water absorbed by untreated flax. To verify if this difference in wicking is actually due to swelling and if the assumption that treated fibres are less sensitive to humidity is valid, tests on elementary fibres were conducted [19].

In order to assess the sensitivity to water sorption, fifteen tests of swelling were carried out on treated and untreated elementary flax fibres with an optical method [19]. Three measurements of diameter were carried out on every fibre, in dry and wet conditions, and for each fibre the mean swelling ratio R_{SW} was calculated with Eq. (6.14):

$$R_{SW} = \frac{D_{f,fin}}{D_{f,ini}} \tag{6.14}$$

where $D_{f,fin}$ is the fibre radius after swelling in water and $D_{f,ini}$ the initial one.

Fig. 6.7 shows the results of swelling tests with water for untreated and treated fibres. The large variability of diameter (typical for elementary flax fibres [25,26]), and the large dispersion in swelling ratio can be clearly observed. However comparison between the two graphs in Fig. 6.7 shows that the treatment does not affect significantly the fibre morphology since the mean dry diameter of untreated flax was found to be 16.8 ± 4.7 m, and 17.5 ± 5.9 m for the treated ones. Moreover the swelling of fibres and its dispersion is lower for treated fibres. The mean swelling ratio for untreated fibres is 1.27 ± 0.13 vs 1.11 ± 0.07 for treated ones. This confirms that the treatment makes fibres less sensitive to water sorption and the swelling is less meaningful for those fibres. It can thus explain differences of wicking with water in untreated and treated fabrics.

6.4 Future trends

Main challenges that have to be faced in near future are the reliability of treatments. Indeed, those treatments can be inhomogeneous along the fibre. Moreover, there is very little information about the durability of those effects on surface properties during storage of the fabrics itself, and then during the lifetime of the composite after processing. Most of these treatments have not been raised to the industrial level and thus, fibres and composites are tested just after preparation mostly in research activities. It has been proved [27] that processing itself can modify fibres properties. So it has to be proved that the surface modification of those fibres last at least until after the manufacturing process. Then the durability of the bonding properties under composites service conditions have to be evaluated. Again, a large part of literature deals with newly formed bonds. Little information is available on the evolution of bonding between natural fibres and polymer matrix in service condition and especially in humid atmospheres.

Another significant challenge is to find reliable ways to measure the surface energy of the fibres which are not widely used currently [12,16]. Researches are ongoing to allow measurement of natural fibres surface energy with a simple method that could allow to minimize the scatter on contact angles and thus on surface energy values [12,16]. Classical methods cause very large scatters and lead to a reasonable doubt

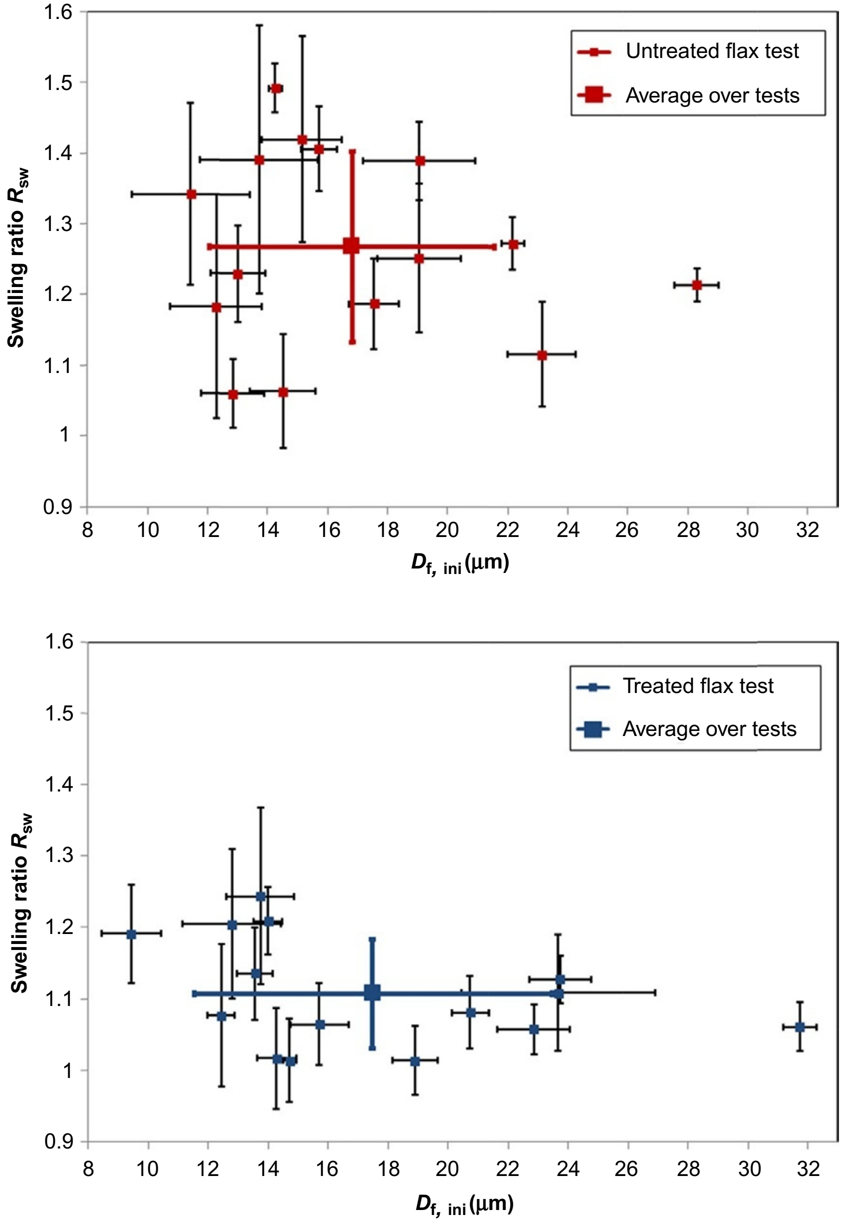

Fig. 6.7 Swelling factor against fibre initial diameter for both untreated and thermal treated fibres.

on the modification induced by the different treatments. Also, variations in fibre composition and morphology have to be taken into account to assess a reliable value of surface energy. This point should be solved in the upcoming years; the question of the durability may stay an open one for longer. At the industrial scale, fabrics or preforms have to be considered. At this scale, the morphology of the yarns and the interaction between fibres is determinant. Research is ongoing on propagating the effect of fibres surface energy modification to higher scales (the scale of the composite reinforcement first, and then the scale of the manufacturing process) [12,15,16,19,24]. It will become mandatory to take those parameters into account into robust simulation tools [28] to reliably predict the manufacturing strategy in order to obtain suitable and durable biobased composite parts.

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Environmental degradation in biocomposites

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7.1 Introduction

7.1.1 Biocomposites

The emergence of biocomposites as an alternative to petroleum-based composites has largely been due to superior technical properties along with problems associated with depleting petroleum resources and increasing environmental legislations. The biocomposite industry has found acceptance (mainly as nonload bearing structures) in the construction and automotive sector and reports suggest a projected growth rate of 22% per year [1]. Biocomposites—mainly containing natural reinforcements in a petroleum/biopolymer-based matrix possess many appealing characteristics such as high specific properties, lightweight, positive environmental impact, and biodegradable nature. However, the problems associated with biocomposites/bioplastics and in particular natural fibres are its degradation behaviour in the presence of moisture, temperature, sunlight, and microbial attack which restricts its increased use in industrial applications. Research on studies related to degradation behaviour of biocomposites in different environmental conditions is increasing indicating that it is currently a very relevant research topic.

Natural fibre reinforced composites are currently being used in the furniture, construction, and transport industry mainly in the interior and as nonstructural applications. Recent studies report on the development of natural fibre-based sandwich panels for use as side panels in aircrafts [2]. It is apparent that the use of NFC for exterior applications is not prevalent as they face a high risk of degradation when they are exposed to outdoor elements. Another issue that is limiting the use of biocomposites in industrial applications is that there are currently no international testing standards available for assessing the durability of biocomposites. In most cases, standards for wood and synthetic fibre reinforced composites are used for biocomposites which may not be technically appropriate. Moreover ageing studies for wood-based panels for use as interior panels does not exist and most accelerated ageing techniques make use of Arrhenius equation which only takes into account temperature variations and not humidity parameters and moisture content of natural fibres [3]. As a result most of the studies related to ageing of natural fibre composites use standards for wood-based materials with simplification of test methods. The ASTM D 1037

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test on accelerated ageing consists of cycles of six treatment steps, i.e., immersion in water at 49°C for 1 h, steaming at 93°C for 3 h, freezing at −12°C for 20 h, drying at 99°C for 3 h, steaming at 93°C for 3 h, and drying at 99°C for 18 h. Several studies attempted the ageing by shortening the number of cycles [4] and eliminating certain ageing conditions [5].

The degradation behaviour is attributed to the inherent characteristics and chemical composition of natural fibres [6]. The degradation behaviour of natural fibres in composites can be related to structure and composition of natural fibres. Natural fibres comprise of cellulose, hemicellulose, lignin, and pectins. Cellulose is formed of cellulose microfibrils aligned along the length of the plant fibre and is hydrophilic. Hemicellulose comprises of a mixture of sugars and functions as a cementing material. Being hydrophilic hemicellulose can be easily hydrolysed by acids and bases.

Lignin is a mixture of complex aromatic and aliphatic hydrocarbons and gives rigidity to the plant structure. It is hydrophobic and is resistant to the attack of microorganisms. Pectins are mixture of complex polysaccharides that are present in the cell walls and nonwood parts of terrestrial plants. The function of pectin is to aid in cell wall extension and plant growth. In natural fibres, the responsible constituent for water uptake is hemicellulose. The presence of voids within the natural fibre structure also increases water absorption. As the content of hemicellulose increases, water uptake and rate of biodegradation in natural fibres increase. The component in fibres responsible for photodegradation is lignin. When biocomposites are exposed to sunlight, the ultraviolet radiation causes changes on the surfaces leading to colour fading and yellowing followed by deterioration in mechanical properties. It is the lignin present in natural fibres that mainly absorbs the UV light resulting in the formation of quinones and coloured chromophoric groups.

This chapter aims to review the different types of environmental degradation conditions that biocomposites can be exposed to. Recent studies dealing with mechanical and morphological data before and after ageing have been highlighted.

7.2 Types of environmental degradation

The response of composite materials towards different environmental factors is different. The effect of environmental factors on the performance of composite materials must be well thought in the initial stages of design and tailoring of polymer composites [7]. The short-term and long-term response of composites towards environmental factors such as temperature, moisture, and biological attack can limit the usefulness of composites by retarding their mechanical properties during service. The main types of environmental degradation that will be reviewed in this chapter are:

- Temperature and moisture

  Amongst all the different environmental factors, temperature and moisture are the most important and studies have revealed that when polymer composites are subjected to a combination of both temperature and moisture it results in a more aggressive and adverse effect on the properties of composites. Composite materials can be exposed to cryogenic temperatures, elevated temperatures, and thermal cycling between these extremes. Natural fibres in particular are susceptible to both high temperature and moisture and are the primary points of attack followed by the interface and the matrix which exhibits transitions from glassy stage to a rubbery stage at its glass transition temperature.

- Weathering

  Composites commonly used in automotive and aerospace applications are subjected to varying conditions of sunlight, rain, moisture, and humidity during their service life. The effect of weathering on properties of composites depends upon what type of materials has been used and on the presence of surface coating agents. As the effect of weathering needs to be assessed over a long period, test methods have been developed to simulate natural weathering conditions at an accelerated rate so that long-term weathering effects can be estimated in a shorter time. However, these types of accelerated weathering test results do not reflect accurate response as that of materials in actual use.
- Biological attack

  The biological attack on polymer composite materials consists of fungal growth or marine fouling. Fungal growth is only possible in moist conditions and mechanical properties are affected after long-term exposure to micro-organisms. The degradation of polymer composites due to biological factors depends on the chemistry of the composites and the presence of acidic or basic entities. Natural fibres are prone to attack by microbes and promote the rate of degradation in composites. The effect of biological attack on biocomposites is usually analysed through soil burial tests and testing in a bioreactor.

The common methods to protect biocomposites from water uptake and weathering include the use of chemical treatments on natural fibres and/or resin and bio-based coatings on composite surfaces. A review of hygroscopic ageing on cellulosic fibres and biocomposites elaborates on the different techniques for providing moisture and weathering resistance for natural fibre composites [8]. Chemical treatments on natural fibres deal with acetylation and mercerization treatments where decline in water absorption is related to changes in physical and chemical morphologies of natural fibres. Bio-based coatings on composite panels comprise of silica and furanic coatings where the hydrophobicity of the coatings play an important role in imparting water resistant characteristics to the composites. A recent study on the use of furanic-based coating on flax fabric reinforced phenolic panels was undertaken by Mokhothu and John. Composite samples with and without coating were conditioned at 90°C and 90% R.H for 3 days and water sorption and strength properties were analysed. Samples coated with furans exhibited lower water uptake and improved strength retention properties after ageing [9]. In a similar study, the researchers focused on the use of external coatings on the biocomposite panels prepared from woven flax fabric and furan based resin. The coatings were found to have good adhesion with the substrate and exhibited good properties when compared to uncoated samples [10]. Another approach is the development of superhydrophobic surfaces using nanoparticle coatings. Researchers have explored the use of nanosilica-based coatings produced by sol-gel technique for cotton fabrics. Hydrophobic properties are induced on the textile substrates by reducing surface energy and formation of covalent bonds between hydroxyl groups of nanosilica and hydroxyl groups of natural fibres.

7.3 Case studies

7.3.1 Effect of temperature and moisture

Natural fibre composites are prone to moisture uptake when exposed to humid and wet conditions. This is mainly due to the hydrophilic nature of natural fibres imparted by the cellulosic and hemicellulosic groups present in them. Water attaches onto the hydroxyl groups present in cellulose/hemicellulose and forms intermolecular hydrogen bonding with the fibres. This in turn reduces the interfacial adhesion between fibres and matrix resulting in debonding between the fibre and matrix and leads to impaired mechanical properties. The water absorption pattern in natural fibres has been reported to be 0.7%–2% after 24 h, 1.5% after a week, and upto 22% upon prolonged exposure (several months) [11]. The nature of the fibre, matrix, processing technique, and exposed surface area determine the water absorption capacity of composites.

The transport of water in polymer composites occurs via three main mechanisms:

Diffusion within the matrix

Diffusion through pores or cracks in the matrix

Capillary flow along the interface between fibre and matrix

In a study dealing with lignocellulosic fibres, flax fibres were exposed to a range of various temperatures from −40 to 140°C and relative humidities ranging between 25% and 85% in an environmental chamber. It was observed that the mechanical properties drastically decreased with hygrothermal ageing. Scanning electron micrographs revealed changes in flax fibre microstructures due to water uptake [12].

The behaviour of flax fibres and flax fibre reinforced polypropylene composites when exposed to moisture were investigated by Stamboulis et al. [13]. The authors chose two types of flax fibres: untreated green flax fibres and duralin flax fibres where flax fibres were subjected to steam or water-heating at temperatures above 160°C for 30 min in an autoclave. The fibres were placed in dessicators at different relative humidities followed by weighing the fibres at regular intervals. The authors placed the flax-PP composites in water for 60 days at room temperature and measured the water uptake. The moisture uptake and swelling of the duralin treated fibres was found to be 30% lower than that of untreated fibres. In the case of the composites, improved performance was observed for the composites containing duralin treated fibres. This was attributed to the formation of a water resistant system from the depolymerization of hemicellulose and lignin which cements the cellulose microfibrils.

Anuar et al. [14] investigated the degradability of kenaf fibre reinforced PLA biocomposites immersed in river water, tap water, and sea water. The water uptake of the samples was measured every day for 3 days. The authors made the general observation that water absorption generally depended on the amount of fibre content and water uptake increased with immersion time. In the present study, it was observed that the PLA biocomposite samples exhibited a higher water uptake when immersed in tap water.

In a similar study, the effects of long-term immersion of flax-PLA biocomposites in sea water were investigated by Le Dugiou et al. [15]. The injection moulded samples were immersed in sea water at a depth of 5 m for 2 years where temperatures ranged from 8°C to 19°C. The weight gain of the samples was periodically measured. Fig. 7.1

Fig. 7.1 Biological development on the surface of Flax/PLA biocomposite.

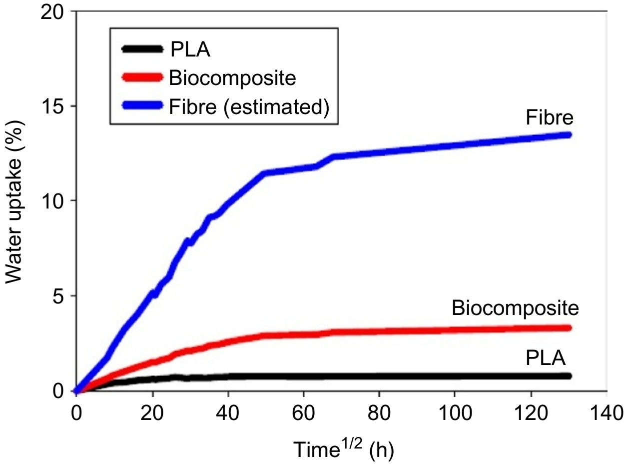

Fig. 7.2 Water uptake in PLA, flax fibre, and the biocomposite.

presents the biological development on the surface of the samples. The water uptake in the samples is shown in Fig. 7.2. It was observed that water uptake in biocomposites reaches plateau values of 3.3% within 2 months. The water uptake in fibres was theoretically calculated and the saturation weight value was found to be 12% which is in accordance with values obtained from dynamic vapour sorption [16] and gravimetric methods [8].

In a similar study, Krasowska et al. [17] investigated the degradation behaviour of two types of biocomposites in Baltic sea water. The two systems chosen were: ramie reinforced Ecoflex biocomposites and ramie fibre reinforced corn starch resin which contained cellulose nanofibers. The samples were immersed in a perforated basket and placed at a depth of 2 m in the Baltic sea. The authors observed that ramie reinforced

Ecoflex biocomposites degraded at a faster rate than the biocomposites containing cellulose nanofibres. The authors also carried out experiments in compost and observed that degradation was faster in compost when compared to sea water as the former provided an ideal environment for the growth of fungi.

Dixit et al. [18] investigated the influence of water sorption on coir fibre-epoxy composites containing fillers of cow dung, wheat husk, and rice husk. The authors immersed samples in water at 100°C for 24 h. Samples were also placed in water at room temperature for a week and the resulting changes in tensile properties were monitored. The first observation was that reduction in mechanical properties (tensile, flexural, and impact) was higher when samples were submerged in water at 100°C. Amongst all the fillers, it was observed that tensile strength decreased the maximum (60%–90%) in the case of composites containing cow dung while a reduction in the range of 30%–70% was observed for wheat husk and rice husk containing composites. The same trend was observed for impact strength with cow dung containing composites registering the maximum decrease (65%) compared to wheat husk and rice husk samples. Immersion experiments at 100°C resulted in a maximum decrease of 94% for cow dung containing composites. This was attributed to the presence of nitrocellulose in cow-dung which being hydrophilic promoted water uptake.

The effect of immersion of kenaf fibre reinforced polyester composites in different types of water solutions for 260 days was investigated by Nosbi et al. [19]. In this particular case, samples were prepared by pultrusion technique and solutions chosen were distilled water, sea water, and acidic solution at ambient temperature. The weight change of the samples was regularly monitored. The authors observed that irrespective of the type of solution, all the samples exhibited a Fickian water absorption pattern. The samples immersed in distilled water recorded the maximum moisture uptake as there was no interference to the diffusion path followed by water molecules while in acidic and sea water, the presence of acidic ions blocked the diffusion of water into the biocomposites. Samples immersed in distilled water registered the minimum decrease in compressive strength.

Polypropylene composites containing wheat flour and saw dust were immersed in brine solution and water for a period of 15 weeks and the resulting surface and mechanical properties were evaluated [20]. The authors observed that samples immersed in the brine solution exhibited maximum crazing, discolouration, and reduction in mechanical properties. This was attributed to the presence of chloride ions affecting the interfacial strength in composites. Another observation was that composites containing sawdust exhibited greater reduction in mechanical properties and higher moisture uptake. The authors attributed this to greater hydrophilic character of sawdust, however the particle size of the fillers would also have played a role.

The effect of chemical treatment of natural fibres and fillers on the water sorption has been investigated extensively. It has been noted that several chemical modification techniques such as—alkali treatment, acetylation, and cyanoethylation—have proved to reduce the water uptake in biocomposites during short-term immersion experiments. A detailed review on the hygroscopic ageing in lignocellulosic fibres and its composites has been documented by Mokhothu and John [21]. The authors are of the view that a higher level of hydrophobicity needs to be introduced to natural fibres so that they can withstand long-term environmental ageing. These include the use of bio-based coatings and development of superhydrophobic surfaces.

7.3.2 Effect of weathering

An in-depth review on the degradation behaviour of natural fibre composites under various conditions was documented by Azwa et al. [5]. The exposure of biocomposites to sunlight results in colour and weight loss and deterioration of mechanical properties which occurs due to degradation of fibres and matrix. In the case of biocomposites, both natural fibres and the polymer matrix absorb the ultraviolet rays from the sunlight. This leads to changes in the chemical structure of the polymers via molecular chain scission, surface oxidation, and breakdown of molecules to form active radicals. The main degradation processes occurring by weathering includes photoradiation, thermal degradation, photooxidation, and hydrolysis [22,23]. The effect of sunlight and oxygen on the polymers causes density gradients leading to stresses and in combination with macromolecular chain scission results in propagation of cracks. These cracks cause light diffusion leading to a whitening effect in appearance and an adverse effect on mechanical properties [24].

The lignin present in natural fibres absorbs ultraviolet radiation resulting in the formation of chromophoric groups, quinones, and hydro-peroxy radicals that cause the yellow colour associated with ageing of polymers. In the case of wood fibre reinforced polymer composites, it was observed that upon UV exposure, two competing reactions occurred namely, formation of paraquinone chromophoric structures generated by oxidation of lignin leading to yellowing and reduction of paraquinine structures to hydroquinones leading to photobleaching [25].

The photodegradation of natural fibre reinforced polymer composites depends on various factors such as amount of fibre, presence of compatibilizers, processing techniques, and weathering conditions. Generally it has been observed that oxidation rate of the composites increases with fibre content and decreases with the presence of compatibilizers. The presence of moisture along with ultraviolet radiation results in greater loss of mechanical properties and colour change. Processing techniques also affect the rate of degradation and it has been seen that biocomposites manufactured by extrusion degrade more than injection moulded composites due to the presence of a surface layer of the polymer matrix.

Natural fibre composites can be subjected to natural weathering conditions which relates to the action of the environment in which the material is subjected to during its service life. The behaviour of materials subjected to environmental exposure is evaluated over a duration of several years. Ageing of composites can also be studied by accelerated weathering studies where samples are placed in an ageing chamber that simulates a natural environmental condition and exposes the samples to ultraviolet radiation, heat, and moisture in a controlled manner.

Accelerated weathering studies were conducted on banana fibre reinforced PLA biocomposites in an Xenon Arc Weatherometer [26]. The specimens were subjected to specified weathering cycles of light and darkness [3.8 h light and 50% relative humidity, 1 h dark and 95% RH at 38 black panel temperature]. The samples were taken out at intervals and tested for tensile and impact properties. The main observations were that after weathering the tensile strength of PLA and PLA biocomposites decreased by 45% and 53%, respectively. However it was observed that composites containing nanoclay exhibited lower reduction rate in tensile strength. This was attributed to the fact that nanoclay penetrates into the microvoids at the PLA-banana fibre interface and prevents the weakening of the interface. A similar trend was observed in the case of impact strength. The surface of the biocomposites also exhibited blisters after weathering while the composite containing nanoclay displayed microcracks.

In another study [27], poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)/poly(butylene adipate-*co*-3-terephthalate) (PHBV/PBAT) biocomposites containing nanoclay were subjected to alternating cycles of UV light, rain, and dryness according to ISO standards. After weathering the samples were tested for thermal stability and changes in colour. The authors observed that all the samples [100/0: PHBV/0, 0/100:0/PBAT, 50/50: 50PHBV/50PBAT, 50/50/OMMT: 50PHBV/50PBAT/3Organomodified montmorillonite, 50/50/OMMT/P1: 50PHBV/50PBAT/3Organomodified montmorillonite/Propolis siccum extract, 50/50/OMMT/P2: 50PHBV/50PBAT/3Organomodified montmorillonite/Propolis powder with SiO_2, 50/50/OMMT/IR: 50PHBV/50PBAT/3Organomodified montmorillonite/Irgaguard B1315 & F3000] registered a decrease in thermal stability after weathering (Fig. 7.3). Certain samples containing antimicrobial agents (propolis) showed a reduced degradation during weathering. Regarding colour change, most of the samples exhibited a slight decline in brightness and colour, however samples containing propolis changed from brown colour to a neutral shade.

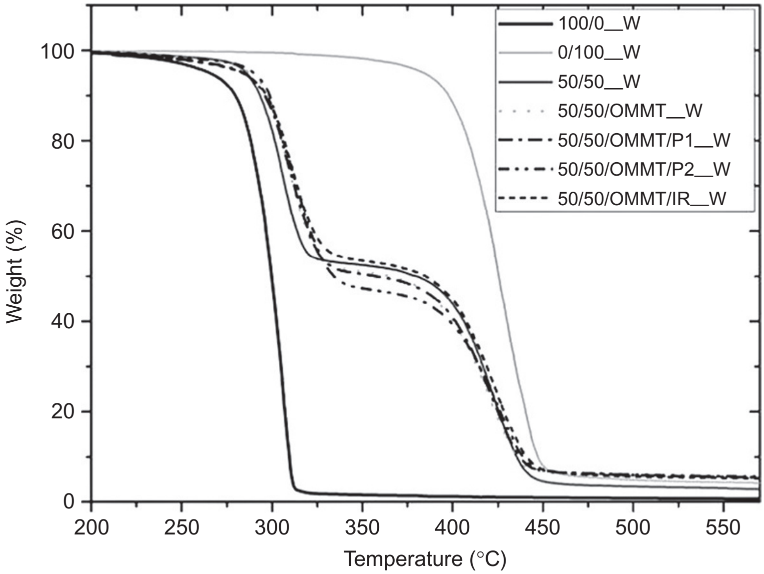

Fig. 7.3 TGA results of specimens after weathering test.

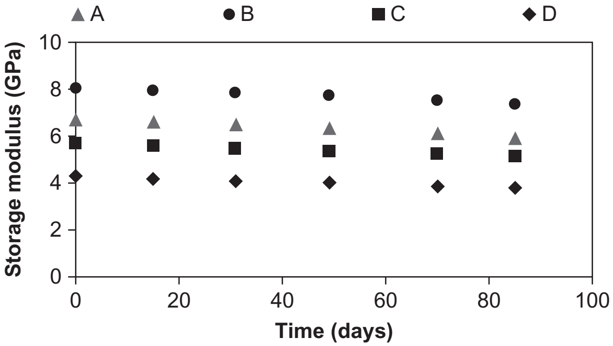

Fig. 7.4 Change in storage modulus over time for biocomposites (A) untreated hemp mat-unsaturated polyester resin (UPE), (B) acrylonitrile treated hemp mat-UPE, (C) silane-treated bi blue steam grass-$CaCO_3$, and (D) silane-treated BBSG and green flax core-$CaCO_3$-UPE.

Information on durability behaviour is very important for use in certain applications such as the building sector. A number of studies on weathering behaviour of wood-based composite samples have been documented in literature [28,29]. Mehta et al. [30] investigated the long-term effects of weathering on biocomposites (hemp fibre reinforced unsaturated polyester) used as building components. The samples were exposed to ultraviolet radiation for 2016h. The authors observed that as the exposure time of the samples to weathering conditions increased, storage modulus decreased (Fig. 7.4) and the surface roughness of the samples also increased.

Acrylonitrile butadiene styrene (ABS) samples containing four different types of fillers [carbon-black-filled, sunflower hull (SFH) and distillers' dried grains with solubles (DDGS)] were subjected to weathering under ultraviolet (UV)/condensation conditioning [31]. The authors observed that impact properties of the ABS samples containing SFH and DDGS exhibited higher property retention in comparison to neat ABS.

In a study focusing on protein-based composites, silk fibre reinforced gelatin biocomposites were subjected to alternating cycles of sunshine and condensation for a period of 60h; the authors observed a loss of tensile strength of about 70% for composites containing 30% silk fibre [32].

Researchers suggest that it is difficult to corelate data acquired from accelerated weathering experiments with natural weathering process. Though an understanding of the basic degradation mechanisms of composites is obtained, it is crucial to run natural weathering tests to obtain accurate data.

7.3.3 Effect of biological attack

Several studies measure the biodegradation in biocomposites by means of soil burial test and testing in a bioreactor. Soil burial test comprises of placing samples in soil/compost for long durations and testing the mechanical properties/dimensional changes/morphology before and after soil burial. In a bioreactor, samples are placed in a composting vessel containing a mixture of compost and the percentage of biodegradation is theoretically calculated by measuring the amount of CO_2 evolved from the composting vessel for a period of 45 days.

Silk fibre reinforced gelatine composites were subjected to soil burial for days and mechanical properties determined before and after burial. It was found that the tensile properties underwent a drastic reduction in properties with time. Another observation was that the gelatin matrix degraded from the composites within 24 h. This was attributed to the attack of microorganisms present in soil on gelatine and silk which are both natural polymers.

In another study [33], PLA composites containing oil palm empty fruit bunch fibre was compounded with a slow releasing fertilizer and was subjected to soil burial tests at a temperature of 30°C and relative humidity of 80%. The samples were recovered at different stages of degradation and weighed to ascertain the mass loss during soil burial. The surfaces of the samples were also analysed using scanning electron microscopy. The biodegradation rate of the samples containing fibres and fertilizer was found to be lower than that of neat PLA. The scanning electron micrographs depicted the changes that occurred during the degradation period. The surface of the composite samples exhibited traces of shrinkage and roughness and exposed the natural fibre bundles. The scanning electron micrographs also revealed the presence of cracks and holes which were produced by the degradation of oil palm fibres (Fig. 7.5).

Soil burial test of biocomposites from wheat gluten and rubber wood sawdust were carried out by Bootklad et al. [34]. Compression moulded samples were buried in soil for 15 and 30 days and the subsequent weight loss was measured. The authors observed that this type of green biocomposites could be degraded within 15 days. During

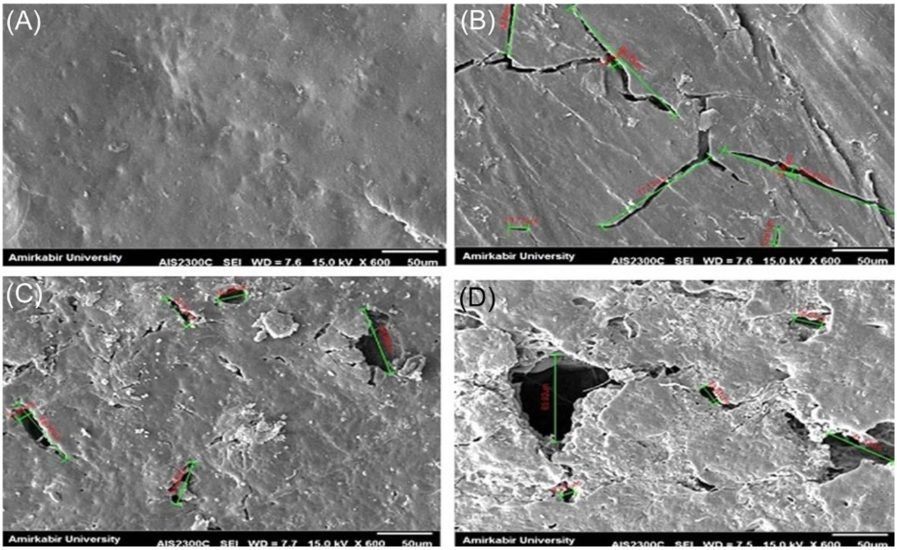

Fig. 7.5 Scanning electron micrographs, (A) PLA10/NPK15/EFB15 (0 weeks), (B) PLA10/NPK15/EFB15 (2 weeks), (C) PLA10/NPK15/EFB15 (4 weeks), and (D) PLA10/NPK15/EFB15 (8 weeks).

the first 15 days, the weight loss was attributed to the leaching of glycerol which was used as a plasticizer in the system. The authors also observed that the biodegradation rate of composites containing 20 weight percent of rubber-wood waste was slower than that of wheat gluten biocomposites.

In another study, Pantyukhov [35] investigated the biodegradation behaviour of a range of lignocellulosic filler reinforced low-density polyethylene composites. The lignocellulosic fillers included flax shives, sunflower husk, hay, birch leaves, and banana skin. Soil mixture comprising of sand, garden soil, and horse manure were prepared and samples were placed in the soil for a period of 1 year. The authors observed the greatest weight loss was in the case of hay filled composites followed by lignosulfonate, husk, banana, leaves, and shives. This was attributed to the chemical, fractional, and particle size composition of the fillers. It is generally known that fibrous particles have a larger surface area than spherical particles and in that respect, hay particles having a fibrous structure would undergo biodegradation at a faster rate and hence register the higher mass loss.

In an interesting study, samples of okra fibre reinforced corn starch composites were immersed in soil containing a variety of microbial species. The weights of the samples were monitored every week. The authors observed that increasing the weight of the okra fibres decreased the rate of biodegradation; this was attributed to the slower degradation of okra fibres when compared to corn starch matrix. Changes in morphology were also observed and a highly rough and heterogeneous surface for the corn starch matrix was observed [36].

The effect of different additives on the biodegradation of flax fibre reinforced polylactic acid composites was investigated by Kumar et al. [37]. The samples were subjected to soil burial test for long periods of time. The authors observed that biodegradation occurred at a faster rate in presence of mandelic acid (which was used as a compatibilizer) while degradation slowed down in presence of dicumyl peroxide. This was attributed to the amphiphilic characteristics of the mandelic acid. Another interesting observation was that flax composites containing nonwoven flax biodegraded at a faster rate than those samples containing woven flax.

In a study involving the use of bioreactor, the biodegradation in polycaprolactone (PCL)/eggshell (ES) biocomposite (50/50, w/w) was studied by Gonzalez Petit et al. [38] for 8 weeks, where several parameters such as temperature, moisture, soil pH, light, and anaerobic condition were monitored during composting. The morphological changes observed in scanning electron micrographs showed that the degradation process occurred mainly on the surfaces of biocomposite samples. A higher weight loss and degradation was registered for the PCL/ES samples than for pure PCL. It was observed that soil pH, heat, and an aerobic environment accelerated the degradation process, while a photo-controlled, anaerobic, and moisture-saturated environment reduced microbial activity and delayed the biodegradation process.

Similar studies were performed by Muniyasamy et al. [39] on green composites from poly(butylene-*co*-adipate terephthalate) and distillers dry grains with solubles (DDGS). The authors observed that the presence of DDGS increased the rate of degradation of biocomposites as DDGS was the preferential point of attack by microorganisms.

7.4 Conclusions

This chapter analyses the performance characteristics of natural fibre reinforced composites under various environmental conditions. The different environmental factors covered are exposure to moisture, temperature, and humidity along with weathering elements. The response of natural fibres to various weathering elements depends on the chemical composition of the fibres. Of all the environmental elements, combined exposure to moisture and temperature were found to have a drastic decline in the performance of biocomposites. This is attributed to the absorption of moisture by hydrophilic natural fibres resulting in fibre debonding from the matrix leading to a weak interface. The long-term exposure of biocomposites to sunlight results in absorption of ultraviolet radiation leading to colour change, surface roughening, and mechanical property deterioration which is further aggravated in the presence of moisture. The presence of natural fibres increases chances of biological attack (bacterial and fungal attack) and accelerates the degradation of biocomposite materials.

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In situ processing of biocomposites via reactive extrusion

8

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Abbreviations

AA	acrylic acid
ABS	acrylonitrile-butadiene-styrene copolymer
ABS-g-GMA	glycidyl methacrylate grafted acrylonitrile-butadiene-styrene copolymer
AFM	atomic force microscopy
CA	crotonic acid
CL	ε-caprolactone
CNC	cellulose nanocrystals
CP	carboxyl-ended polyester
DCP	dicumyl peroxide
DMA	dynamic mechanical analysis
EF-PLA	epoxy functionalized-PLA
EGMA	poly(ethylene-co-glycidyl methacrylate)
EPR-g-MA	maleic anhydride grafted ethylene propylene rubber
EOR-g-MA	maleic anhydride grafted poly(ethylene-co-octene) rubber
ESO	epoxidized soybean oil
ETPB	ethyltriphenyl phosphonium bromide
EVA	poly(ethylene-co-vinyl acetate)
FTIR	Fourier transform infrared spectroscopy
GMA	glycidyl methacrylate
HDI	hexamethylene diisocyanate
HIPS	high-impact polystyrene
LTI	lysine triisocyanate
LDI	lysine diisocyanate
MA	maleic anhydride
MDI	methylene diphenyl diisocyanate
mTMI	*m*-isopropenyl-α,α-dimethylbenzyl-isocyanate
PBAT	poly(butylene adipate-co-terephthalate)
pbCNC	phenylbutyl isocyanate modified cellulose nanocrystals
PBNCO	polybutadiene isocyanate
PBS	poly(butylene succinate)
PBSA	poly(butylene succinate-co-adipate)
PC	polycarbonate
PCL	poly(ε-caprolactone)
PE-epoxy	epoxy terminated polyethylene
PHB	poly(3-hydroxybutyrate)

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PHBV	poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PHBV-g-MA	maleic anhydride grafted poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	poly(lactic acid)
PLA-g-MA	maleic anhydride grafted poly(lactic acid)
PLA-g-GMA	glycidyl methacrylate grafted poly(lactic acid)
PLA-g-CNC	cellulose nanocrystal grafted poly(lactic acid)
PLA-g-PBAT	poly(butylene-adipate-co-terephthalate) grafted poly(lactic acid)
PMDI	polymeric methylene diphenyl diisocyanate
PMMA	poly(methyl methacrylate)
PO	polyolefin
PO-g-MA	maleic anhydride grafted polyolefin
POE-g-GMA	glycidyl methacrylate grafted poly(ethylene-co-octene) rubber
PP-g-MA	maleic anhydride grafted polypropylene
PP-g-VF	vinylformamide grafted polypropylene
PP-g-VTES	vinyltriethoxysilane grafted polypropylene
PVC	poly(vinyl chloride)
PVOH	poly(vinyl alcohol)
RC	reactive comb
ROP	ring-opening polymerization
SAN-g-MA	maleic anhydride grafted styrene-acrylonitrile copolymer
SAN-g-GMA	glycidyl methacrylate grafted styrene-acrylonitrile copolymer
SE	solid epoxy
SEBS	styrene-ethylene-butylene-styrene copolymer
SEBS-g-MA	maleic anhydride grafted styrene-ethylene-butylene-styrene copolymer
SEM	scanning electron microscopy
TBT	tetrabutyl titanate
TDI	toluene diisocyanate
TEM	transmission electron microscopy
TPS	thermoplastic starch
WF	wood flour

8.1 Introduction

Preparation of polymer blends and composites via melt blending is solvent-free, time-saving, and environmentally-friendly method to produce new materials with unique properties [1–3]. Main advantages of this method are reduced costs due to elimination of complicated processes (e.g., polymerization reactions, purification of final products, etc.) and application of widely available components. Wide range of possible selection of compositions can be a valuable tool for tailoring of polymer blends and composites with desired properties [4–6].

Melt blending is usually performed on extruders commonly used in industry, which allows reduction of investment costs and has a beneficial impact on diversity and versatility of this method. Continuity of the process, short cycle time, high efficiency, and suitable quality of the obtained products have made extrusion one of the fastest growing methods of polymer processing [7–9]. However, physical blending defined as simple compounding in the melt state without any chemical reactions between components, results in weak interfacial adhesion between matrix and the dispersed phase. This results in unsatisfactory performance properties of the obtained polymeric materials, which limits their industrial applications. In order to prevent such technological difficulties, most of the polymeric materials (including bio-based blends and biocomposites) require further compatibilization [10,11], resulting in enhancement of their properties. One of the most efficient methods to improve matrix-filler/fibre interfacial interactions in biocomposites is in situ processing via reactive extrusion, which involves carrying out a designed chemical reaction between the used components. Although reactive extrusion is known for many years, its application during processing of bio-based polymeric materials is a relatively new field of research. According to our knowledge, first comprehensive literature overview about reactive processing of biodegradable polymers was presented by Raquez et al. in 2006 [12] and updated in subsequent years [13,14].

Reactive extrusion can be successfully applied during in situ polymerization of biodegradable polymers [12–14], modification of biodegradable materials [15,16], or modification/functionalization of biofillers [17,18], which confirm versatility of this industrial processing method.

In the present chapter, reviews of reactive extrusion are limited to modification, functionalization, or compatibilization of biocomposites, which were categorized according to the used polymer matrix. A special attention is given to the advantages and limitations of reactive extrusion, which determine its future development.

8.2 Parameters affecting reactive extrusion

The final properties of biocomposites obtained through extrusion depend on two factors. First factor is the type of used components, which determine physico-chemical properties of the materials. It should be pointed out that used components must be in a physical form suitable for thermo-mechanical processing. Otherwise, elevated temperature and high shear forces during extrusion could cause degradation of the applied components with emission of volatile, low molecular weight compounds [19–21]. This phenomenon may cause instability during the extrusion and could significantly increase pressure inside the extruder barrel, which can be a serious threat for extruder operator.

Second factor is processing conditions during extrusion (e.g., barrel temperature, screw speed, shear forces, residence time distribution, etc.), which affect the homogeneity of produced biocomposites. Residence time distribution is the time that flowing material spends inside the extruder and can be successfully changed by variable throughput, screw speed or screw configuration. The parameters affecting the quality of biocomposites obtained via melt blending are presented in Fig. 8.1.

Exothermic character of reactions occurring during reactive extrusion indicate that mass and heat transfer should be performed with the highest efficiency, what is related to aforementioned residence time distribution and shear forces acting on the material inside barrel. The main parameters affecting shear forces generated during extrusion are: extruder construction, screw configuration, and screw speed. A comparison between a single-screw, twin-screw, and triple-screw extruder is presented in Table 8.1.

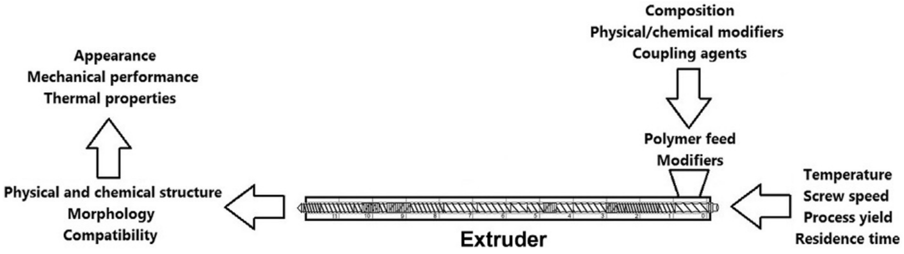

Fig. 8.1 Parameters affecting the quality of biocomposites obtained via extrusion.

Table 8.1 **Comparison between single-, twin-, and triple-screw extruder**

Item	Single-screw extruder	Twin-screw		Triple-screw
		Counter-rotating	**Co-rotating**	
Screw design	Nonmodular	Nonmodular[a]	Modular	Modular
Feeding	Fair	Good	Good	Good
Melting	Good	Good	Very good	Excellent
Distributive mixing	Good	Fair	Very good	Excellent
Dispersive mixing	Good	Very good	Very good	Excellent
Heat generation capability	Very good	Good	Very good	Very good
Pressure generation capability	Good	Very good	Good	Good
Wiping	Poor	Good	Very good	Very good
Degassing	Fair	Good	Good	Good

[a] In conical twin screw extruders.

Single- and twin-screw extruders are commonly used in industry during processing of polymers, food, pharmaceuticals, and other complex compositions. Generally, twin-screw extruders have higher melting, mixing, and devolatilization capability than single-screw extruders. This is a main reason for their more frequent use during reactive extrusion. Twin-screw extruders are classified depending on whether the screws are rotating in the same direction (a co-rotating) or in the opposite directions (a counter-rotating) and the distance between the screws (intermeshing or nonintermeshing (rarely used)). The most popular type of twin-screw extruders is equipped with co-rotating and intermeshing screws. Furthermore, screws in this type of extruders usually have modular design. This allows easy modification of screw design, which enhances flexibility of their potential applications in different branches of industry.

It is well known that melting efficiency of extruded material is correlated with the speed of plastic deformation (shear rate), which can be described as gradient of the transverse velocity dv/dy [22,23]. For twin-screw extruders approximate values of this parameter are as follows:

- for counter-rotating extruder:

$$\frac{dv}{dy} = \frac{V_1 - V_2}{S_w} \tag{8.1}$$

- for co-rotating extruder:

$$\frac{dv}{dy} = \frac{V_1 + V_2}{S_w} \tag{8.2}$$

where V_1 is the peripheral speed on outer diameter of the screw, m/s; V_2 is the peripheral speed of the screw core, m/s; and S_w is gap between screws, m.

It is clearly seen that highest values of shear rates are obtained in co-rotating twin-screw extruders. Furthermore, a co-rotating twin-screw extruder works at much higher screw speed than counter-rotating twin-screw extruder, what is related to limitation in screw distance during their construction [24]. This causes the shear rate (and the corresponding shear stress) acting on the material to be several times higher in co-rotating twin screw extruder than that in the counter-rotating one.

At present, counter-rotating twin-screw extruders are widely used for polymers with low thermal stability during processing, mainly poly(vinyl chloride) (PVC) and its copolymers. Therefore, this type of twin-screw extruders could be successfully applied for processing of selected biopolymers and biodegradable polymers characterized by low resistance to thermo-mechanical degradation. However, data published in this field are very limited [25–27].

Compared to single- and twin-screw extrusion, triple-screw extrusion is a relatively new technology. First triangle-arrayed triple-screw extruder was designed by Jiang Nan et al. in 2000 and patented in 2001 [28,29]. Researchers from Beijing University of Chemical Technology completed original conceptive plot, design, manufacture, and production of triple-screw extruders, which were successfully applied in trial industrial production in 2006 [30,31]. This new equipment for polymer processing provides advantages in compounding of polymeric blends and composites. Superior mixing performance of triple-screw extruder is due to higher efficiency in flow and mixing characteristics from traditional single- and twin-screw extruders. A comparison of free areas of flow channels between single-, twin-, and triple-screw extruders is presented in Fig. 8.2. As observed, in triple-screw extruder free area in the centre region is variable during screw rotation and calculations showed that the ratio of area change is 6:1. This characteristic makes the melt flowing through the gap between screws experience an extensional flow field. In minimal area of centre region, high pressure acts on the extruded material, while further increase of area in the centre region reduces this effect. Consequently, when the area of centre region is maximal, the impact of screws pressure on the polymer melt is negligible due to its relaxation. This phenomenon increases residence time

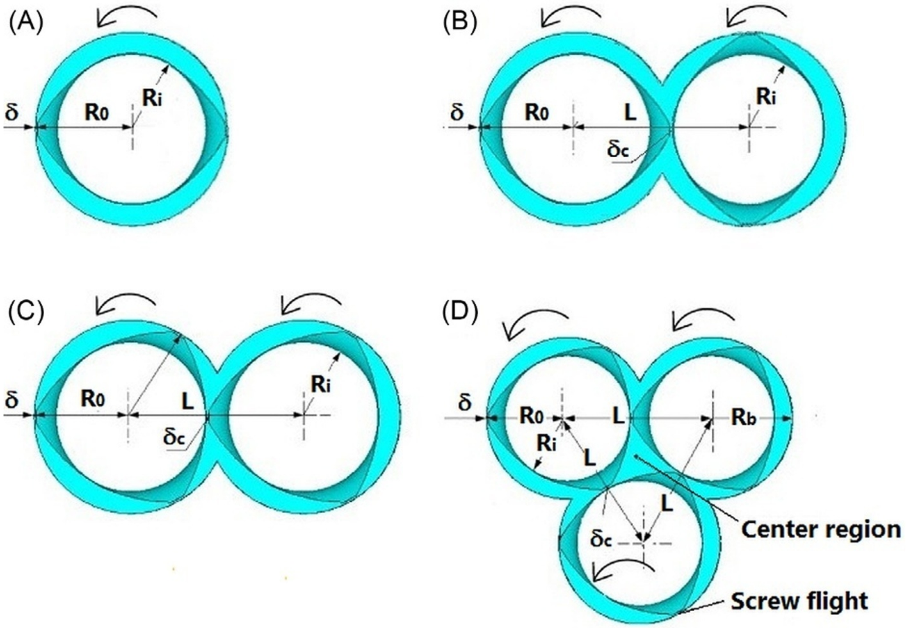

Fig. 8.2 A comparison of free area of flow channel between: (A) single-screw, (B) twin-screw (double-flight), (C) twin-screw (triple-flight), and (D) triple-screw extruder
Reproduced with permission from Elsevier – licence number 3954300163729 Ref. [Zhu XZ, Yuan HQ, Wang WQ. Numerical simulation of flow characteristics in new co-rotating triangle arrayed triple screw extruders. J Mater Process Technol 2009;209:3289–99].

of polymer inside the barrel and outperforms shear flow acting on the processed material [32]. Triple-screw extruders have higher efficiency of plasticization and mixing than co-rotating intermeshing twin-screw extruders [33]. This indicates that triple-screw extrusion is suitable for processing of high viscosity polymers or polymers with higher content of fillers [34]. Furthermore, according to published data, in triple-screw extruders the power consumption is 1.5 times of twin-screw extruders, while simultaneously their productivity is around 1.3 times higher than in twin-screw extruders [35].

Despite the above mentioned advantages of triple-screw extrusion compared to single- or twin-screw extrusion, research about its application in polymer technology are still very limited [36–38] due to its high costs related to complicated screw geometry and barrel construction. Therefore, this type of extruder is not commonly available in research laboratories. However, recently triple-screw extruders were successfully applied for preparation of microcellular poly(lactic acid)/talc biocomposites [39], poly(lactic acid)/poly(vinyl alcohol) blends [40], or poly(lactic acid)/poly(ethylene glycol) porous scaffolds [41–43]. To the best of our knowledge, reactive processing using a triple-screw extrusion is currently unknown, however its application in this field should be developed in near future.

8.3 State of the art in reactive extrusion of biocomposites

The economic and environmental factors, related to limited petroleum resources, growing amounts of polymer wastes, and higher awareness of the society influenced the dynamic development of bio-based polymer blends and composites. However, their impact on the environment is usually variable and depends mainly on polymer matrix, fillers, or other additives (e.g., cross-linking agents, stabilizers, etc.) used during their preparation. Therefore, bio-based polymer blends and composites can be classified in three ways. First classification is based on the origin of polymer matrix, as natural and synthetic polymers. Second classification is related to biodegradability of the biocomposites, which can be fully, partially, or not biodegradable. The last classification is based on content of renewable components in biocomposites, which can be prepared from petroleum-based, partially or fully bio-based components [44–46]. Based on the above mentioned classifications, we describe the state of the art of reactive extrusion according to used polymers and their biodegradability, including biodegradable and partially biodegradable polymer blends and composites.

8.3.1 Ring-opening polymerization of biodegradable polyesters

Reactive extrusion can produce polymers with high molecular weight since it is able to overcome polymerization problems in bulk polymerization such as long mixing and inefficient heat transfer during reaction, which significantly delays the chain growth. Continuous development in construction of extruders and their additional equipment (e.g., new screw elements, extrusion dies, gear pumps, feeding systems, etc.) help reactive extrusion to be successfully applied for many high conversion polymerization processes, including synthesis of biodegradable polymers. In this field, the most promising route is using reactive extrusion for synthesis of biodegradable aliphatic polyesters following ring-opening polymerization (ROP) of lactones [47–49]. In the literature, different metal-based catalysts were applied to perform ROP via reactive extrusion. For example, Mercerreyes et al. [49] showed that poly(ε-caprolactone) (PCL) with high molecular weight ($M_n = 200{,}000$ g/mol) can be produced by reactive extrusion in presence of aluminium triisopropoxide catalyst where the residence time in extruder barrel was about 5 min.

Bonnet et al. [50] reported comparative study between bulk polymerization and reactive extrusion polymerization in a twin-screw micro-extruder. The authors investigated the possibility of the synthesis of the polylactide (PLA) using five different metal catalysts; $Mg(BH_4)_2$, $Ca(BH_4)_2(THF)_2$, $Nd(BH_4)_3(THF)_3$, $Sm(BH_4)_3(THF)_3$, and $La(BH_4)_3(THF)_3$. The obtained results indicated that all five catalysts show good activities reaching ~77% conversion in 20 min in the case of bulk polymerization and ~73% conversion in 20 min in the case of reactive extrusion. The authors showed that reactive extrusion can form macrocyclic structure with molecular weight up to 30,000 g/mol with narrow molecular weight distribution (1.23–1.79). Furthermore, it was demonstrated that application of $La(BH_4)_3(THF)_3$ as catalysts allows to reduce the reaction temperature to 130°C, while reactive extrusion polymerization of lactide being usually conducted at 185°C. This could open new way to synthesize of macrocyclic polyesters via continuous process, however the scale-up of the reaction on a high-output extruder is in progress.

Kim et al. [51] performed continuous polymerization of ε-caprolactone (CL) using a co-rotating twin-screw extruder. The authors studied the influence of different variables, such as the screw speed, throughput, and ratio of ε-caprolactone to the initiator, on the molecular weight of the obtained PCL. The authors showed that reactive extrusion conditions have crucial impact on mechanical degradation of the synthesized PCL and consequently on decreasing of the final molecular weight of the polymer. The presented results showed that higher molecular weight PCL can be obtained at higher screw speed and flow rate, which is related to reduced residence time of material in the extruder. Furthermore, it was observed that longer chains of PCL (synthesized at high ratio of ε-caprolactone to the initiator) are more liable to be mechanically degraded due to high shear forces generated inside extruder barrel.

Very interesting and novel route for preparation of biodegradable polyester is enzymatic reactive extrusion employing ring-opening polymerization. This kind of polymerization has been recently described by Spinella et al [52]. Authors have successfully used immobilized enzyme-catalysts instead of metal catalysts to obtain high molecular weight ω-pentadecalactone. In particular, immobilized *Candida antarctica* Lipase B was used at high temperature (in range from 90ºC to 130ºC) to get high molecular weight polyester. The efficient mixing by reactive extrusion in presence of immobilized enzyme-catalysts lead to shorter reaction time, lower reaction temperature, and results in higher molecular weight polyester.

However, it should be pointed out that research works published in the field of ring-opening polymerization of biodegradable polyesters are still very limited. This is due to the complexity of technological operations during combined polymerization and extrusion processes, which are very difficult to control (even in the laboratory). Most of the technical problems in this field are related to precise, repeatable, and constant feeding of used components characterized by different physico-chemical properties (e.g., physical form (gas/solid/liquid), viscosity, chemical stability, etc.) and optimization of their processing conditions. The appropriate solutions to these issues need a lot of time consuming experimental efforts performed on very advanced and expensive equipment, which limits the application of this technology in industry, especially by small and medium companies.

8.3.2 Biodegradable polymer blends and composites

In the field of biodegradable polymeric materials processed via reactive extrusion, commercial aliphatic polyesters such as poly(lactic acid) (PLA), poly(ε-caprolactone) (PCL), poly(3-hydroxybutyrate) (PHB), poly(butylene-adipate-co-terephthalate) (PBAT), poly(butylene succinate) (PBS), and thermoplastic starch (TPS), were extensively studied due to high interest in developing biocompatible and biodegradable polymer blends. In this chapter we present selected examples of biodegradable polymer blends and composites obtained via reactive processing.

8.3.2.1 Aliphatic polyester blends and composites

Recently, Yang et al. [53] proposed new, green, and industrially viable two-step method of in situ processing of blends of two commercially available aliphatic polyesters, poly(3-hydroxybutyrate) (PHB) and poly(lactic acid) (PLA). The first step consists of controlled thermal degradation of PHB in an extruder to form PHB oligomers with functional end-groups suitable for further reactions. As shown in Fig. 8.3, PHB can thermally degrade to crotonic acid (CA) which results in PHB oligomers with crotonate end groups. These groups are able to covalently link with methanetriyl carbon in the main chain of PLA during reactive extrusion in second step process, as presented in Fig. 8.4.

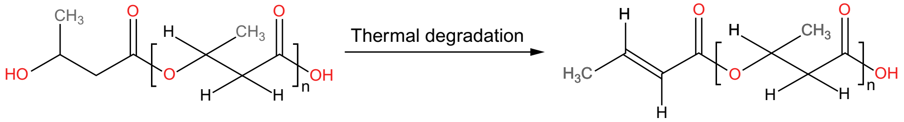

Fig. 8.3 Schematic presentation of the thermal degradation of PHB to oligomers with crotonate end group.
Scheme based on [Yang X, Clénet J, Xu H, Odelius K, Hakkarainen M. Two step extrusion process: from thermal recycling of PHB to plasticized PLA by reactive extrusion grafting of PHB degradation products onto PLA chains. Macromolecules 2015;48:2509–18].

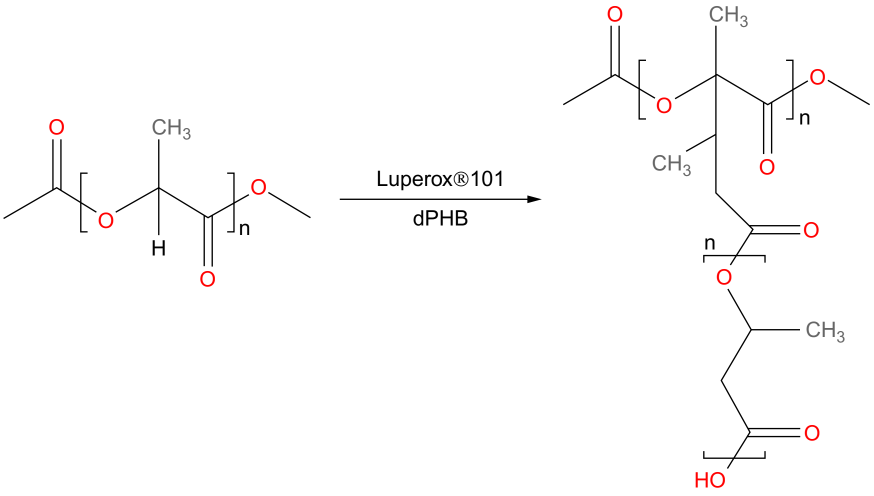

Fig. 8.4 Schematic presentation of the most likely grafting of the thermally degraded PHB with unsaturated end groups to the main chain of PLA.
Scheme based on [Yang X, Clénet J, Xu H, Odelius K, Hakkarainen M. Two step extrusion process: from thermal recycling of PHB to plasticized PLA by reactive extrusion grafting of PHB degradation products onto PLA chains. Macromolecules 2015;48:2509–18].

The 2,5-dimethyl-2,5-di(tert-butylperoxy)-hexane organic peroxide, known under trade name Luperox 101, was used as radical initiator for the reactive extrusion. The results indicate that PHB/PLA blends prepared by reactive extrusion showed higher mechanical properties than nonreactive processed blends. In particular, when 20 wt% thermally degraded PHB was added to PLA matrix, high elongation of 538% was reached, which is 66 times higher than the elongation of pure PLA.

Dong et al. [54] examined PHB/PLA blends dynamically cured with dicumyl peroxide (DCP). Branching and partial cross-linking occurred in PHB/PLA blends during reactive processing. This suggests that use of DCP as cross-linking agent significantly enhanced the compatibility between PLA and PHB phases and improved performance of the studied blends. Wei and McDonald [55] proved that addition of DCP (in range: 0.25–1 wt%) to PHB/PLA blends increased their cross-link density. This lowers the glass transition temperature, melting temperature, and degree of crystallinity for the studied blends. Furthermore, it was noticed that cross-linking of PHB/PLA blends with DCP improves their melt strength and thermal stability, which have beneficial influence on their further thermo-mechanical processing. Ma et al. [56] used DCP as a free-radical initiator during in situ compatibilization of poly(lactic acid) and poly(butylene adipate-co-terephthalate) (PLA/PBAT) blends. The authors showed that addition of DCP initiated free radicals in the blends leading to complicated products such as PLA-g-PBAT copolymers. These copolymers can act like interface compatibilizers between PLA and PBAT, which improve mechanical properties of PLA/PBAT blends. For example, notched Izod impact strength for PLA/PBAT blends after in situ compatibilization with DCP was 110 J/m, while this value for pure PLA/PBAT blend was only 60 J/m. The research about PHBV/PBS and PHB/PBS blends compatibilized using DCP was presented in work [57]. The tensile strength, impact toughness, and elongation at break of PHB/PBS blends increased after their in situ compatibilization with DCP. This is due to considerable reduction in PBS particle size and a significant improvement of the interfacial adhesion between the PHB and PBS phases confirmed by microstructure analysis using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Semba et al. [58] evaluated the effect of DCP cross-linking on the structure and mechanical properties of PLA/PCL blend. The schematic diagram of PLA/PCL blend (in ratio 70/30) compatibilized with DCP is shown in Fig. 8.5. It can be seen that the diameter of the PCL particles decreased with higher content of DCP during in situ compatibilization, which corresponds to improvement of mechanical properties of PLA/PCL blend. The authors suggest that mechanical properties of PLA/PCL blend in ratio 70/30 modified with 0.3 phr of DCP are comparable to those of popular engineering polymers such as acrylonitrile-butadiene-styrene (ABS) and high-impact polystyrene (HIPS).

Signori et al. [59] used DCP for modification of commercial aliphatic polyesters blend (based on PLA and PBAT) with trade name Ecovio from BASF. Authors indicated that besides free radical promoted radical chain branching and cross-linking of PLA/PBAT blend, transesterification mechanism may occur during processing at high temperature. This phenomenon promotes polymer chains rearrangements to form linear, soluble PLA-PBAT covalently bound chains, which may also act like a compatibilizer in the examined blend. Based on above presented data, schematic diagram of interactions between two different aliphatic polyesters in situ compatibilized with DCP is presented in Fig. 8.6.

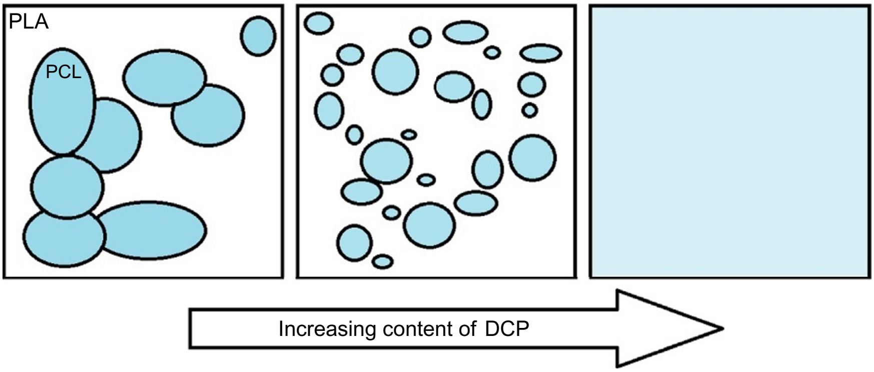

Fig. 8.5 Schematic diagram of PLA/PCL blend (in ratio 70/30) compatibilized with DCP. Scheme is adapted based on [Semba T, Kitagawa K, Ishiaku US, Hamada H. The effect of crosslinking on the mechanical properties of polylactic acid/polycaprolactone blend. J Appl Polym Sci 2006;101(3):1816–25].

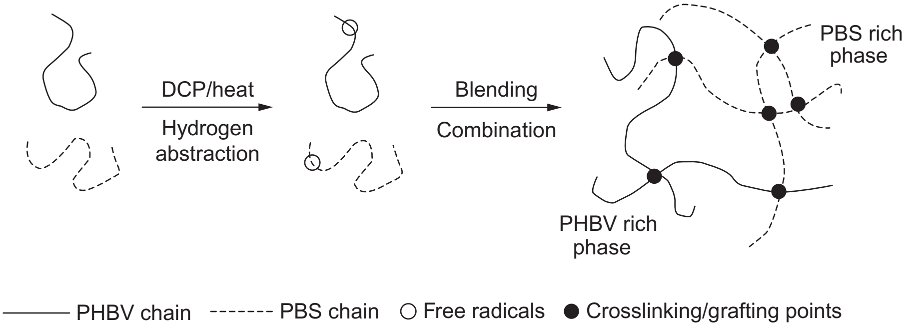

Fig. 8.6 Schematic illustration of the in situ compatibilization of aliphatic polyester blends using dicumyl peroxide (in presented case PHBV/PBS blends).
Scheme is adapted based on [Ma P, Hristova-Bogaerds DG, Lemstra PJ, Zhang Y, Wang S. Toughening of PHBV/PBS and PHB/PBS blends via in situ compatibilization using dicumyl peroxide as a free-radical grafting initiator. Macromol Mater Eng 2012;297(5):402–10].

Recently, DCP was successfully applied to improve interfacial adhesion in poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/lignin biocomposites [60] due to the formation of PHBV-g-lignin copolymer and decrease of biocomposites' crystallinity related to grafting. The probable mechanism of the reaction between PHBV, lignin, and DCP is presented in Fig. 8.7.

Dhar et al. [61] described a single step reactive extrusion process for fabrication of thermally stable, polylactic acid grafted cellulose nanocrystal (PLA-g-CNC) nanocomposites modified with DCP as cross-linking agent. This methodology is a novel approach for fabricating CNC-reinforced-PLA nanocomposites that can be easily recycled and reused for multiple cycles. The scheme of reactions occurring during manufacturing of PLA-g-CNC is presented in Fig. 8.8.

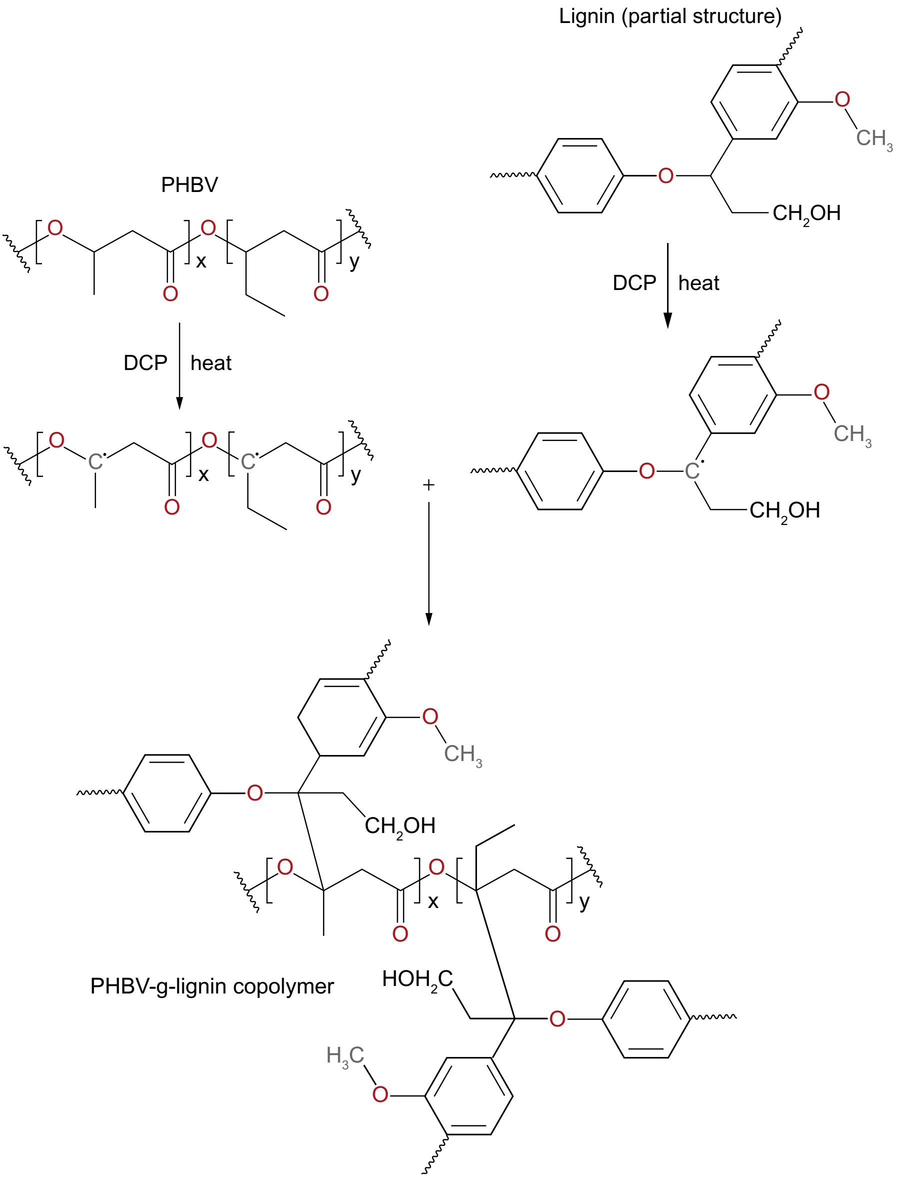

Fig. 8.7 Possible reactions between PHBV, lignin, and DCP.
Scheme based on [Luo S, Cao J, McDonald AG. Interfacial improvements in a green biopolymer alloy of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) and lignin via in-situ reactive extrusion. ACS Sustain Chem Eng 2016;4(6):3465–76].

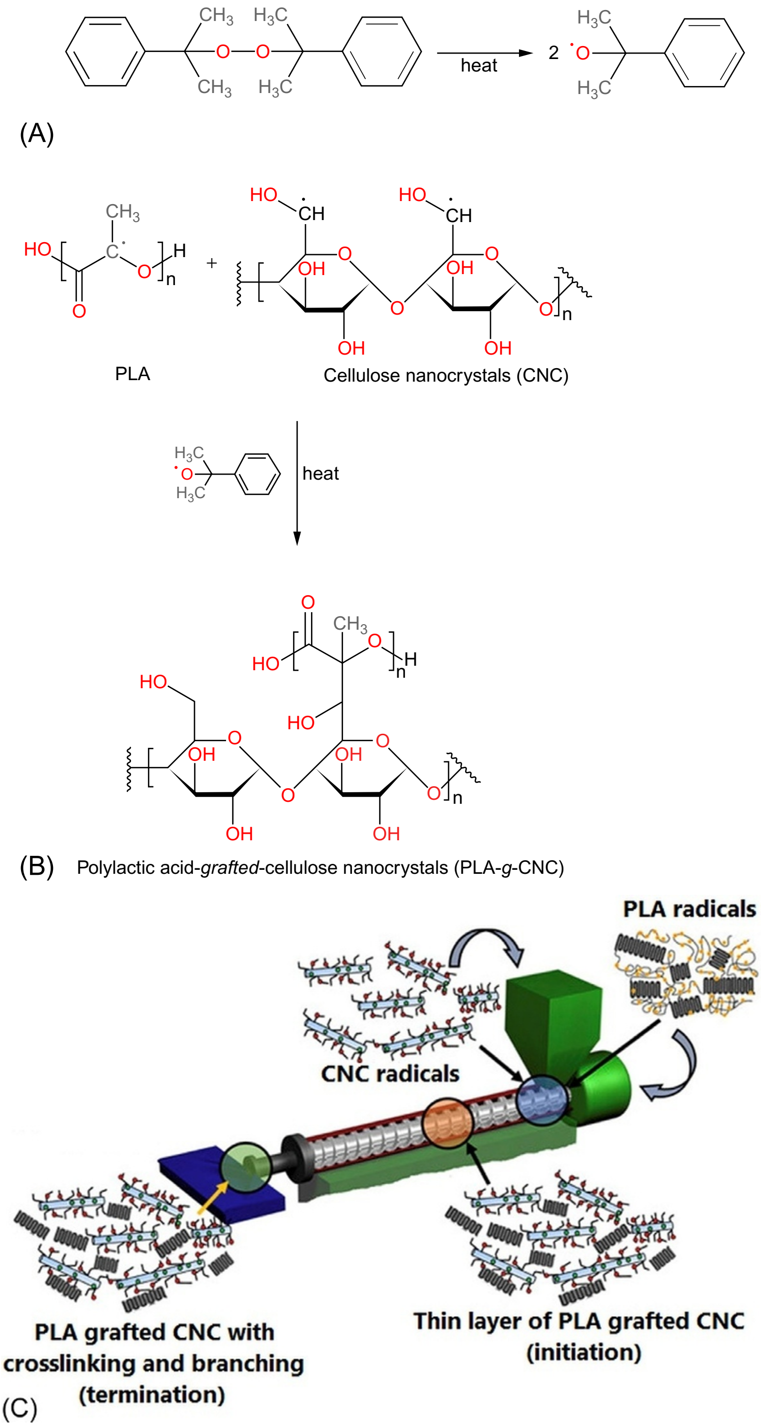

Fig. 8.8 See figure legend on next page.

On the other hand, the results presented in work [62] indicate that using DCP is an ineffective way to improve interfacial adhesion between PLA and short flax or hemp fibres. These opposite conclusions can be related to complexity of chemical reactions between PLA, natural fibres, and DCP occurring during reactive extrusion. Moreover, diversity of physico-chemical characteristics of natural fibres/fillers has significant impact on the interfacial interactions in biocomposites [63,64].

Chikh et al. [65] examined PHBV/PBS blends and PHBV/PBS/sepiolite nanocomposites compatibilized with maleic anhydride grafted poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV-g-MA). Presented results highlighted that interfacial interactions between PHBV and PBS are enhanced due to synergistic effect of chemical compatibilizer (PHBV-g-MA) and sepiolite nanofiller, which could be applied during further research in the field of reactive extrusion.

Zhang and Zhang [66] showed recently that thermal stability, static, and dynamic mechanical properties of PBS/PLA blend can be successfully improved by reactive processing with DCP and PBS-g-cellulose nanocrystals. This is due to the limited molecular segmental mobility of PBS/PLA matrix related to its cross-linking with DCP and physical bonding with PBS-g-cellulose nanocrystal as reinforcement filler.

In work done by Sajna et al. [67] the combined impact of nanoclay and glycidyl methacrylate grafted poly(lactic acid) (PLA-g-GMA) on the thermal and flammability properties of PLA/banana fibre biocomposites was evaluated. Obtained results indicated that the PLA-g-GMA and nanoclay in PLA/banana fibre biocomposites enhanced their thermal stability and resistivity towards the flame due to formation of a protective surface layer.

Lin et al. [68] studied morphology and mechanical properties of PLA/PBAT blends compatibilized by transesterification during melt-extrusion. Tetrabutyl titanate (TBT) at varying concentrations was applied as transesterification catalyst. It was proved that incorporation of TBT in PLA/PBAT blends improved significantly their toughness and stiffness. This method could find application during processing of biocomposites.

Eslami and Kamal [69] prepared poly(lactic acid)/poly(butylene succinate-co-adipate) (PLA/PBSA) blends in the presence of commercial chain extender with trade name CESA Extend, which is multifunctional epoxy-based copolymer produced by Clariant. The linear viscoelastic properties showed that the chain extender promoted the development of chain branching in PLA/PBSA blends. On

Fig. 8.8 (A) Mechanism of thermal decomposition of the DCP into peroxide radicals during extrusion at T = 180°C (initiation step), (B) Generation of CNC and PLA radicals followed by reactive extrusion at screw speed = 50 rpm and recycle time = 2 min (propagation step) leading to the formation of PLA grafted CNC structures (termination step), and (C) Pictorial representation of the grafting mechanism of initiation, propagation, and termination of the reactive extrusion process for PLA-g-CNC along the different zones of the extruder. Reproduced with permission from Elsevier – licence number 3951161193447 Ref. [Dhar P, Tarafder D, Kumar A, Katiyar V. Thermally recyclable polylactic acid/cellulose nanocrystal films through reactive extrusion process. Polymer 2016;87:268–82].

the other hand, the effect of chain extender on the elastic modulus and elongation at break was negligible. Consequently, used chain extender enhanced ductility and melt strength of PLA/PBSA blends, which made this blend more suitable for many applications. Similar observations were also described by Arruda et al. who used commercial chain extender Joncryl (BASF) in PLA/PBAT blends [70].

Mirzadeh et al. [71] modified PLA/PBSA biocomposites with CESA Extend chain extender and nanoclay Cloisite 30B from Southern Clay Products, Inc. It was observed that nanoclay Cloisite 30B in PLA/PBSA biocomposites modified with chain extender increased the viscosity compared to the same blends without nanoclay, however a more visible effect was noticed for blends with higher PBSA content. The presence of nanoclay in PLA/PBSA blends has strong impact on the mechanical properties of the obtained biocomposites, but is simultaneously related to its barrier role to control the local concentration of chain extender in the PLA phase.

Epoxy functionalized-PLA (EF-PLA) has been used as reactive modifier for PLA and PBAT blends [72]. In this case, in situ copolymerization takes place during reactive extrusion between the epoxy groups of the EF-PLA modifiers and PBAT forming strong interphase between the blended components, which resulted in significant improvement in mechanical and rheological properties of PLA/PBAT blends. SEM analysis confirmed that addition of EF-PLA to PLA/PBAT provided better and more stable dispersion of the two phases with a more diffused and compatibilized interfaces. The schematic reaction mechanism between PLA, PBAT, and epoxy functionalized-PLA is presented in Fig. 8.9.

Harada et al. [73] studied the effect of lysine triisocyanate (LTI) content on rheological, mechanical, and morphological properties of poly(lactic acid)/poly(butylene succinate) blends. The obtained results indicated that application of lysine triisocyanate enhanced the compatibility of PLA/PBS blends, resulting in their almost 2-4 times higher impact strength compared to pure PLA. Furthermore, the results of rheological measurements and morphology analysis confirmed that LTI reacts with PLA and PBS. The scheme of possible reaction between lysine triisocyanate and terminal hydroxyl or carboxyl groups present in PLA and PBS is presented in Fig. 8.10.

Recently, Morelli et al. [74] prepared biocomposites with PBAT and phenylbutyl isocyanate modified cellulose nanocrystals (pbCNC), whose properties were compared with unmodified cellulose nanocrystals (CNC). It was noticed that PBAT biocomposites reinforced with modified CNC (pbCNC) were more homogeneous and similar to the pure PBAT. During further research in this area, the process could be performed in a one step reactive extrusion.

8.3.2.2 Aliphatic polyesters/starch blends

Zhang and Sun [75] have studied mechanical properties of PLA and wheat starch composites compatibilized by maleic anhydride (MA) in the presence of 2,5-bis(tert-butylperoxy)-2,5 dimethylhexane (L101) as radical initiator. As illustrated in Fig. 8.11, PLA free radicals induced by the radical initiator are highly reactive with MA and the anhydride groups of MA are able to react with the hydroxyl groups of

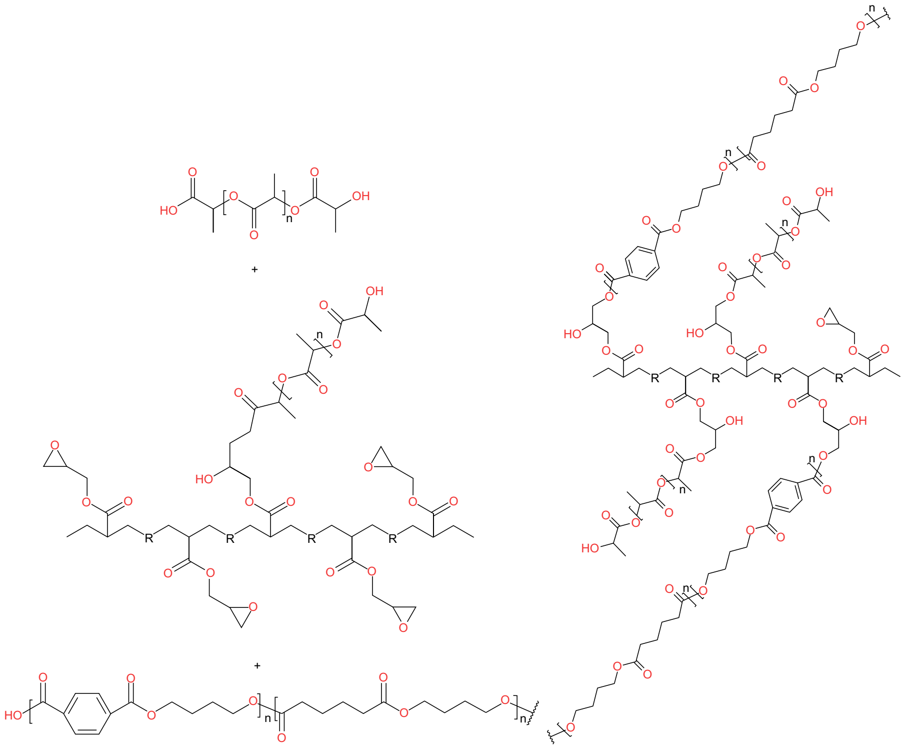

Fig. 8.9 Possible mechanism of reaction between PLA, PBAT, and epoxy functionalized-PLA. Scheme based on [Schneider J, Manjure S, Narayan R. Reactive modification and compatibilization of poly(lactide) and poly(butylene adipate-co-terephthalate) blends with epoxy functionalized-poly(lactide) for blown film applications. J Appl Polym Sci 2016;133:43310].

starch leading to ester linkages. The carboxylic groups of the hydrolyzed anhydride can also form hydrogen bonds with the hydroxyl groups of starch. Furthermore, additional hydrogen bonds can be formed between carbonyl groups of PLA and hydroxyl groups of starch.

Authors indicated that reactive extrusion of PLA/starch blends in ratio of 55/45 with 1 wt% MA (and 10 wt% L101 (MA basis)) produces biocomposites with mechanical properties (tensile strength of 52.4 MPa and 4.1% elongation) comparable to pure PLA. Hwang et al. [76] confirmed that using MA as compatibilizer is an effective way to enhance mechanical properties of PLA/starch biocomposites. Similar observations were presented in works [77,78]. Furthermore, this strategy was successfully applied for other biodegradable aliphatic polyesters and their composites [79,80].

To promote the compatibilization between PLA/starch blends, Jun [81] used methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), and hexamethylene diisocyanate (HDI) as reactive agents proving that the more effective

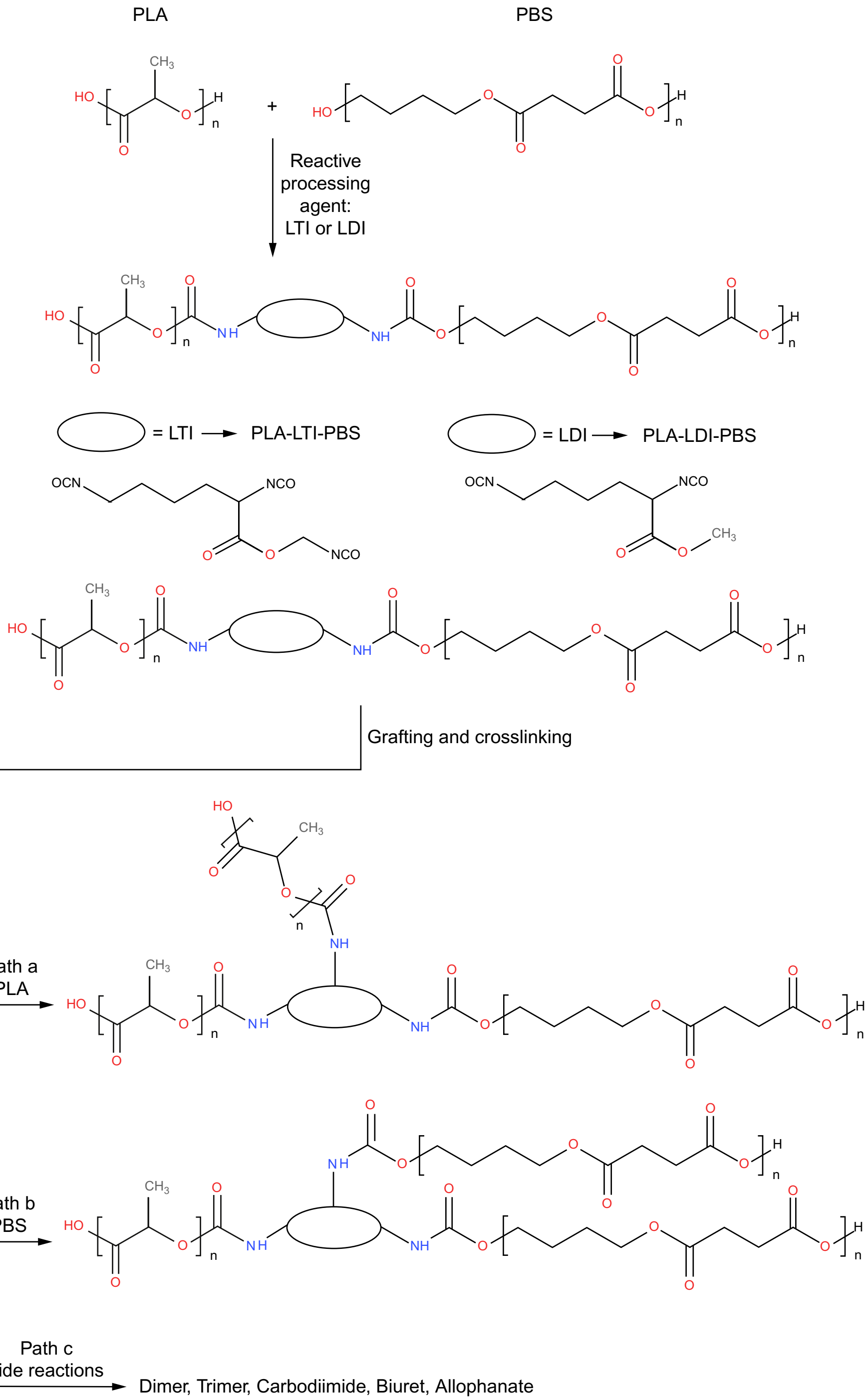

Fig. 8.10 Possible reaction between PLA, PBS, and isocyanate reactive modifier. Scheme based on [Harada M, Ohya T, Iida K, Hayashi H, Hirano K, Fukuda H. Increased impact strength of biodegradable poly(lactic acid)/poly(butylene succinate) blend composites by using isocyanate as a reactive processing agent. J Appl Polym Sci 2007;106:1813–20].

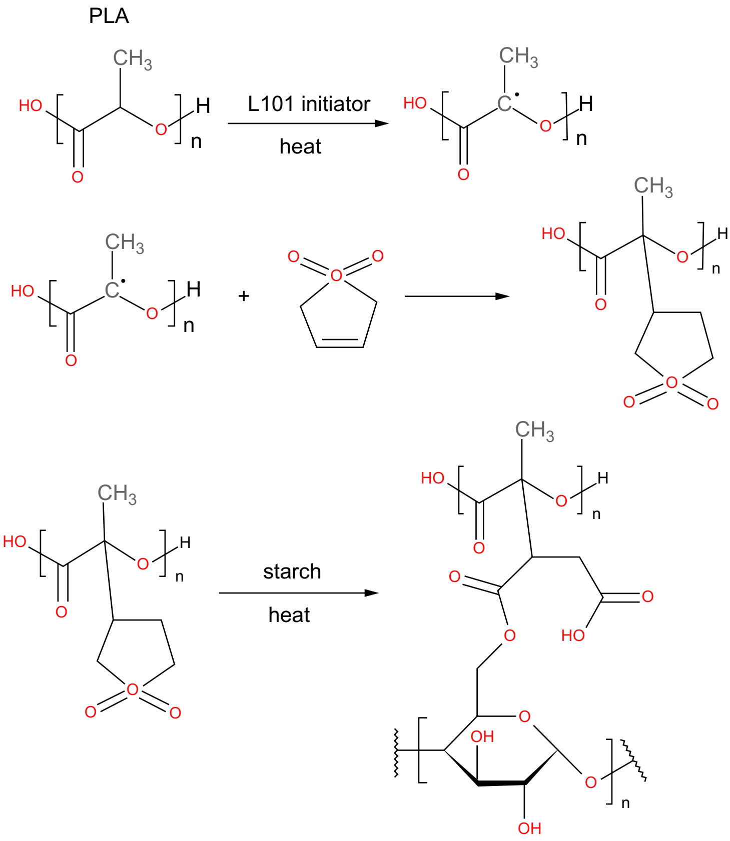

Fig. 8.11 Proposed chemical reactions between PLA, starch, MA, and initiator L101. Scheme based on [Zhang J-F, Sun X. Mechanical properties of poly(lactic acid)/starch composites compatibilized by maleic anhydride. Biomacromolecules 2004;5:1446–51].

way of preparation of reactive blends is the two-step process, in which the reactive agent was added after all other reactants. They also showed that aliphatic HDI is a more effective reactive agent for the PLA/starch blends compared to MDI and TDI. Similar observations were described by Karagoz and Ozkoc [82], who used 1,4-phenylene diisocyanate as compatibilizer of PLA/citric acid modified TPS blends. Furthermore, authors indicated that combinatorial usage of 1,4-phenylene diisocyanate and modification of TPS by citric acid enhanced dispersion of TPS particles into PLA matrix, resulting in significant improvement of the mechanical properties of PLA/TPS blends.

Epoxidized soybean oil (ESO) was employed as a reactive compatibilizer for PLA/starch blends by Xiong et al. [83]. In this particular case, the starch was grafted with maleic anhydride (MA) to enhance reactivity with ESO. Consequently, the reaction can take place between the epoxy groups of ESO, the MA groups of MA-grafted starch, and the end carboxylic acid groups of PLA forming a compatible

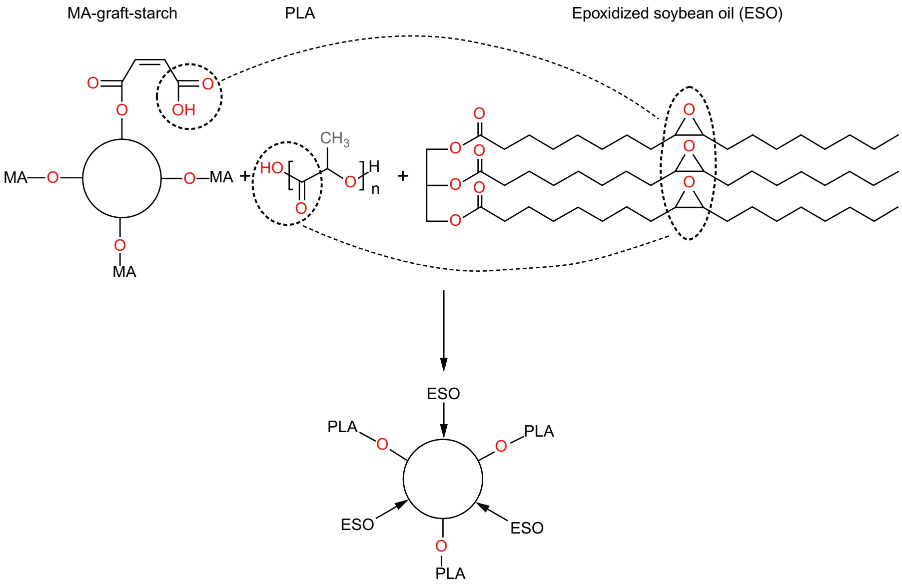

Fig. 8.12 The possible chemical reaction diagram in PLA/MA-grafted starch blends compatibilized by ESO.
Scheme based on [Xiong Z, Yang Y, Feng J, Zhang X, Zhang Ch, Tang Z, et al. Preparation and characterization of poly(lactic acid)/starch composites toughened with epoxidized soybean oil. Carbohydr Polym 2013;92:810–6].

region of PLA, MA-grafted starch, and ESO around the grafted starch, as visualized in Fig. 8.12.

Authors investigated the effect of addition of MA-grafted starch and ESO on the mechanical properties of the obtained blends. The tensile and impact properties decreased with increase of MA-grafted starch in PLA/MA-grafted starch/10 wt% ESO, which is related to decrease of interfacial adhesion between components as proved by morphological study performed using SEM measurement. In this system, ESO acted as a plasticizer to toughen PLA and also as a compatibilizer to improve the interaction of PLA and MA-grafted starch. Therefore, the increased ESO content caused plasticization of PLA and made the blends softer leading to lower tensile strength and higher elongation at break and impact strength. The addition of ESO as compatibilizer allows to improve interfacial interaction between PLA and MA-grafted starch, which leads to more brittle blends reflected in the elongation at break and impact strength.

Świerz-Motysia et al. [84] studied the effect of maleic anhydride grafted poly(lactic acid) (PLA-g-MA) on structure and performance properties of PLA/TPS blends. It was observed that PLA-g-MA had positive impact on mechanical properties of PLA/TPS blends, while their biodegradation rate decreased with an increased content of compatibilizer.

PCL/starch bionanocomposites were extensively investigated by Kalambur and Rizvi [85–87]. They proposed a procedure to fabricate this PCL/starch blends in

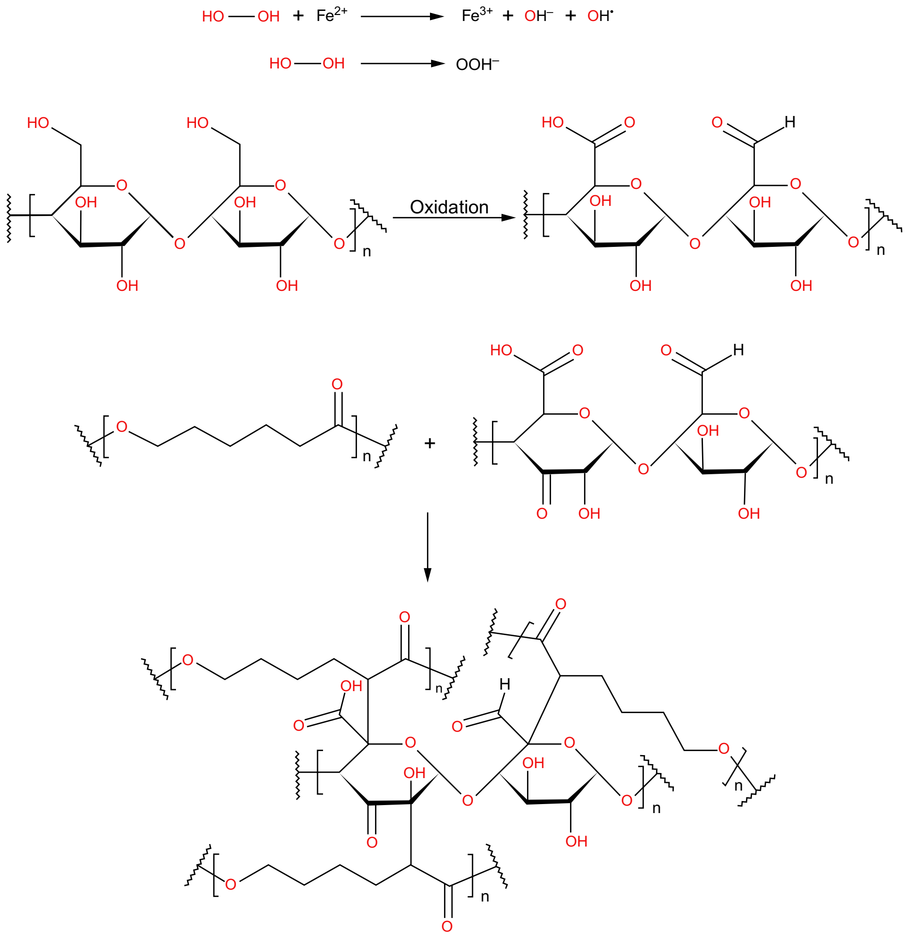

Fig. 8.13 The scheme of starch oxidation and cross-linking pathway of oxidized starch. Scheme based on [Kalambur SB, Rizvi SSH. Biodegradable and functionally superior starch–polyester nanocomposites from reactive extrusion. J Appl Polym Sci 2005;96:1072–82].

two steps but in a single extrusion process. The first step is related to oxidation of starch by the replacement of hydroxyl groups by carboxyl and carbonyl groups. Then, PCL can react with the carbonyl and/or carboxyl groups in oxidized starch through a peroxide-initiated free radical process, as shown in Fig. 8.13. Fenton's reagent (hydrogen peroxide with iron and copper catalysts) was used as the oxidizing/cross-linking agent. The single oxidizing/cross-linking agent was added in both steps.

This research group developed reactive processed PCL/starch bionanocomposites containing high amounts of starch (~40 wt%) modified by MMT nanoclay, which result in toughness and elongation properties similar to pure PCL.

Campos et al [88] investigated PCL/starch biocomposites modified with sisal fibres bleached with sodium-hydroxide followed by hydrogen peroxide treatment prepared by extrusion processing. Authors studied the influence of the addition of sisal fibres on morphology, water absorption properties, and the biodegradability of PCL/starch biocomposites. They proved that the interaction between sisal fibres and polymers increased with rise in crystallinity in the composites with fibres, confirmed also by Fourier transform infrared spectroscopy (FTIR). Biodegradation tests indicated faster biodegradation in biocomposites compared to neat PCL. Additionally, PCL/starch biocomposites modified with sisal fibres showed decrease in hydrophilic character as a positive impact of PCL and fibres.

Li and Huneault [89] used a multifunctional epoxy-acrylic-styrene copolymer with trade name CESA Extend as reactive compatibilzer of PLA/TPS blends. It was observed that CESA Extend modifier can effectively increase the viscosity of PLA/TPS blends, which improves their melt strength and further processing via variable techniques (e.g., foaming, blowing, casting, etc.). On the other hand, the application of CESA Extend modifier had only a marginal impact on the mechanical properties and morphology of PLA/TPS blends. This indicates that CESA Extend modifier reacts mostly with PLA end groups, while its reactions with TPS are very limited. Increasing molecular weight of chain extended PLA improves the stress transfer between PLA and TPS phases and leads to significant increase of ductility of PLA/TPS blends.

Bossard et al. [90] evaluated the rheological and morphological properties of PCL/formic acid modified TPS blends. Proposed blends were obtained by one-step reactive extrusion process, which allows their industrial applications in standard processing equipment and limits their thermo-mechanical degradation during prolonged (two- or more steps) processing. The presented results indicated that modification of TPS with formic acid and application of hydroxyl ended polyester oligomers significantly enhanced compatibility between PCL matrix and TPS phase.

Recently, Cardoso et al. [91] applied reactive extrusion during modification of oat hull fibres with alkaline hydrogen peroxide. This process could be fast, solvent-free, and low-cost alternative to conventional modification methods of natural fibres. The obtained modified oat hull fibres were further compounded with a PBAT/TPS blend. The presented results showed that rougher surfaces observed in the treated fibres improved their interfacial adhesion with the polymeric matrix, which surprisingly did not improve the mechanical properties or thermal stability of the studied biocomposites. This phenomenon could be explained by intense chemical process associated with high shear forces acting on the fibres during shearing. Reactive extrusion promotes weakening of the fibre structure and affecting its size and aspect ratio. On the other hand, Yang et al. [92] compared use of bleached, extruded chemo-mechanical pulp fibre (PF) and wood flour (WF) as reinforcement in PLA matrix. The mechanical tests showed that these cellulosic fillers increased the tensile and flexural moduli, but decreased the tensile, flexural, and impact strengths of the biocomposites. However, the tensile strengths of the PLA/PF composites were higher than that of PLA/WF composites, especially at lower fibre content (up to 10 wt%). This might be due to the higher aspect ratio of

PF (as noted previously), higher crystallinity, and dynamic viscosity of the PLA/PF composites, which confirmed that PF can be a more efficient reinforcement than WF in PLA matrices

Zeng et al. [93] published recent extensive work about current strategies during compatibilization in poly(lactic acid)-based blends. Presented solutions could also find application for biodegradable aliphatic polyester based blends and composites.

8.3.3 Partially biodegradable polymer blends and composites

Partially biodegradable polymer blends and composites could be defined as polymeric materials with at least one fully biodegradable component. The current research in this field shows two main trends focused on: (i) commercial and engineering polymer based biocomposites and (ii) natural fibre and wood polymer composites. In this chapter selected examples of partially biodegradable polymer blends and composites obtained via reactive processing are presented.

8.3.3.1 Commercial and engineering polymer based biocomposites

In this field, partially biodegradable composites based on commercial polyolefins (polyethylene, polypropylene) are extensively studied due to their relatively low price and easy manufacturing. Huneault and Li [94] examined structure and property development in uncompatibilized and compatibilized blends of TPS with high-density polyethylene, polypropylene, polystyrene, poly(lactic acid), and poly(ε-caprolactone). The scheme of process configuration for TPS/polymer blending is presented in Fig. 8.14. Functional polymers containing maleic anhydride were used as compatibilizers. Generally, TPS/polymer blend morphology and tensile properties are greatly improved when a maleated compatibilizer is added. This is related to better dispersion of TPS due to partial replacement of the polymer matrix by the maleated analogues, which was confirmed in other works [95–97].

Ma et al. [98] used glycerol (plasticizer), maleic anhydride, and benzoyl peroxide (compatibilizers) during reactive extrusion of poly(lactic acid)/poly(ethylene-co-vinyl

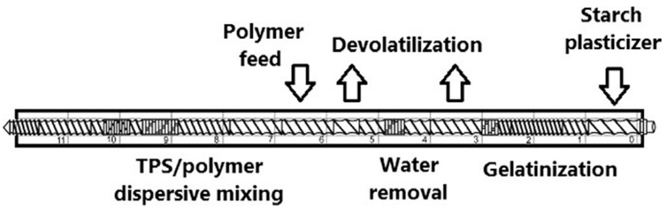

Fig. 8.14 Scheme of production processes of TPS/polymer blends.
Reproduced with permission from Elsevier—licence number 3953020660363 Ref. [Huneault MA, Li H. Morphology and properties of compatibilized polylactide/thermoplastic starch blends. Polymer 2007;48:270–80].

acetate)/starch blends (PLA/EVA/starch). The authors showed that plasticization and compatibilization provided a synergistic effect to PLA/EVA/starch blends, resulting in a significant reduction in starch particle size and an increase in interfacial adhesion. Consequently, the toughness of studied blends, their tensile properties and stability during storage (common issue for starch based biocomposites) were significantly improved.

Korol et al. [99] pointed out the technical problems with feeding of native starch during extrusion. The authors studied the impact of mixing and granulating conditions of native starch and evaluated the possibility of its further application in TPS/polyethylene biocomposites. The granulation of native starch eliminates the dust emissions and increases its density. This allows easy dosage, transportation, and storage of native starch, which is crucial from a technological point of view and potential industrial application. The appearance of granulated native starch and glycerin is presented in Fig. 8.15.

Liu et al. [100] used thermogravimetry and differential scanning calorimetry to evaluate thermal properties of PHB/PP-g-MA blends and PHB/PP-g-MA/vermiculite bionanocomposites after biodegradation in simulated soil. The obtained results indicated that possible interactions between maleic anhydride groups and vermiculite enhanced biodegradation of the biocomposites and consequently decreased their crystallinity. Furthermore, it was observed that biodegradation process decreased thermal stability of the studied blends.

Lee et al. [101] investigated mechanical, rheological, and morphological properties of polycarbonate/poly(lactic acid) (PC/PLA) blends. During processing three types of

Fig. 8.15 The appearance of granulated form of native starch and glycerin.
Reproduced with permission from Elsevier—licence number 3951170405386 Ref. [Korol J, Lenża J, Formela K. Manufacture and research of TPS/PE biocomposites properties. Compos Part B Eng 2015;68:310–6].

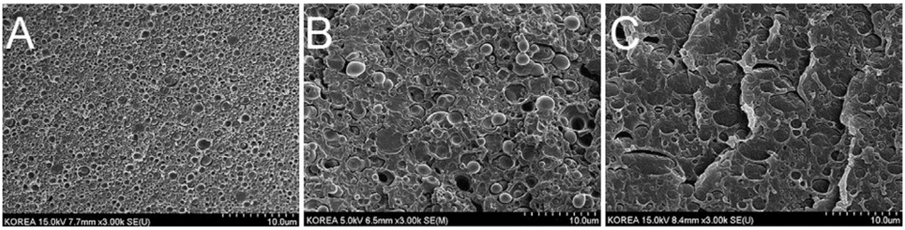

Fig. 8.16 SEM images of the PC/PLA blends (70/30) with the 5 phr of compatibilizer: (A) SAN-g-MA; (B) EOR-g-MA; (C) EGMA.
Reproduced with permission from Elsevier—licence number 3951171217637 Ref. [Lee JB, Lee YK, Choi GD, Na SW, Park TS, Kim WN. Compatibilizing effects for improving mechanical properties of biodegradable poly(lactic acid) and polycarbonate blends. Polym Degrad Stab 2011;96(4):553–60].

reactive compatibilizers were applied: maleic anhydride grafted styrene-acrylonitrile copolymer (SAN-g-MA), maleic anhydride grafted poly(ethylene-co-octene) rubber (EOR-g-MA), and poly(ethylene-co-glycidyl methacrylate) (EGMA). The presented results suggest that SAN-g-MA is the most effective compatibilizer to improve the mechanical strength of the PC/PLA (70/30) blends among the three compatibilizers used in this study. This is due to improved distribution of PLA particles into PC matrix, as presented in Fig. 8.16.

Kuo et al. [102] prepared ABS/TPS blends compatibilized with maleic anhydride grafted styrene. The mechanism of reaction between the used components is presented in Fig. 8.17.

The obtained ABS/TPS blends were characterized by high thermal stability, good processability, low volatile compounds emissions, and excellent mechanical properties. The primary results presented by authors showed that ABS/TPS blends can be successfully used as filaments in 3D printing. This indicates development of new materials for 3D printing, which can be used in many applications such as biomedical engineering, industrial design, automobiles, architecture, mechanical engineering, etc.

Yoo et al. [103] evaluated the impact of commercial compatibilizers (PP-g-MA and SEBS-g-MA) on selected properties of PP/PLA blends in ratio 80/20. Presented results indicated that addition of PP-g-MA improves tensile strength of the PP/PLA blends (80/20), while SEBS-g-MA enhances their impact strength.

Feng et al. [104] prepared poly(ethylene octene) grafted with glycidyl methacrylate (POE-g-GMA), which was further blended with PLA. The results showed that the end carboxyl groups of PLA reacted with the epoxide groups of POE-g-GMA during blending. This improved dispersion of POE-g-GMA particles in PLA matrix, which significantly increased impact strength of PLA/POE-g-GMA blends compared to unmodified POE.

Oyama [105] modified PLA by reactive blending with poly(ethylene-co-glycidyl methacrylate) (EGMA). The obtained PLA/EGMA blends showed elongation at break 40 times higher and impact strengths over 50 times higher compared to pure

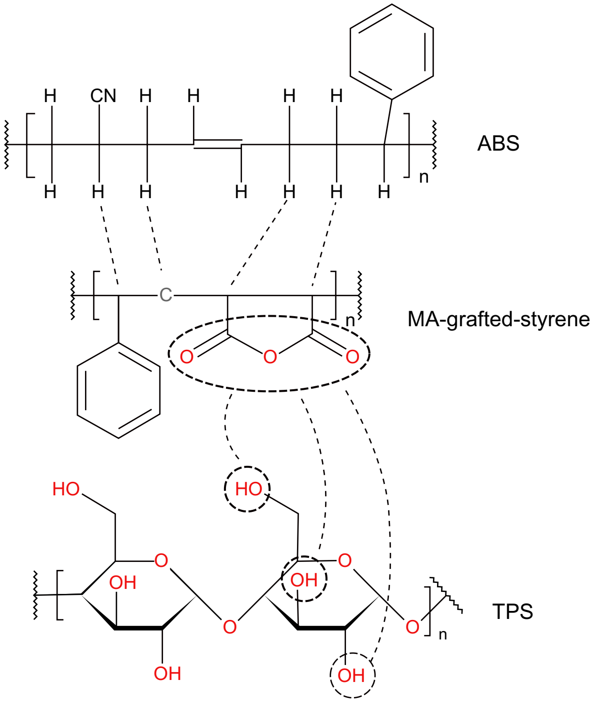

Fig. 8.17 The possible reaction between ABS, TPS, and maleic anhydride grafted styrene. Scheme based on [Kuo C-C, Liu L-C, Teng W-F, Chang H-Y, Chien F-M, Liao S-J, et al. Preparation of starch/acrylonitrile-butadiene-styrene copolymers (ABS) biomass alloys and their feasible evaluation for 3D printing applications. Compos Part B Eng 2016;86:36–9].

PLA. The proposed method of PLA modification produces materials tougher than acrylonitrile-butadiene-styrene copolymer (ABS), without loss of other important properties, such as heat resistance or partial biodegradation.

Partial replacement of ABS with PLA in automotive industry increases content of renewable components in the automobile interior parts, which reduces consumption of petroleum-based resources and decreases their impact on environment [106].

Li and Shimizu [107] used glycidyl methacrylate grafted styrene-acrylonitrile copolymer (SAN-GMA) with ethyltriphenyl phosphonium bromide (ETPB) catalyst as the in situ formed compatibilizer for PLLA/ABS blends. The scheme for possible reaction of PLLA end groups with SAN-GMA under the catalyst ETPB is presented in Fig. 8.18.

The obtained results showed that compatibilized PLLA/ABS blends were characterized by improved impact strength and elongation at break, while only marginal loss in the modulus and tensile strength was noticed.

Jo et al. [108] evaluated the impact of different compatibilizers on mechanical properties of PLA/ABS composites. Commercially available additives such as maleic anhydride grafted ethylene propylene rubber (EPR-g-MA), maleic anhydride grafted

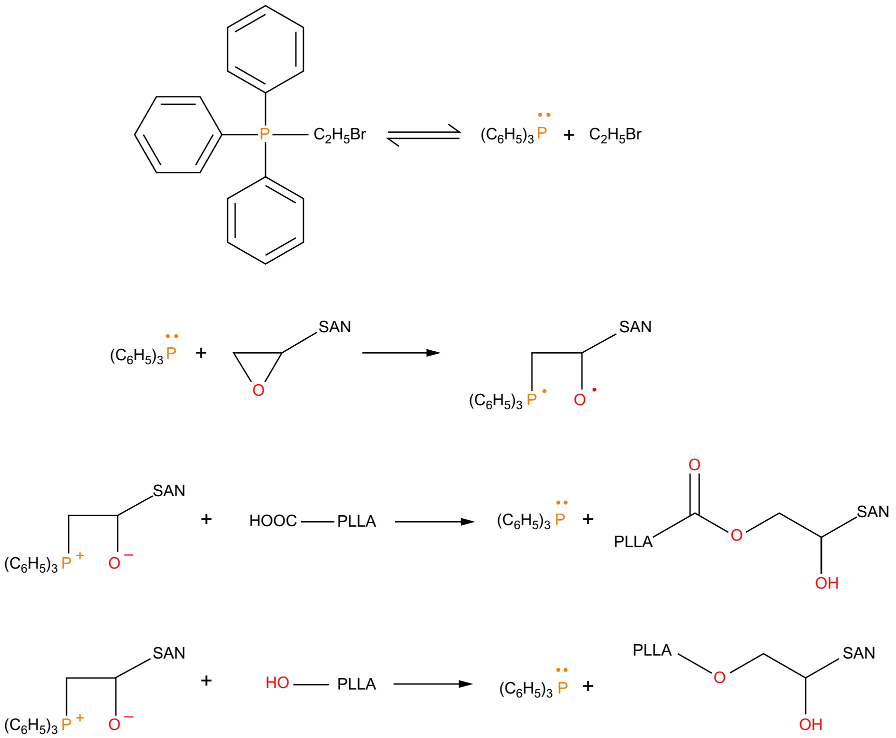

Fig. 8.18 Scheme for the reaction of PLLA end groups with SAN-g-GMA under the catalyst of ETPB.
Scheme based on [Li Y, Shimizu H. Improvement in toughness of poly(L-lactide) (PLLA) through reactive blending with acrylonitrile-butadiene-styrene copolymer (ABS): morphology and properties. Eur Polym J 2009;45(3):738–46].

styrene-acrylonitrile copolymer (SAN-g-MA), glycidyl methacrylate grafted styrene-acrylonitrile copolymer (SAN-g-GMA), epoxy terminated polyethylene (PE-epoxy), and polycarbonate (PC) were applied to improve mechanical properties of PLA/ABS composites. It was observed that mechanical properties of the PLA/ABS composites were significantly improved with increasing content of SAN-g-GMA, which was more effective than other applied compatibilizers. For example, tensile strength increased from 37.3 MPa for PLA/ABS composites 50/50 wt%, to 50.9 MPa for sample with 20 phr SAN-g-GMA.

Recently, Dong et al. [109] synthesized a reactive comb (RC) polymer composed of one poly(methyl methacrylate) (PMMA) backbone, two PMMA side chains, and a few epoxy groups distributed randomly along the backbone, which found application as a reactive compatibilizer in PLLA/ABS blends. The authors showed that in situ formed PLLA grafted RC polymers at the PLLA/ABS interface drastically improved the interfacial adhesion between these two phases. On the other hand, decrease of double glass transition temperature (T_g) in the

RC-compatibilized PLLA/ABS blend was observed. This is related to the presence of free volume voids formed during cooling from the melt to the solid state due to internal pressure, derived from the differentiation of the thermal contraction between the PLLA and the ABS phase. This phenomenon increased the chain mobility of both the PLLA and ABS phase, which resulted in improvement of toughness of the studied blends. Scheme of the generation of the internal pressure and the enlargement of the free volume in the uncompatibilized and compatibilized PLLA/ABS blend is presented in Fig. 8.19.

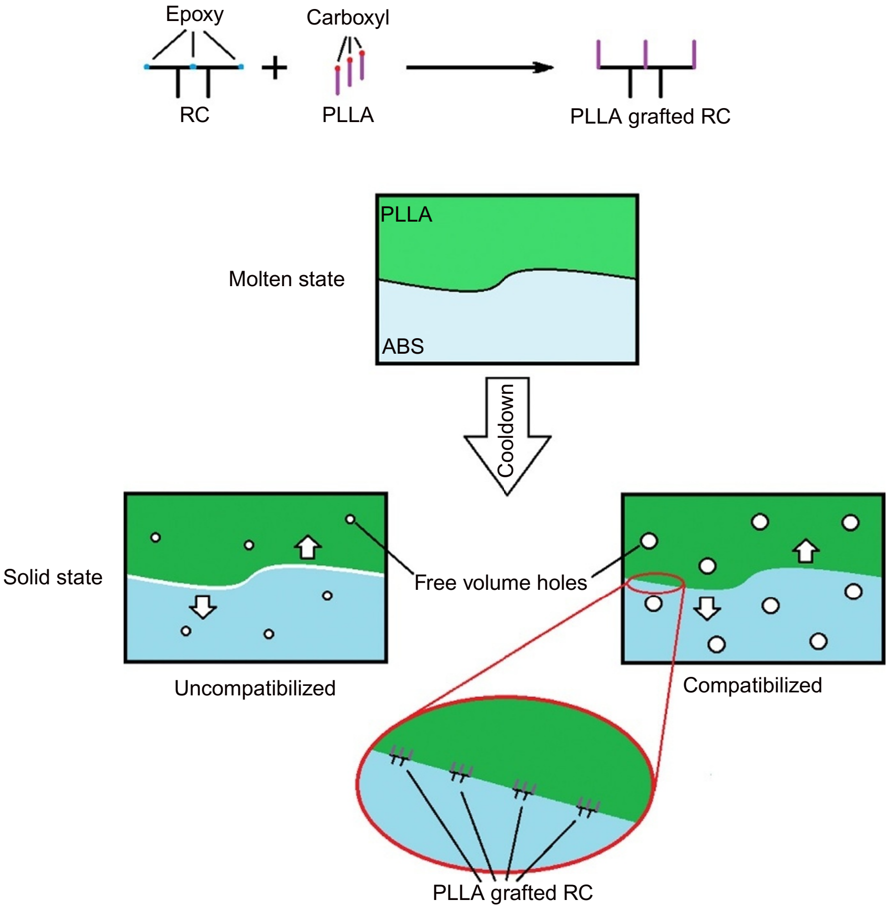

Fig. 8.19 Scheme of the generation of the internal pressure and the enlargement of the free volume in the uncompatibilized and compatibilized PLLA/ABS blend.
Scheme is adapted from [Dong W, He M, Wang, H, Ren F, Zhang J, Zhao X, et al. PLLA/ABS blends compatibilized by reactive comb polymers: double Tg depression and significantly improved toughness. ACS Sustain Chem Eng 2015;3(10):2542–50].

Vadori et al. [110] compatibilized PLA/ABS blend by using two commercial additives: acrylic copolymer Biostrength 900 (processability enhancer dedicated for PLA) from Arkema and styrene-acrylic oligomer with epoxy functional groups Joncryl ADR-4368C (chain extender) from BASF. The obtained results indicated that synergic combination of acrylic copolymer and chain extender resulted in increase of the impact strength by almost 600%, which is related to the decreased tension between the PLA and ABS. Furthermore, the authors showed that the chemical structure of ABS remains unchanged during reactive processing, which suggests that interactions between PLA and ABS are mostly physical. The scheme with possible reaction between PLA and Joncryl ADR-4368C chain extender is presented in Fig. 8.20.

Sun et al. [111] used glycidyl methacrylate grafted acrylonitrile-butadiene-styrene copolymer (ABS-g-GMA) particles to improve toughness of PLA. The presented results confirmed chemical reactions between PLA and ABS-g-GMA particles, which increased the viscosity and decreased the degree of crystallization of PLA. It was observed that notched impact strength determined for the PLA/ABS-g-GMA blend with 1 wt% GMA was 27 times higher than the impact strength of pure PLA. Moreover, further increase in the GMA content in the ABS-g-GMA particles did not improve the toughness of PLA/ABS-g-GMA blend.

Walha et al. [112] showed that Joncryl ADR-4368C (BASF) can be applied as compatiblizer in PLA/polyamide 11 blend, however its compatibilization efficiency is related to the compounding method.

Zhang et al. [113] used various compositions of carboxyl-ended polyester (CP) and solid epoxy (SE) as reactive modifiers of PLA. The results showed that addition

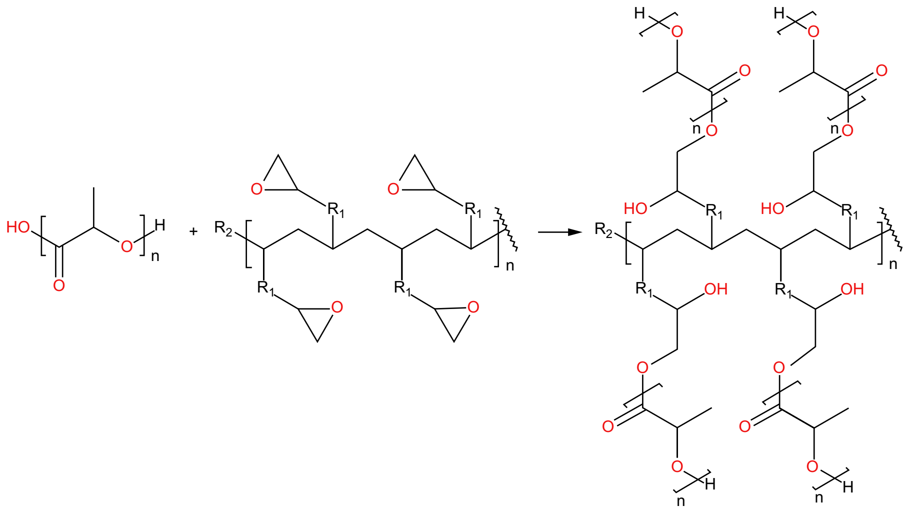

Fig. 8.20 The mechanism of possible reaction between PLA and Joncryl ADR-4368C chain extender.
Scheme based on [Vadori R, Misra M, Mohanty AK. Sustainable biobased blends from the reactive extrusion of polylactide and acrylonitrile butadiene styrene. J Appl Polym Sci 2016, doi: 10.1002/app.43771].

of CP/SE can improve the melt viscosity and elasticity of PLA, which have beneficial effect on its processing via different methods (e.g. blow-film, blow-moulding or foaming). Furthermore, the application of CP/SE hinders the crystallization of PLA, while the tensile strength of PLA is increased. The scheme of reactive blending of PLA and solid epoxy resins is shown in Fig. 8.21.

The reactive modifiers with epoxy groups were also successfully used for other biodegradable aliphatic polyesters or their blends [114,115].

8.3.3.2 Natural fibre and wood polymer composites

Strong interfacial interactions between filler and matrix are crucial to achieve satisfactory mechanical performance of biocomposite materials. It is especially important in the case of natural fibre and wood polymer composites, because of the nonpolar character of matrix phase and its incompatibility with hydrophilic natural fibres or wood. Numerous ways to improve the interfacial interactions have been developed with varying success. Both filler-based and matrix-based strategies have been employed. First category

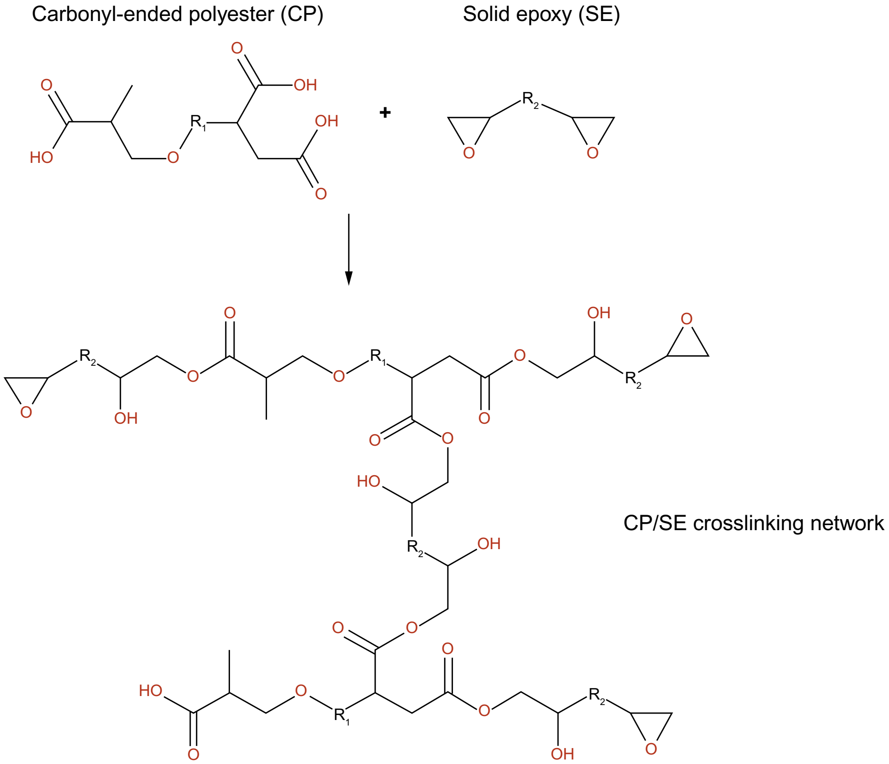

Fig. 8.21 The mechanism of reactive blending of PLA and solid epoxy resin.
Scheme based on [Zhang J, Li G, Su Y, Qi R, Ye D, Yu J, et al. High-viscosity polylactide prepared by in situ reaction of carboxyl-ended polyester and solid epoxy. J Appl Polym Sci 2012;123:2996–3006].

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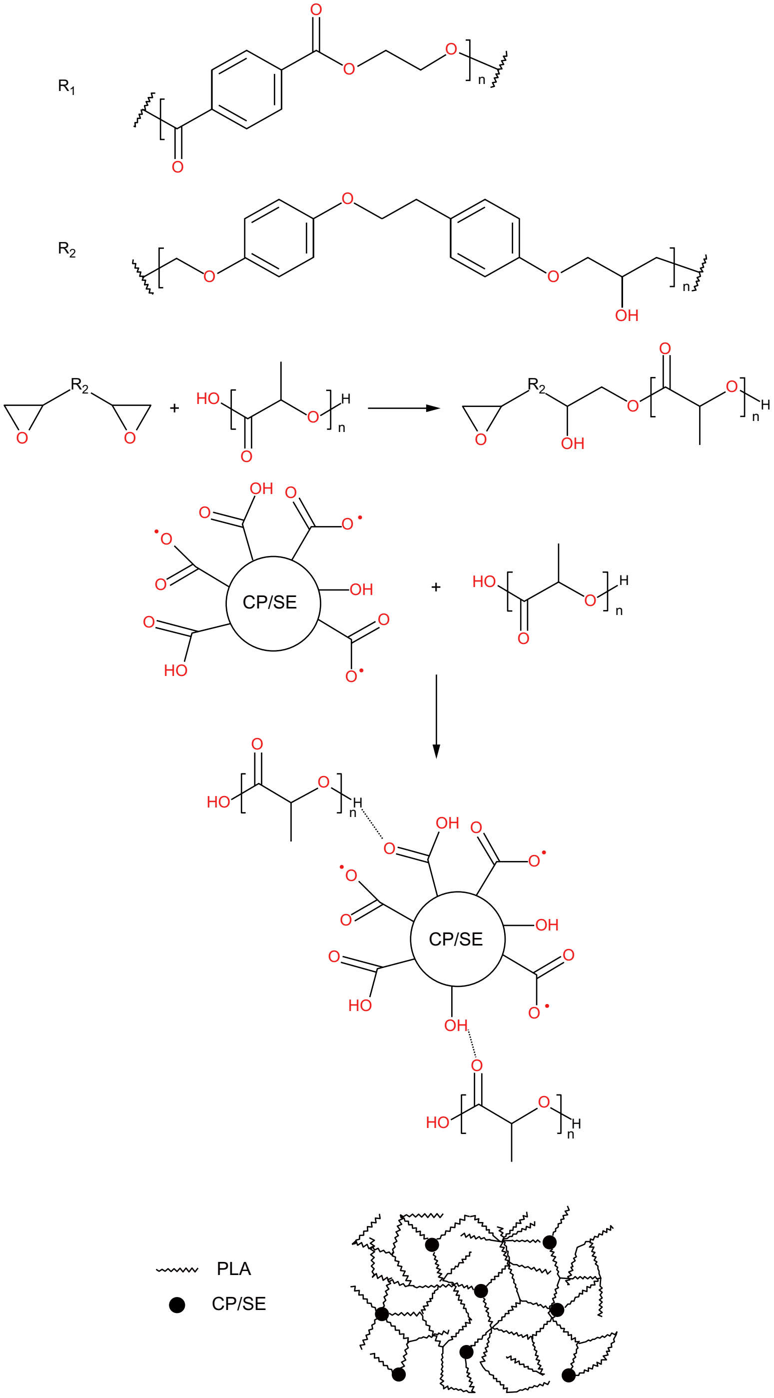


Fig. 8.21, continued

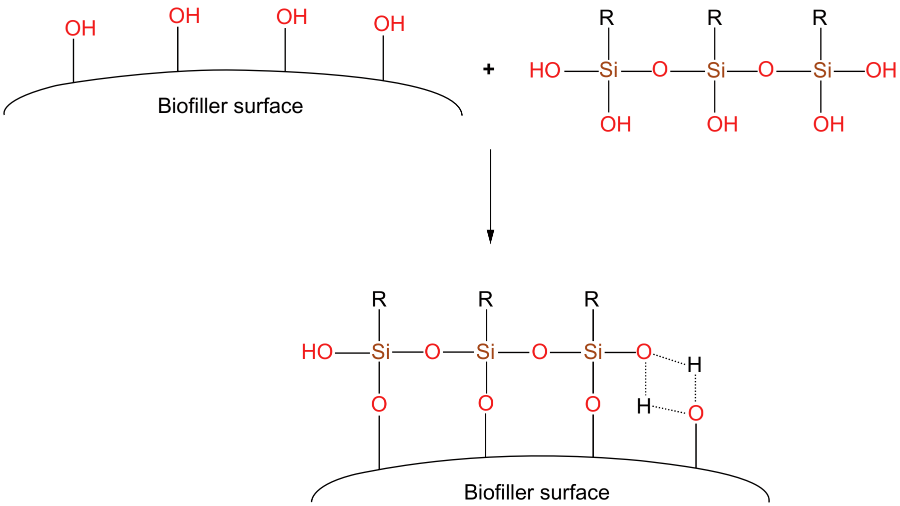


Fig. 8.22 Bonding mechanisms in silane cross-linked biocomposites.
Scheme based on [Karnani R, Krishnan M, Narayan R. Biofiber-reinforced polypropylene composites. Polym Eng Sci 1997;37:476–83].

includes various methods of filler treatment, most common are silanization [116,117], mercerization [118,119], acetylation [120,121], or maleic anhydride treatment [122]. Such treatments can significantly improve characteristics of resulting biocomposites. Fig. 8.22 shows schemes of fibre silanization and its interaction with polymer matrix.

Second route is matrix-based strategies, which are associated with the application of compatibilizers, usually modified polymers. Backbone of the compatibilizer needs to be compatible with the matrix in order to provide sufficient miscibility, while functional groups, usually grafted to the main chain should be able to interact and bond with the reinforcement. The easiest way of providing compatibility with the matrix is the use of the similar polymer as the backbone of compatibilizer. Modifiers can be fed directly into the extruder with initiator during preparation of biocomposites, however it is hard to control the efficiency of polymer grafting. Another most common approach is separate preparation of grafted polyolefin (PO) and its incorporation into extrusion process. In PE- and PP-based composites, by far the most common are polyolefins functionalized with maleic anhydride (MA) [123–125]. Except polyolefins, mainly styrene-ethylene-butylene-styrene copolymer (SEBS) is used as a backbone for MA-based compatibilizers in PO-based biocomposites [126].

As mentioned before, the most popular compound used to enhance compatibility of PO-based biocomposites is maleic anhydride. The advantage of its application is that there is no need for additional filler modification or pretreatment in order to provide sufficient level of interfacial interactions. Functional groups of MA can react with hydroxyl groups present in almost all kinds of biofillers. Schematic pathways of maleic anhydride grafting onto polyolefin chain and reaction of anhydride groups with bio fillers are shown in Fig. 8.23.

Reactions presented above may lead to noticeably enhanced level of interfacial interactions which result in improved mechanical performance. Moreover, presented

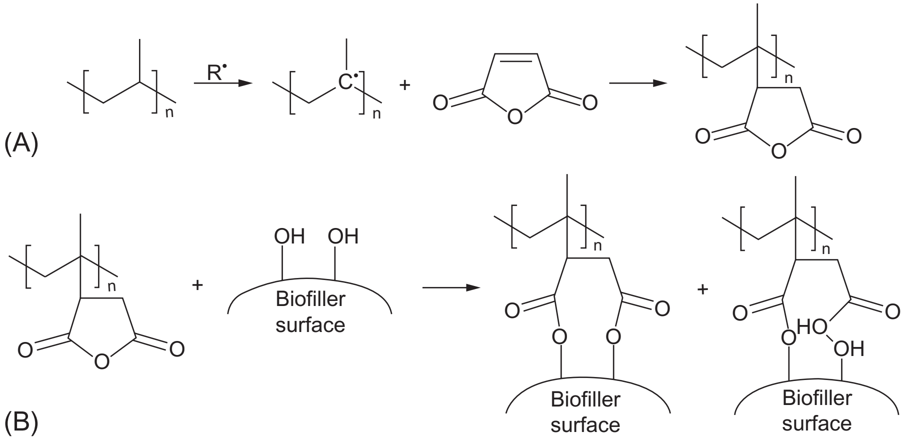


Fig. 8.23 Scheme of reaction: A, grafing of maleic anhydride onto polypropylene; B, between maleic anhydride grafted polypropylene and hydroxyl groups present on surface of biofiller. Scheme based on [Snijder MHB, Bos HL. Reinforcement of polypropylene by annual plant fibers: optimisation of the coupling agent efficiency. Compos Interf 2000;7:69–75; Karnani R, Krishnan M, Narayan R. Biofiber-reinforced polypropylene composites. Polym Eng Sci 1997;37:476–83; Hornsby PR, Hinrichsen E, Tarverdi K. Preparation and properties of polypropylene composites reinforced with wheat and flax straw fibres: Part II Analysis of composite microstructure and mechanical properties. J Mater Sci 1997;32:1009–15].

scheme of compatibility improvement is independent of the way of MA addition. Whether maleic anhydride is used to modify filler particles or grafted to polymer backbone, it is connecting with biofiller through ester bonds and hydrogen bridges (see Fig. 8.23), while interactions with matrix are originate from chain entanglements. Nevertheless, application of PO-g-MA into biocomposites can be considered more convenient than pretreatment of fillers with maleic anhydride, because grafting can be easily performed in the same extruders, so no additional apparatus is required. Efficiency of these methods is debatable. Nuñez et al. [127] reported that incorporation of PP-g-MA resulted in improved tensile and flexural performance of composites in comparison to those containing wood flour pretreated with MA, while Arbelaiz et al. [128] achieved the same enhancement of mechanical properties for both ways of composites' modification.

Generally majority of reported studies based on the use of PO-g-MA resulted in significant enhancement of mechanical performance of biocomposites obtained via reactive extrusion, which can be seen in Table 8.2.

As shown in Table 8.2, incorporation of compatibilizer into biocomposites results in superior mechanical properties than those containing only neat or unmodified biofiller. Such effect is related to the fact that backbone of the compatibilizer is usually miscible with the matrix and grafted compounds are able to create not only hydrogen bonds, but also covalent bonds with functional groups present on the biofillers' surface. Apart from maleic anhydride, other compounds can also be used to modify PO

Table 8.2 Comparison of properties of biocomposites based on polyolefins and compatibilized by PO-g-MA

	Filler		Compatibilizer			Mechanical properties				
Polymer matrix	Type	Content (wt%)	Type	Content (wt%)	Extrusion conditions	Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m^2)	Composition with the highest mechanical properties	Ref.
Polypropylene	Kenaf fibre	20–60	PP-g-MA (2 wt%)	0–5	Twin screw extruder, 175°C, 150 rpm	26.9–61.2	3–6	–	PP + 5 wt% of PP-g-MA + 60 wt% of kenaf fibre	[124]
Polypropylene	Flax straw	25	PP-g-MA (0.55 wt%)	0–5	Twin screw extruder, 155–185°C, 100 rpm	32.9–39.1	4–5	3.0–3.6	PP + 5 wt% of PP-g-MA + 25 wt% of flax straw	[125]
	Silanized flax straw[a]					36.4	5	3.4		
	Wheat straw					29.7–32.3	3–4	2.2		
	Silanized wheat straw[a]					29.8	4	2.2		
Polypropylene	Wood flour	10–30	PP-g-MA (0.4 wt%) SEBS-g-MA (2 wt%)	0–4.5	Twin screw extruder, 200°C, 300 rpm	30.1–42.3	–	1.9–2.7	PP + 3.5 wt% of SEBS-g-MA + 30 wt% of wood flour	[126]
Polypropylene	Flax fibre	15–30	PP-g-MA (0.6 wt%)	0–5	Single screw extruder, 190°C, 45 rpm	19.3–25.3[d]	8–35[d]	–	PP + 5 wt% of PP-g-MA + 30 wt% of alkaline treated flax fibre	[129]
	Bleached flax fibre[b]					20.5–28.5[d]	7–28[d]	–		
	Alkaline treated flax fibre[c]					19.5–28.9[d]	7–28[d]	–		
Polypropylene	Pineapple skin	10–30	PP-g-MA (1 wt%) PP-g-AA (6 wt%)	0–3	Twin screw extruder, 185°C, 200 rpm	31.4–35.0	29–30	3.6–4.4	PP + 3 wt% of PP-g-MA + 30 wt% of nondestarched cassava root bioflour	[130]
	Nondestarched cassava root bioflour					28.6–36.6	26–30	3.4–3.9		
	Destarched cassava root bioflour					29.7–36.1	27–31	3.4–3.8		

Continued

Table 8.2 Continued

	Filler		Compatibilizer			Mechanical properties				
Polymer matrix	Type	Content (wt%)	Type	Content (wt%)	Extrusion conditions	Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m^2)	Composition with the highest mechanical properties	Ref.
Polypropylene	Sawdust	20	PP-g-MA (1 wt%)	0–2	Twin screw extruder, 160–180°C, 120 rpm	32.1–33.0	7–8	–	PP + 2 wt% of PP-g-MA + 20 wt% of silane treated sawdust	[131]
	Silane treated sawdust[e]					31.8–36.0	7	–		
Polypropylene	Bamboo fibre	10–50	PP-g-MA (5 wt%)	0–3	Twin screw extruder, 180°C, 150 rpm	29.6–44.3	–	–	PP + 3 wt% of PP-g-MA + 50 wt% of bamboo fibre	[132]
Polypropylene	Bleached sulphite cellulose fibre	40–60	PP-g-MA (1 wt%)	0–3	Twin screw extruder, 175–190°C, 100 rpm	24.9–50.8	2–5	–	PP + 3 wt% of PP-g-MA + 50 wt% of bleached kraft cellulose fibre	[133]
	Bleached kraft cellulose fibre					25.2–51.6	2–4	–		
Polypropylene	Wood flour	30–60	PP-g-MA (7 wt%)	0–3	Twin screw extruder, 120–180°C, 200 rpm	9.9–27.2	2–5	–	PP + 3 wt% of PP-g-MA + 60 wt% of wood flour	[134]
Polypropylene	Wood flour	40	PP-g-MA (1 wt%)	0–3.345	Twin screw extruder, 165°C, 110 rpm	37.0–43.0	2–3	–	PP + 3.345 wt% of PP-g-MA + 40 wt% of wood flour	[135]
	Alkali treated wood flour[f]					38.0	3	–		
	Silane treated wood flour[g]					36.0	3	–		

High density polyethylene	Wood flour	40	PP-g-AA (6 wt%) HDPE-g-AA (6 wt%) HDPE-g-MA (1 wt%) LLDPE-g-MA (1 wt%) PP-g-MA (1 wt%)	0–5	Single screw extruder, 150–160°C, 40 rpm	9.3–21.6	1–3	–	HDPE + 5 wt% of HDPE-g-MA + 40 wt% of wood flour	[136]
High density polyethylene	Wood flour	20–50	PE-g-MA (1.1 wt%)	0–5	Twin screw extruder, 80–170°C, 35 rpm	17.8–34.4	3–8	6.1–9.9	HDPE + 5 wt% of PE-g-MA + 50 wt% of wood flour	[137]
Recycled high density polyethylene	Wood flour	60	PE-g-MA (0.9 wt%)	0–1	Twin screw extruder, 155–180°C, 40 rpm	13.6–19.2	1	–	HDPE + 1 wt% of PE-g-MA + 60 wt% of wood flour	[138]

[a] Modified with vinyltrimethoxysilane.
[b] Fibres treated in 0.25% sodium hypochlorite (NaOCl) solution for 1 h.
[c] Fibres treated in 5% sodium hydroxide (NaOH) solution for 3 h.
[d] Values estimated from graphs.
[e] Modified with (3-aminopropyl)triethoxysilane.
[f] Flour treated with 18% sodium hydroxide (NaOH) solution for 0.5 h.
[g] Modified with 10% solution of vinyltris(2-metoxietoxi)silane.

backbone in order to enhance the compatibility with various biofillers and have been investigated by many researchers.

Nachtigall et al. [139] investigated effects of PP/wood flour composites compatibilized with PP-g-MA and PP grafted with vinyltriethoxysilane (PP-g-VTES). Latter coupling agent was found to be twice more effective with 30 wt% of biofiller in terms of tensile performance of the material. SEM analysis revealed that samples containing PP-g-VTES had the most homogenous structure with low voids content, which resulted also in significantly decreased water uptake compared to unmodified sample or the one containing PP-g-MA.

Furthermore, grafting of polyolefins with AA [135], GMA [140], cardanol [141], as well as their oxidation [142,143], or carboxylation [144] were investigated as methods of coupling agents' synthesis, however their impact on the mechanical performance of biocomposites was not very substantial. Improvements in tensile or flexural strength were lower than 20%, often with deterioration of other properties. Other groups of chemical compounds which can be successfully applied as coupling agents for PO-based biocomposites are isocyanates. This group of chemicals is well known in polymer area, since it is commonly used in manufacturing of polyurethanes. They react with hydroxyl groups present on the surface of the biofillers generating urethane groups, enhancing the compatibility.

The most common chemical from this group used to enhance the performance of PO-based composites is polymeric form of methylene diphenyl diisocyanate (pMDI) [145–147]. Research group from Oregon State University used it to improve properties of PP- and PE-based composites containing 40 wt% of wood flour. For PP-based biocomposites [145], authors investigated incorporation of pMDI, PP-g-N-vinylformamide (PP-g-VF), and their combinations. Results were also compared with composites compatibilized with commercial PP-g-MA. The best results were obtained for combination of pMDI and PP-g-VF, which were superior to those obtained with maleic anhydride. Microscopic analysis of these materials suggested that the enhancement of mechanical performance was due to the improved interfacial adhesion between matrix and the filler. Moreover, such coupling agents resulted in significant decrease of water uptake, which can be considered beneficial because it reduces the degradation of biocomposites. The same coupling agent was used by Pickering and Ji [146] during investigation of PP-based composites filled with 0–50 wt% of thermo-mechanical pulp wood fibre. When pMDI was used alone, only slight improvements were achieved. Noticeably better results were obtained when pMDI was combined with PP-g-MA, tensile strength, and moduli were increased by 115% and 85%, respectively. Nevertheless, these results were very similar to those obtained for composites compatibilized with PP-g-MA alone.

In case of polyethylene composites [147], pMDI was used solely or in combination with stearic acid. Addition of 1.5 wt% of pMDI resulted in ~10% increase of modulus of rupture and modulus of elasticity, while combination with 0.5 wt% of stearic acid led to ~90% and ~20% improvement of these properties. Enhanced compatibility of the investigated composites was also evident in SEM images. Such coupling agents were more effective than commercially available PE-g-MA.

Research group of Ashori and Nourbakhsh [148,149] studied the influence of polybutadiene isocyanate (PBNCO) on the properties of PP-based biocomposites. Addition of 5 wt% of PBNCO in combination with 3 wt% of PP-g-MA to the PP/mechanical pulp wood fibre composite enhanced tensile stress by 40%, which is twice more than in the case of a sample containing only 3 wt% of PP-g-MA. The same phenomenon was observed in case of composites' impact strength. In case of PP/bagasse fibre composites, combination of 3 wt% of PP-g-MA with 4 wt% of PBNCO increased tensile strength and impact strength by more than 100% and 200%, respectively. Maleic anhydride grafted polypropylene was more effective in enhancing tensile properties, while isocyanate addition resulted in higher improvement of impact strength. Nevertheless, the best results were obtained for combination of both coupling agents, which suggests synergistic effect of PBNCO and PP-g-MA.

Karmarkar et al. [150] investigated the influence of the novel coupling agent obtained by grafting *m*-isopropenyl-α,α-dimethylbenzyl-isocyanate (*m*-TMI) onto isotactic PP on the properties of PP-based WPCs. Schematic reaction occurring during biocomposite's preparation is shown in the Fig. 8.24. Depending on the level of reinforcement, significant enhancement of tensile strength, tensile modulus,

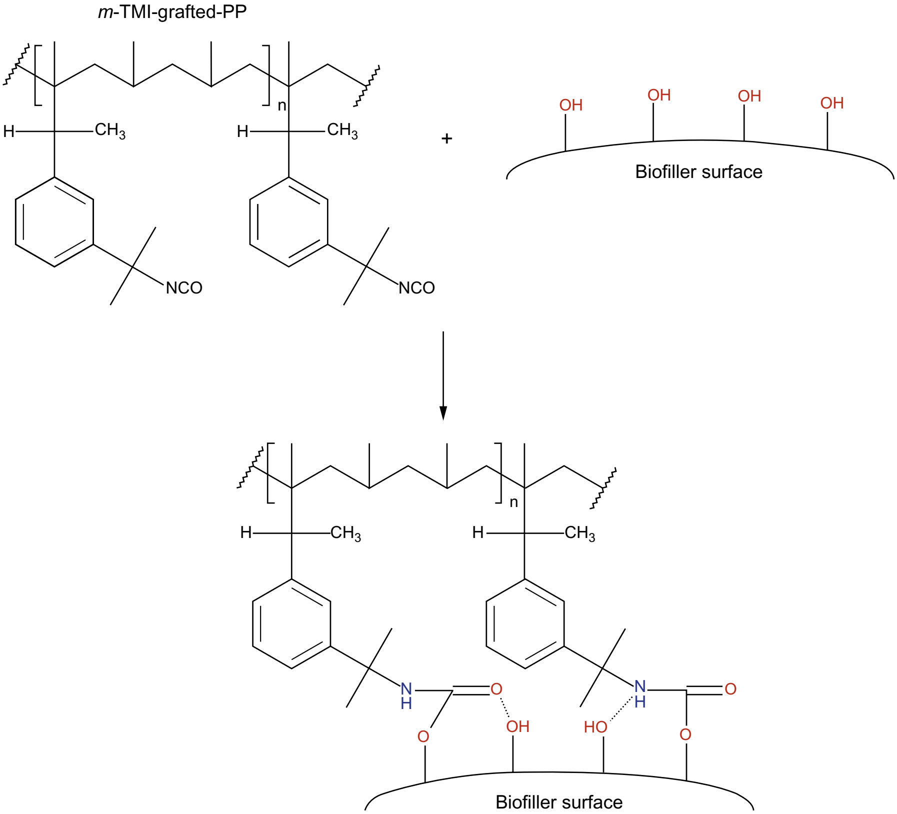


Fig. 8.24 Scheme of reaction between PP, biofiller, and *m*-isopropenyl-α,α-dimethylbenzyl-isocyanate (*m*-TMI) grafted onto isotactic PP.
Scheme based on [Karmarkar A, Chauhan SS, Modak JM, Chanda M. Mechanical properties of wood–fiber reinforced polypropylene composites: effect of a novel compatibilizer with isocyanate functional group. Compos Part A Appl Sci Manuf 2007;38:227–233].

and flexural strength was observed, exceeding even 80% in some cases. Isocyanate grafted PP was found to be very effective compatibilizer for PP-based biocomposites.

Isocyanates can be considered as quite effective compatibilizers for PO-based biocomposites, however the best results can be obtained when they are used in combinations with other coupling agents. Except grafted polyolefins and isocyanates, other chemicals have also been investigated as potential coupling agents for PO-based biocomposites, such as so-called titanium-derived mixture [144], stearic acid [146], or cellulose palmitate [151], however majority of them did not result in enhancement of mechanical performance of the resulting materials. Luo et al [152] modified biocomposites with kraft lignin. Generally, small contents of lignin (0.5 and 1 wt%) were found to enhance the flexural properties, impact strength, and tensile modulus of the composites. Further addition of lignin did not have any positive effect on the mechanical performance. At lignin content of 1 wt%, the flexural strength and modulus increased by 29% and 20%, respectively, while the impact strength was increased by 25%. The best tensile properties were obtained for lignin content of 0.5 wt%. Dynamic mechanical analysis (DMA) and SEM analysis also indicated that matrix/filler adhesion could be improved at lower lignin content. Presented results suggest that kraft lignin is a potential compatibilizer candidate for PP-based biocomposites. Compatibilizers reported in literature are summarized and presented in Table 8.3 together with their chemical structures.

Table 8.3 **Chemical structure of compatibilzers commonly used for biocomposites based on polyolefin matrix**

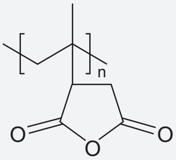
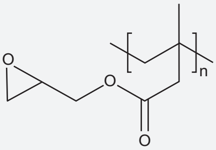
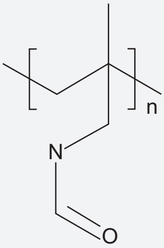
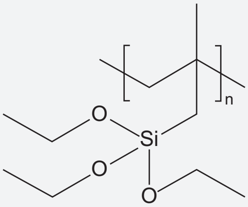
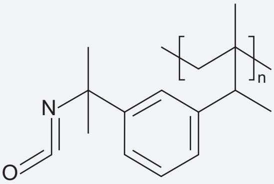
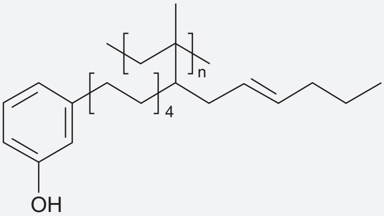
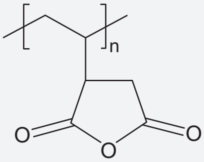
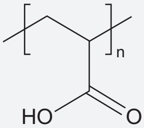
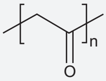
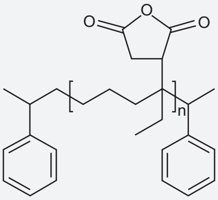
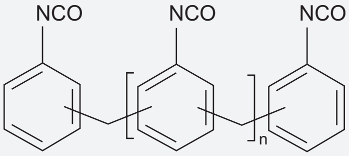
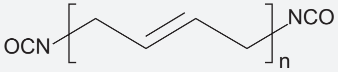
Backbone	Modifier	Chemical structure
PP	Maleic anhydride	
	Glycidyl methacrylate	
	N-vinylformamide	

Table 8.3 Continued

Backbone	Modifier	Chemical structure
	Vinyltriethoxysilane	
	Isocyanate[a]	
	Cardanol	
PE	Maleic anhydride	
	Acrylic acid	
	Oxidation	
SEBS	Maleic anhydride	

Continued

Table 8.3 Continued

Backbone	Modifier	Chemical structure
Polymeric Methylene Diphenyl Diisocyanate	–	
Polybutadiene isocyanate	–	

[a] *m*-Isopropenyl-*a,a*-dimethylbenyl-isocyanate.

8.4 Commercially available biocomposites produced by reactive extrusion

Biocomposites produced by reactive extrusion, the technology controlling the matrix-fibre interface, can be categorized as thermoplastic biocomposites, designated for injection moulding or extrusion. They can be processed with traditional equipment with some adjustments to process settings and no physical hardware modification. This technology based on a variety of natural fibres is utilized up to 50–60 %. The end-product possesses great structural rigidity, dimensional stability, an aesthetically pleasing finish, and highly marketable performance capabilities.

The market for injection moulding and extrusion grades of biocomposites is still ascending. Wood polymer composites, well established at extruded decking and fencing boards, are now moving into injection moulding together with biocomposites utilizing cellulose fibres, rice hulls, flax, or palm fibre waste. Many components such as the casings for computers, monitors, and mobile phone cases could be to a greater extent produced from biocomposite materials. Considerable growth has been seen in the use of biocomposites in the automotive market over the past decade. In view of a considerable research in this area, the commercial use of thermoplastic biocomposites is still at the beginning. In Table 8.4 leading producers and examples of commercial thermoplastic biocomposites are presented.

Melting point and viscosity of biocomposites are influenced by the type of polymer matrix, while mechanical properties are governed to a large extent by the type and amount of filler. With the help of additives additional properties can be introduced or enhanced, like weather resistance, antiaging protection, UV resistance, insect resistance, impact strength, flexural strength, tensile strength, water absorbency, etc.

The applications of biocomposites are based on their physical, mechanical, and processing properties. Examples of successful commercialization are presented below.

Biocomposites from FKuR Plastics are applied for disposable catering items, for office articles, as breathable and waterproof films, for use as e.g., diaper backsheet or femcare products, as packaging for cosmetic products, mulch films in agriculture, padded envelopes, bubble wrap, and air pillows.

Table 8.4 Examples of commercial biocomposites obtained by reactive extrusion

Commercial name	Characteristics	Producer
NCell	Polypropylene or polyethylene matrix reinforced with up to 40% natural cellulosic microfibres	GreenCore Composites (Canada) www.greencorenfc.com
Bio-Res	Biobased resin additive in the form of master batch pellets, which blend easily with polyethylene, polypropylene, polylactic acid, and polyhydroxyalkanoate matrices	Laurel BioComposite (USA) www.laurelbiocomposite.com
Aqvacomp	Combination material that uses natural cellulose fibre and plastics	Metsä Fibre (Finnland) cwww.metsafibre.com
Trifilon FCP	Natural fibre reinforced polypropylene for injection moulding	TRIFLON (Sweden) www.triflon.com
Bio-Flex	Blends of copolyester and polylactic acid with a very high content of natural resource material, depending on the particular grade	FKuR (Germany) www.fkur.com
Biograde	Product based on cellulose and predominantly composed of natural resource materials, especially designed for injection moulding applications	FKuR (Germany) www.fkur.com
Fibrolon	Wood-Plastics-Composites for injection moulding, characterized by a high strength and stiffness when compared to wood	FKuR (Germany) www.fkur.com
ARBOBLEND	Depending on the application, the product contains different biopolymers like e.g., polyhydroxyalkanoate, polyester, lignin, starch, cellulose, organic additives, natural resins, or waxes and natural reinforcing fibres	TECNARO GmbH (Germany) www.tecnaro.de
BioCom	Composite of rice husks and recycled polyethylene	Biocomposite Extrusions (Malaysia) www.bcextrusions.com
Terratek SC	Blend of wheat starch and polypropylene for injection moulding applications. Formulations containing from 30% to 65% starch are available upon request	Green Dot (USA) www.greendotpure.com
Terratek WC	Blend of pine wood fibre and reprocessed polypropylene for injection moulding applications Formulations containing 30%–60% wood are available upon request	Green Dot (USA) www.greendotpure.com
WPC BIO PE WPC BIO PP WPC BIO TPS	Wood-Plastic Composite granulates for injection moulding and extrusion (wood or cellulose fibres, polymer matrix: polyethylene, polypropylene or thermoplastic starch)	JELUPLAST (Germany) www.jeluplast.com

Starch biocomposites from Green Dot include types, that are suitable for injection moulding, profile extrusion, sheet extrusion, blow moulding, and blown film, typical use in manufacture of packaging materials and containers.

Thermoplastic Wood Plastic Composites from JELUPLAST are suitable for both outdoor and indoor applications and can be processed, for example, to high-quality seats, decorative elements, or adjustable feet for shelves and cabinets by injection moulding. Using pressing technology, the biocomposites can be processed into stable panels, for example the substructure of upholstered furniture, for shelves, boards, side and rear panels, and cabinet doors. Plates and injection moulded parts made of the material can be glued, screwed, stained, painted, and welded. Due to its resistance to moisture, this type of furniture is suitable for damp rooms such as bathrooms, kitchens, and saunas. The weather resistance makes this bioplastic also available for outdoor use. It can be used for garden furniture, railings, fences, facade cladding, and decking.

8.5 Advantages-disadvantages of reactive extrusion of biocomposites

The advantages and disadvantages of reactive compounding of biocomposites are summarized in Table 8.5. The main advantage of reactive extrusion (similar like conventional extrusion) is its continuity, which helps in time-saving, cost-effectiveness, repeatability, and environment-friendliness. Some technical problems with continuous and stable feeding of selected components (e.g., starch, liquid plasticizers, nanofillers, long fibres etc.) may occur during extrusion, however this issue is usually omitted in the literature.

Table 8.5 A summary of advantages and disadvantages of reactive extrusion of biocomposites

Advantages	Disadvantages
Versatility of the modular design of twin- and triple screw extruders, which allows easy change of screw configurations and optimize processing conditions	High cost of twin-screw/triple-screw extruders and additional equipment
Possible processing of viscous polymers and highly filled biocomposites	Some problems with heat removal from material during exothermic reactions occurring in reactive processing
Continuous, time-saving, cost-effective, repeatable, and environment-friendly process commonly used in industry	Problems with continuous and stable feeding of selected components
High productivity and good quality of obtained biocomposites	Complexity of reactions between used components, which are very difficult to control precisely and might affect storage stability
Limited costs of employment due to automatization of process	Volatile compounds formed during processing, which could limit commercialization of selected technologies due to environmental regulations

Modular design of twin- and triple-screw extruders allows easy change of screw configurations and optimizing the processing conditions of viscous polymers and highly filled biocomposites. On the other hand, this solution increases the cost of twin-screw/triple-screw extruders, which also need additional equipments (e.g., gravimetric feeders, extrusion dies, vacuum dryers, grinders etc.). Reactive extrusion allows high productivity and good quality biocomposites and at the same time limits the costs of employment due to process automatization. Furthermore, single-screw and twin-screw extruders are commonly used in industry, therefore the transition of results from laboratory to industrial scale is much easier compared to other processing methods.

The main disadvantage of reactive extrusion is the complexity of reactions between used components, which is very difficult to control precisely. The uncontrolled changes in structure and properties might cause problems with storage stability, future processing, or recycling of the biocomposites. Moreover, technical issues with heat transfer from material during reactive processing (to prevent its degradation) and some problems with volatile compounds formed during exothermic reactions could limit commercialization of selected technologies due to environmental regulations.

8.6 Future trends and developments in reactive extrusion of biocomposites

The data presented in this chapter indicate that application of reactive extrusion during processing of biocomposites is a very promising alternative to conventional production. Reactive extrusion is fast, solvent-free, and low-cost method for the production of chemically modified biodegradable polymers, functionalized wood dust, and natural fibres or effective compatibilization of polymer blends. Therefore, it is expected that the production and processing of biodegradable polymers and composites via reactive extrusion will continue to grow in the future. Among new applications of biocomposites obtained in reactive extrusion technology, the most promising direction seems to be 3D printing technology (production of new filaments based on different kind of biocomposites) which is related to versatile usage. Other promising direction is reactive modification/functionalization of cellulose-rich fillers (e.g., wood dust, natural fibres, agriculture waste, etc.) due to their widespread industrial applications. Furthermore, reactive extrusion could find application during material and chemical recycling of biocomposites, which allows to improve the quality of recycled products and reduce their impact on the environment.

However, appropriate designing of reactive extrusion processes requires comprehensive knowledge about impact of variable processing conditions on the efficiency of chemical reactions inside the extruder barrel. The complexity of extrusion process indicates that optimization of processing conditions based on empirical results should be assisted by theoretical calculations. Moreover, optimization of extrusion conditions using existing theoretical basis requires knowledge of the physical and rheological properties of the polymeric materials being processed, and mixtures thereof with various additives (e.g., fillers, stabilizers, plasticizers, etc.). Unfortunately, often lack of those data combined with limited technological knowledge, seriously limits theoretical calculations in practice, especially in case of multicomponent blends/composites prepared in twin screw extruders. Therefore, nowadays experimental test design methods and computer simulations (e.g., response surface method (RSM), artificial neural network (ANN), etc.) are gaining increasing importance in extrusion technology, which reduces cost- and time-consuming experimental work. Additionally, new methods for quick quality control of biocomposites obtained via reactive extrusion should be investigated. At present, the most promising solutions in this field are “on-line” and “in-line” systems based on rheological measurements, near-infrared spectroscopy, Raman spectroscopy, ultrasonic, and dielectric spectroscopy, UV/Vis spectroscopy, optical measurements, or combination of at least two of the above mentioned methods. Interesting alternative is evaluation of volatile organic compounds emitted during reactive extrusion, which could be applied as “markers” for preliminary assessment of biocomposites thermo-mechanical degradation.

Other crucial factors affecting reactive extrusion are shear forces in the extruder, which should be sufficient for reactive groups to encounter one another. Therefore, reactive extrusion should be performed in co-rotating twin screw extruders with segmented/modular construction and in near future in the triple-screw extruders, rather than in single-screw extruders. Further research in this field should be focused on enhancement of mixing efficiency during extrusion, which could be achieved by application of high speed extruders, modification of screws or extrusion process assisted by ultrasounds, supercritical fluids, or other solutions.

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Rapid processing possibilities of biocomposites: microwave, ultraviolet, and e-beam

9

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Composite components must be cured under very strict processing conditions due to the need of having a reproducible polymerization of the resin.

Currently polyester, vinylester, and epoxy resins are cured by heat. The thermal process is the most common in this sector. The conventional thermal process through electric resistance, infrared, or oil involves energy transfer by conduction. So, thermal gradients and nonhomogeneous exothermic reactions can be produced along the thickness of the part. This produces curing variations, external–internal solidification, thermal degradation, and residual stresses related to the process. Thus, it is necessary to work at low temperatures and low heating speed. This involves large curing cycles and external–internal curing that produces the tension and the contraction of the resin, and can cause delamination and/or matrix breaking.

These inconveniences have enhanced the development of processes based on rapid processing technologies. The use of other energy sources such as radiation is very interesting. A lot of interest is detected in microwave radiation, ultraviolet radiation, or electron beam (EB) as a new curing technology for polyester, vinyl ester, and epoxy resins adapted to different processes. These technologies can obtain two important effects:

- Volumetric heating
- Separation between filling and curing steps

Therefore, the main objectives of the use of rapid processing technologies in composite processes are:

- Reduction of curing time
- Reduction of manual work
- Optimize resin polymerization
- Reduce the production cycle time, increasing the productivity, and costs efficiency
- Decrease energy consumption
- Lower styrene emissions

The fibre-reinforced polymer composite (FRP) materials require the use of strict conditions to obtain a reproducible polymerization process. At present, thermosetting resins can be cured by different techniques including heating, UV radiation, and EB [1–3]

Although there is considerable interest in the field of natural fibre composites in structural applications, there has been little research on alternative rapid curing processes of these composites [4].

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9.1 UV curing

The photochemistry in polymers is one area that has been developed most noticeably at an industrial scale. This is not only due to the great number of applications but also due to the economical, technical, and ecological advantages. At industrial scale, the research and development of solvent-free systems have been developed due to their low energy costs and fast application at room temperature.

The photopolymerizable systems imply modifications in their formulations in order to produce materials with specific properties. As an example, the basic components in the coatings area are:

(a) Photoinitiator system (1–3 wt%)
(b) Oligomers (25–90 wt%)
(c) Monomers (15–60 wt%)
(d) Additives (1–50 wt%)

The monomers have generally a low molar extinction coefficient, so it is necessary to add to the system a photoinitiator that absorbs the UV radiation, producing reactive species (radicals or ions) to initiate the polymerization. The substrates acquire specific properties when the oligomers are added to them, obtaining a great variety of resins with different applications. The choice of the monomer depends on the following points:

- Viscosity control
- Effect on the polymerization rate and the final properties of the material, volatility, odour, and toxicity

9.1.1 Description of the UV curing process

The UV curing process needs a UV radiation source to expose the system to the UV light. The photoinitiator absorbs UV energy from the radiation source, initiating a chemical reaction that instantly converts the liquid formulation in a solid.

The UV curing uses permeable resins and reinforcements to the radiation and it is produced from the surface to the interior of the material. The monomers are instantaneously cross-linked, forming a protective surface that produces a reduction of 60%–90% in VOCs emissions.

The polyester, vinlyester, and acrylic resins reinforced with glass fibre can be cured by UV curing. However, the epoxy resins reinforced with carbon or aramid fibres are not permeable to the UV light, although they can be modified to be adapted to the UV radiation. Moreover, there are pigments and fillers that can inhibit or decrease the UV light penetration.

9.1.2 Reaction mechanism [5]

The UV radiation decomposes the photoinitiator added to the thermosetting resin when it is exposed to a specific wavelength, producing free radicals or cations that start the cross-linking reaction. Thus, this process is the so-called radical or cationic polymerization mechanism.

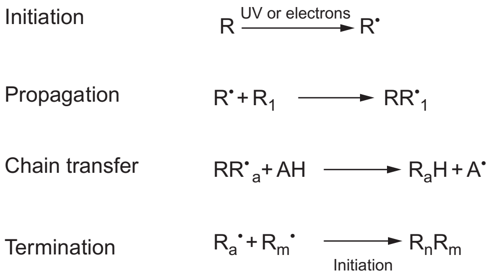


Fig. 9.1 Free radical mechanism.

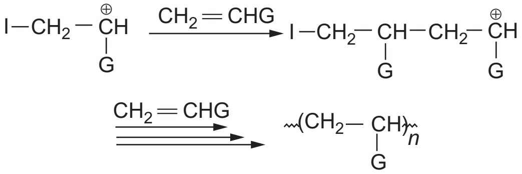


Fig. 9.2 Cationic polymerization.

A radical polymerization mechanism is shown in Fig. 9.1.

An example of cationic polymerization is shown in Fig. 9.2.

9.1.3 Photoinitiators

The photoinitiator is a critical component of UV curing process. It is the additive that initiates the polymerization process to reach rapidly the final cross-linked product. As UV radiation is emitted, it is absorbed by a photoinitiator, producing its split into reactive species. These species can be free radicals or cations. Most of the systems are based on free radicals that react with unsaturated compounds in a liquid form, so the latter can polymerize. This reaction is instantaneous and it is shown in Fig. 9.3.

The radical initiators represent more than 90% of the commercial photoinitiators, while the use of the cationic initiators is more limited.

These radical species are unsaturated molecules, which have aromatic carbon or acrylic rings, and they easily form free radicals. The radical initiators have been widely used in acrylate/methacrylate functional resins, and they can also be used with unsaturated polyester resins.

The cationic curing systems are unsaturated molecules and depend on the use of either epoxy or vinylester functionalized resins.

9.1.4 Radiation to the UV curing

Among all the nonionizing radiations, this section will be focused on the ultraviolet radiation.

The term ‘ultraviolet radiation’ refers to an invisible part of the electromagnetic spectrum, which is spread beyond the visible spectrum next to the violet colour. In Fig. 9.4 the spectrum corresponding to electromagnetic radiation is shown.

Process	Light		Step
[photoinitiator]	►	[photoinitiator]*	
Nonactivated		Activated	Absorption
[photoinitiator]*	►	R*	
Activated		Reactive species	Chemical reaction
R*+Monomers	►	R1*	Initiation
or oligomers		Reactive species	
R1*+oligomers	►	R2*	Propagation
or monomers		Reactive species	
R1*+R1*(or R2*)	►	R-R	Termination
or monomers		Nonreactive species	
		(polymer formed)	

Fig. 9.3 Photoinitiators function.

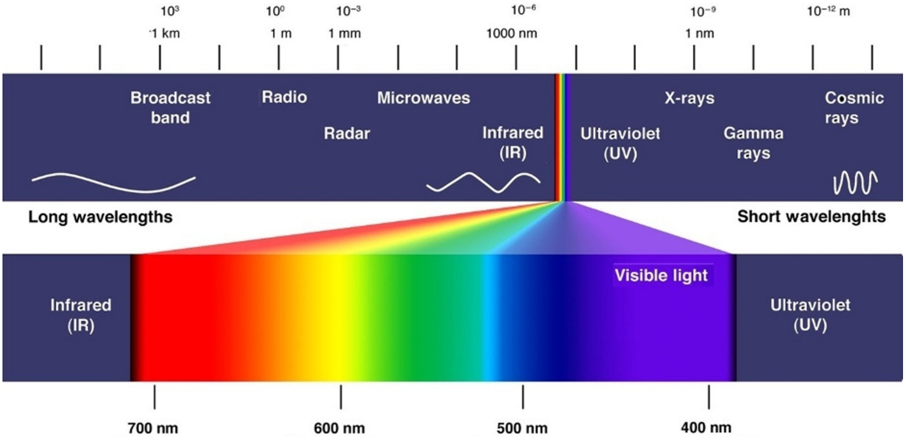


Fig. 9.4 The UV light in the electromagnetic spectrum.

The emission sources of UV light are the sun and man-made artificial sources. The UV light is divided into three groups:

- The ultraviolet light A (UVA), long-wave (320–395 nm), is represented by the sunlight.
- The ultraviolet light B (UVB), medium-wave (295–325 nm), is represented by the tanning lamps.
- The ultraviolet light C (UVC), short-wave (200–295 nm). The natural UVC radiation is completely absorbed by the atmosphere, so it has to be artificially produced by the conversion of electric energy.

9.1.5 Generation of radiation for the UV curing [6]

The first UV radiation source was produced by the mercury-vapour lamp (a gas discharge lamp). These units were replaced by incandescent units with *quartz tungsten halogen* (*QTH*). The emitted radiation is in the range of blue light (400–500 nm). The photoinitiator sensibility used in the composites is within this range.

Two types of light sources of great intensity emerged in the mid-1990s: plasma arc and Argon laser. A new radiation source emerged in the late-1990s: the *light emitting diode unit (LED)*. In comparison with the QTH curing units, the LED units present a radiation spectrum more reduced and they do not need filters. The spectrum ranges from 440 to 490 nm for most of these units. A significant advantage of these lamps is its great energy efficiency in relation to the energy consumption needed and the production of light of the lamp.

The composites curing with thin sections and gel coats, a UV lamp is preferred. Despite the type of light source, the emission spectrum of the lamp must be overlapped with the absorption spectrum of the selected photoinitiator.

Any material heated to a temperature higher than **2500°C** begins to emit UV radiation.

The artificial sources that emit considerable quantities of UV radiation are:

(a) The incandescent sources like quartz-Iodine lamps, which emit some UVA and UVB radiation
(b) Arcs of confined gas discharge
  (i) Germicidal lamps that work with low pressure mercury vapour arc-discharge
  (ii) High-pressure mercury vapour arc-discharge lamps, used in phototherapy, photochemical, and printing reactors
  (iii) High-pressure xenon arc-discharge lamps, used in the same above applications
  (iv) Flash tubes (xenon, krypton, argon, neon, etc.) with specialized uses in the industry
(c) The fluorescent lamps, which convert the UV light into visible light, are basically of two types:
  (i) Fluorescent sunlamps, used in bronzing cosmetics
  (ii) Black light lamps, used in fluorescence in paints and inks
(d) Electric arcs with carbon electrodes
(e) Halogen lamps with quartz ampoule, which are used for illumination and pattern lamps of reference
(f) Plasma, oxyhydrogen, and oxy-acetylene torch

9.1.6 Instrumentation for UV radiation generation

The function of the curing unit is to provide the UV energy that activate the photoinitiators and initiate the polymerization process.

The UV curing units can cost from 5000€ to 250,000€ per instrument. Although the UV curing system is simple, when a UV processing instrument is selected, it is important to bear in mind the following characteristics: type, width, number of parts, samples refrigeration method, and work temperature.

Fig. 9.5 shows a conventional curing unit that may be located in any company.

Fig. 9.5 UV curing tunnel.

Although there are a wide variety of available lamps and reflectors, the medium pressure mercury vapour precision reflectors are very efficient and can work with the conveyor belt working at high velocity. Moreover, they have sufficient energy to cure most of the resins that are available in the market.

In the curing units, the group of the lamp and the reflector that releases UV light is called irradiator. The irradiation is directly related to the electric energy, the lamp conditions and the reflector geometry, which directs and concentrates the lamp production. The irradiation does not vary with the exposition time.

Moreover, it is important to consider that the emitted energy by the lamps diminishes with their lifetime. The lifetime of the lamp must not exceed 1200 h, and it must be replaced after 1000 h of use as a precaution.

9.1.7 Influencing factors on UV curing process

The curing process is initiated with the collision of a photon with a molecule. The success of the UV curing depends on the facility to project photons in a material to activate the photoinitiator molecules. The optic properties of the curable material (polymeric resin) and the optic properties of the lamp must be combined in order for the UV curing to be effective.

There are thermodynamic and optic properties of the material that interact with the radiant energy from the UV lamp and influence significantly the process [7].

These optic properties of the material can be the following:

- *Absorption spectrum*: it is the relative energy as a function of the absorbed wavelength in the material as the depth is increased. More energy absorbed near the surface means less energy available at deeper levels of the part, but this varies with the wavelength.
- *Reflectance and scattering*: it is the reflected energy by the material in relation to the absorbed energy. This reduces the quantity of available UV energy at deeper levels but it can improve the curing efficiency at superior levels.
- *Infrared absorption*: it is a measure of the quantity of radiant energy by the material surface. The infrared radiant energy from the UV lamps is the main heat source for the material.

Regarding the factors that influence the UV curing from the UV lamps are:

- The irradiance or UV intensity
- Espectral distribution of the UV light (wavelengths)
- UV energy (integral of irradiance and time)
- Infrared radiation

The light intensity and the distribution of wavelengths affect the properties after the curing of the photoactivated composite materials.

Some experiments have manifested the influence of (i) the thermoset material type, (ii) the exposition time to the radiation, and (iii) the presence of a filter on the curing depth.

The part can be radiated by the UV light in three different ways [6]:

(a) *Linear exposition*: a tubular lamp with a centred reflector or a row of extended tubular lamps over the work surface, which supply uniform UV energy in that dimension. The motion of work surface provides uniformity in the exposition along the motion direction. Variations of the linear process are the use of printing presses of sheets, machines that apply paint by contact and conveyors.

(b) *Static exposition*: an object or process is located under a UV lamp and the exposition time is controlled according to the required properties.

(c) *Dynamic exposition (3D)*: it is a modified version of the linear exposition. When the surface to be cured is complex, curved or '3D', it is difficult to cover the surface linearly with intense and focused light. If the part is rotated while it passes through the zone where the lamp is, this complex surface will be cured.

9.1.8 Applications

The UV curing is advantageous in the processes of open mould, pultrusion, and filament winding to produce different products like:

- Boats
- Ceiling light panels
- Enclosures for bathtubs and showers
- Recreation vehicles and trucks
- Poles
- Pipelines

Application of the UV curing to different transformation processes of thermosets

9.1.8.1 UV curing in processes of open mould

The UV curing reduces the cycle times and the production rate.

The open mould enters into a UV curing chamber where the whole surface of the part is exposed to the UV radiation, so the curing reaction is initiated in a few seconds. It is possible to cure transparent resins (nonpigmented) together with the glass fibre, and to achieve thicknesses of 12.7 mm or more. Also, it is possible to cure transparent gel coats depending on their thickness and colour.

The manufacturers of polyester resins can add photoinitiators, which generate free radicals when they are exposed to UV light.

The advantages of using UV curing are:

(i) Higher productivity
(ii) Less work of processing
(iii) More consistent parts
(iv) Reduced space necessities
(v) Higher control over the fibre content since the resin has enough time to flow and impregnate the fibre

Sometimes a hybrid curing is needed, especially in parts where the access of the UV light is difficult. In this type of curing, photoinitiators and catalysers are used in conjunction (the UV light reaches rapidly the surface and the curing reaction is initiated).

9.1.8.2 UV curing in the process of infusion [6]

The Resin Infusion between Double Flexible Tooling (RIDFT) process takes place in two stages: resin infusion and vacuum forming.

The capacity to introduce UV radiation to this process is due to the fact that the flexible silicone membranes used are transparent.

A variable that influences the results is the exposition time of the laminates to the UV radiation. An inadequate curing time could reduce the cross-linking reaction.

The properties, like for example the Young's modulus of the material, are better when the curing is produced by UV light. This may be due to the fact that the curing process is faster and the evaporation of the styrene is lower, so there are more styrene molecules available to the cross-linking reaction. This reduction in the evaporation of the styrene molecules is due to the rapid formation of a protective layer on the surface.

The properties like the tensile resistance are not highly influenced by the UV light, since this property is mainly determined by the fibres and is less influenced by the matrix. Therefore, the variation in the composition of the matrix will have less influence on this property.

9.1.8.3 UV curing in the Resin transfer moulding process

One of the advantages of this process is that the curing of the part is initiated when the UV radiation is applied. UV irradiation through a glass window at one side of the Resin transfer moulding (RTM) mould, the cure continuously propagates towards the other side [8].

Since the UV curing is a fast process, i.e., the curing time is a few minutes instead of hours, the part has less risk of fracture.

9.1.8.4 UV curing in filament winding [9]

Parts like low pressure oxygen bottles, baseball bats, and pipelines are obtained with this method.

This process could be used to obtain an intermediate phase in the thermosetting polymerization (the so-called B-stage), a complete curing, or a gel-coat curing. To that end, the lamps are located after the resin bath, previously to the winding in the mandrel, until the resin over the roving achieves the B-stage state. This state does not represent a complete curing, but the resin cures partially to a tacky state.

Some of the applications include cylinders or goal shafts which require an attractive appearance. The resins that can be UV cured using Filament Winding are vinyl ester, polyester, and epoxy resins. Moreover, in the case of polyester and vinyl ester resins, it is possible to avoid the use of styrene with the addition of photoinitiators.

9.2 Microwave (MW) curing

9.2.1 Introduction

In conventional thermal processing, energy is transferred to the material from the surfaces. In microwave processing, the energy is supplied by an electromagnetic field directly to the material. Under the electromagnetic field the energy is absorbed by the reorientation of the polymer dipoles, the energy is then dissipated as heat as a consequence of the movement of the dipoles. Energy can be transfered throughout the whole volume of the composite part to be cured, so this results in rapid heating

[10–13], The use of microwave radiation is a technical alternative to conventional processing for the nonhomogeneous heating of the FRP materials and reduces the processing time.

Microwaves are electromagnetic radiation in the frequency ranging from 300 MHz to 300 GHz. They are used mainly for radar, communication technologies, plasma generation, and heating of materials. For industrial use microwave of a frequency of 2.45 GHz is mostly used. The curing of materials with microwaves is the electromagnetic curing processes. Because of the high frequency of microwaves, transmission through free space is possible. Therefore, three dimensional curing can be done without specific electrodes.

Microwave power irradiation is known as an incredibly rapid and selective, clean and safe, versatile, and energetically convenient heating method. It is useful for application in polyester, vinylester, and epoxy resins to accelerate polymerization processes. Nowadays, at industrial level, this technology is used to cure thermoset elastomers (SBR, NBR, natural rubber, etc.) in a continuous extrusion process.

9.2.2 Description of microwave curing process

Microwave heating, therefore, will couple most efficiently with the strongest dipole in a system and has the potential to selectively heat polar polymers in mixtures. The efficiency of microwave coupling with polymer materials is dependent on the dipole strength, its mobility, and mass and the matrix state of the dipole [14]. Microwave coupling to a given dipole will be greater in a liquid, less in a rubber, and even further reduced in a glassy or crystalline polymer.

Polymer dielectric constants can vary during a processing cycle or when a phase change occurs due to temperature shifts, solvent is removed, and the reaction proceeds changing the type and concentration of dipoles. Generally, several distinct dielectric relaxation processes are present in a solid polymeric material. This is shown in Fig. 9.6, which is a scan of dielectric loss at constant frequency as a function of temperature. Similar relaxation processes are observed in dynamic mechanical properties of polymers, with analogous dispersions in real and imaginary components of viscoelastic response.

From previous studies, it is evaluated that natural and glass fibres have the same dielectric loss factor, it is expected that the same extent of cure for a given cure time occurs when a microwave radiation is applied [4].

9.2.3 Mechanism of microwave coupling in polymers

Microwave processing can be used over a broad range of polymers and products, including thermoplastic and thermoset resins, rubbers, and composites. Many polymers contain groups that form strong dipoles (e.g., epoxy, hydroxyl, amino, cyanate, etc.), however not all polymer materials are suitable for microwave processing.

Initially, thermoset polymers are low-viscosity liquids that can flow into a mould or around fibres. During processing, thermosets react to increase molecular weight

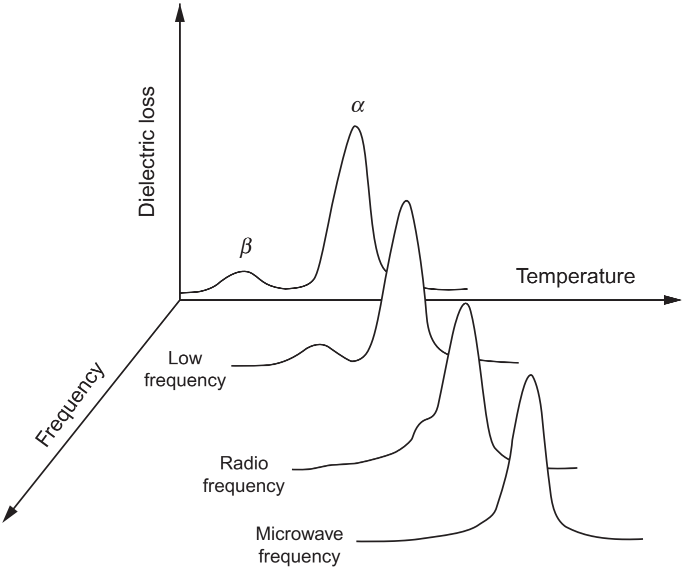


Fig. 9.6 Schematic dielectric loss vs temperature and frequency for polymer materials [15].

and viscosity, becoming eventually highly cross-linked, solid, insoluble, and infusible materials.

Thermoset curing processes consist of three basic steps:

(1) Preheating of the components
(2) Reaction, producing the corresponding exothermic heat
(3) Cooling of the cured materials

Permittivity and dielectric loss factor of thermosets generally increase with the temperature and decrease with the extent of cure. These polymers tend to be efficient absorbers of microwave radiation initially, with ε'' increasing as the resin is heated. As the cure reaction progresses, the temperature may be difficult to be controlled due to the additional heat input caused by the exothermic reaction.

Polymer systems that are candidates for microwave processing are typically not conductive. Particles and fibres that are conductive or unreactive organic additives may be included to aid processing or to modify the mechanical, physical, or optical properties. The presence of these inclusions can strongly influence the way in which the composite material interacts with the microwave radiation.

9.2.4 Polymers for microwave applications

Some functional groups can absorb microwave radiation. These groups have a significant dipolar moment. This dipolar moment represents electronic cloud distortion between two atoms with different electronegativity. If a molecule is composed only of two atoms, more electronegativity difference means higher dipolar moment. Fig. 9.7

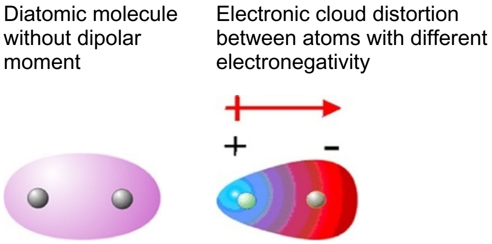


Fig. 9.7 Representation of molecules with and without dipolar moment.

shows two molecules: first one without dipolar moment (left) and second one with evident dipolar moment (right).

Functional groups with strong or medium dipoles are hydroxyls, epoxies, amines, cyanates, imides, chlorine derivates, etc.

The microwave energy transfer is strongly influenced by several parameters, e.g., irradiation power, time of microwave exposure, geometry of the applicator, impulsive or continuous irradiation, frequency of the electromagnetic waves, shape and size of the sample, and so on. In the case of *epoxy resins*, the degree of cure achieved in microwave process is invariantly higher than corresponding value for conventional heating, though the two thermal profiles are kept comparable. The activation energy in microwave field is significantly lower than that calculated from isothermal DSC data. Therefore the claim of an acceleration of reaction rate, due to the effect of the electromagnetic radiations, can be suggested. Moreover physical–mechanical properties of microwave cured samples, such as the glass transition temperature and flexural elastic modulus, are higher than those obtained for thermally cross-linked specimens and this behaviour seems to depend only on specific effects of the microwave heating mechanism [16].

9.2.5 Heating promoters for microwaves

It is common practice to add particles and fibres to the polymer to improve its processing behaviour and modify mechanical, physical, or optical properties of the polymeric matrix. Conductive fillers or those with dielectric properties can influence the effect of the microwave to the polymer matrix. The effect of heating promoters depends on the size, geometry, concentration, and the electric resistance of the additive. Their dispersion and distribution in the polymeric matrix is also very important.

On the other hand, the presence of conductive fillers can inhibit microwave heating because penetration depth can be reduced. However, filler composition, orientation, and concentration can define material response to microwave heating. For example, carbon fibres have a high electric resistivity, but can heat the matrix very effectively, presenting a thermal profile with maximum effect on the fibres surface. This preferential heating behaviour improves interphase adhesion between the fibres and the matrix. This means polymeric materials with higher resistance to failure.

Nonconductive additives such as glass fibres and some pigments can influence the material behaviour through preferential heating mechanisms, depending on dielectric properties of the additives.

It is possible to divide heating promoter additives for microwaves into the following groups:

- *Metallic filler [17,18]*: Metals, metal oxides [19] (including ferrous oxides and ferrimagnetic materials), ferroelectric fillers [20]
- *Organic dipolar additives*: Glycols and related compounds (diethylene glycol, ethylene glycol ethyl ether, polyethylene glycol 200, polyethylene glycol 400), phtalates (dibutyl phthalate, diisodecyl phthalate, diisononyl phthalate, dioctyl phthalate, butyl benzyl phthalate), cyanates (2,4-toluene diisocyanate, 1-naftil isocyanate), amines (triethylamine, diphenylamine, hexamethylenetetramine)
- Inorganic and transparent additives

9.2.6 Electromagnetic field

Microwaves form part of a continuous electromagnetic spectrum that extends from low-frequency alternating currents to cosmic rays [21].

Basically microwave technology provides an alternative to conventional heating methods, with several important advantages like: penetrating radiation, controllable electric field distribution, rapid heating, selective heating of materials, and self-limiting reactions [21].

The energy involved in the process is supplied by an electromagnetic field when it comes in contact with the material. Two major effects are responsible for the heating which results from this interaction [22]: dipolar polarization and conduction.

The material properties are of greatest importance in microwave processing. The complex relative permittivity $\varepsilon = \varepsilon' - j\varepsilon''$ and the loss tangent, $\tan\delta = \varepsilon''/\varepsilon'$ are critical to study the interaction between the electric field and the dipoles of the material. The real part of the permittivity, ε', sometimes called the dielectric constant, mostly determines how much of the incident energy is used in the dipole rotation. The most important for a material is to find the frequency where both the absorption of energy ε', and the energy loss, ε'' will be high (see Fig. 9.8). This equilibrated frequency point is well determined by the loss tangent, $\tan\delta$, or *dielectric loss*, which predicts the ability of the material to convert the incoming energy into heat. For example, for water, the maximum in the dielectric loss is around 2.0 GHz, in the range of the domestic ovens [23–25].

9.2.7 Microwave equipments

The study of the state of the art related to the different microwave heating techniques is useful to select the most interesting equipment for the promoted heating studies. Microwaves form part of a continuous electromagnetic spectrum that extends from low-frequency alternating currents to cosmic rays [21]. Microwaves propagate through empty space at the velocity of light. The frequency ranges from 300 MHz to 300 GHz. Frequencies reserved for industrial applications consist of 915 MHz, 2.45 GHz,

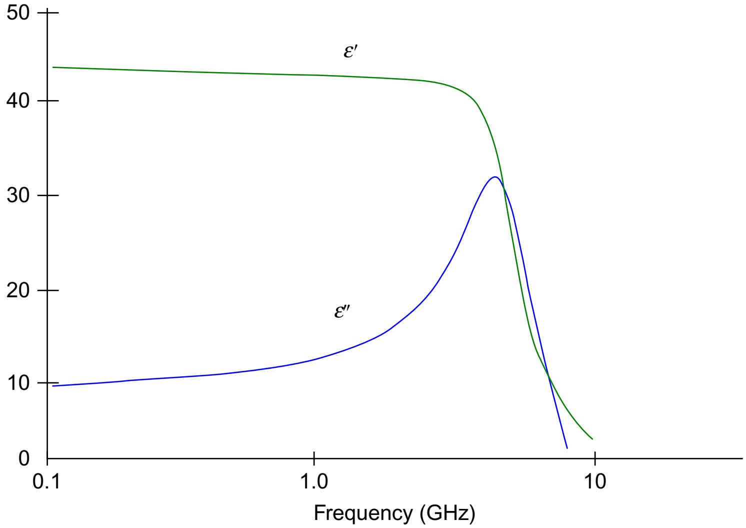


Fig. 9.8 Dielectric spectrum for a microwave absorbing material.

5.8 GHz, and 24.124 GHz. Amongst those bands, 2.45 GHz is the most commonly used in industrial applications. Industrial microwave ovens are operated by a variety of devices such as magnetrons, power grid tubes, klynstrons, klystrodes, crossed-field amplifier, travelling wave tubes, and gyrotrons [26]. In the typical domestic applications the microwave frequency is 2.45 GHz.

Different microwave technologies are available: closed oven technologies, like fixed frequency and variable frequency (VFM), multimode and monomode systems; open microwave spaces as moving antenna system (for big finished parts).

In order to select the most suitable equipment, the different characteristics of each discussed technique has been compared (see Table 9.1) [27–29].

9.2.8 Influencing factors on MW curing process

The microwave energy transfer is strongly influenced by several parameters, e.g., irradiation power, time of microwave exposure, geometry of the applicator, impulsive or continuous irradiation, frequency of the electromagnetic waves, shape and size of the sample, dielectric properties, and so on.

9.2.9 MW curing of thermosetting resins and composites

In the case of epoxy resins, the degree of cure achieved in microwave process is invariantly higher than the corresponding value in conventional heating, though the two thermal profiles are kept comparable. Therefore the claim of an acceleration of reaction rate, due to the effect of the electromagnetic radiations, can be suggested. This behaviour seems to depend only on specific effects of the microwave heating mechanism [30].

Table 9.1 Characteristics of different microwave systems

	Fixed frequency	Variable frequency	Moving antenna system	Monomode system
Heating	Nonuniform heating. Hot places absorb more energy. Some points are exposed to more electric fields creating 'hot spots'	The presence of 'hot spots' is minimized and heating homogeneity is increased. The irradiation with variable frequency creates 'thousand of waves' and appears as a lot of 'hot spots'. This technology does not use magnetrons, but wave tubes	Uniform heating depending on the antenna 'displacement'. Irradiation of 'continuous' and big samples (like commingling or curing processes). Control in the distance between magnetrons and sample	Direct irradiation of the sample without reflections. Ensure heating homogeneity and efficiency of the radiation
Control	Temperature control by IR camera or optical fibre	Temperature control by IR camera or optical fibre and it allows knowing the best microwave frequency to heat the polymeric material	Temperature control by IR camera. Possibility to fix a specific and controlled temperature	Temperature controlled by IR camera or contact probe
Power	Short heating times because high magnetron power level can be used	Lower power level through wave tubes technology	High magnetron power level like fixed frequency oven, but less efficiency because of the open chamber	High magnetron power level can be used at maximum efficiency because of lower wave reflections and wave lost
Cavity	Small cavities. Big cavities are too expensive	Small cavities. Big cavities are too expensive	No limits in the size of the sample or cavity	Very small cavities due to the necessity to direct the wave orientation to the sample
Price comparation	Low	High	Low	Low

In order to evaluate this technology different kinds of resins used in the composite sectors have been examined, such as unsaturated polyester resins (UP-A, UP-B, UP-C), vinylester resins (VE-A), and epoxy resins (EP-A, EP-B).

In order to improve the interaction between microwaves and resin, dielectric additives can be employed, especially in the case of polyester resins. Dielectric additives are polar substances that can be added to the resin mixture in very low proportion (up to 2.5%) to absorb the microwave radiation and transform such radiation into heat, which is transmitted to the resin. In this development, different additives have been evaluated for the polyester resins (glycols, phathalates, etc.) [31].

A set up of the microwave curing technology has been carried out for each neat resin system, taking into account different variables: microwave power, temperature, curing time in microwave, etc.

With dielectric test, an evaluation about suitable matrix has been done. As it is previously mentioned, the dielectric function describes the interaction of microwaves with the material. It is a complex value. The real part describes the electromagnetic energy in the material. The imaginary part describes the electromagnetic energy which is transformed into heat.

The best method to determine the dielectric function is the resonator method. A microwave resonator is put out of tune because of the sample inside the resonator. From the frequency shift and the reduction of the quality of the resonance the dielectric function can be calculated.

Differential scanning calorimetry (DSC) can be used to obtain the enthalpy of cure for the resin. The residual enthalpy for the cured was measured by DIAMOND DSC equipment. DSC samples were heated from 20°C to 250°C at $10°\mathrm{C\,min}^{-1}$ for polyester resin and from 20°C to 340°C at $10°\mathrm{C\,min}^{-1}$ for vinylester and epoxy resins. The enthalpy of residual cure was obtained from the loss part of the heat capacity by integration of the area of the exotherm. From the enthalpy the degree of cure, α, was calculated using:

$$\alpha = 1 - \frac{\Delta Hb}{\Delta Ha} \tag{9.1}$$

where ΔHb is the residual curing enthalpy of a partial cured sample of resin and ΔHa is the curing enthalpy of the reference sample.

An evaluation of different microwave susceptors has been carried out in order to obtain suitable microwave absorbing additives to use in microwave curing. For this, DSC tests have been developed to evaluate the influence in the degree of cure by microwave curing at 1000 W and 60°C.

As a conclusion and taking into account the degree of cure after microwave curing of neat polyester resins, optimum results are obtained with polyester resin, UP-C (Table 9.2).

In order to improve the interaction between microwaves and resin, some additives are evaluated as microwave susceptors. The best results are obtained with following additives:

- Additive 2
- Additive 5
- Additive 6

The addition of additive 6 to the formulation of the polyester resin (UP-C) has an important effect on microwave curing, increasing the degree of cure in the resin.

Table 9.2 Results of DSC tests of UP resins with and without microwave susceptors and processed by microwave [32]

Resin	Microwave absorber	ΔH (reference) (J/g)	ΔH (mw curing) (J/g)	Degree of cure (mw curing) (%)
UP-A	–	−238.4835	−52.7331	77.9
UP-B	–	−258.4405	−121.3589	53.0
UP-C	–	−357.6020	−50.7818	84.8
UP-C	Additive 1	−357.6020	−55.6554	84.4
UP-C	Additive 2	−357.6020	−48.1822	86.5
UP-C	Additive 3	−357.6020	−56.4623	84.2
UP-C	Additive 4	−357.6020	−68.8610	80.7
UP-C	Additive 5	−357.6020	−35.8181	90.0
UP-C	Additive 6	−357.6020	−30.5008	91.5

Comparing with conventional heating and taking into account that same range of degree of cure is achieved, it could be concluded that an important reduction in the cycle time is obtained by microwave curing of polyester resin UP-C (Table 9.3).

A TA Instruments DMA 20980 equipment in dual cantilever mode was used to obtain the dynamic mechanical data applying a heating rate of 3°C/min in the interval of 30–250°C, a frequency of 1 Hz and a strain amplitude of 20 μm. For this purpose, composite test specimens with approximate dimensions of 35, 10, and 4 mm were prepared.

The purpose of dynamic mechanical analysis (DMA) was to provide information about viscoelastic properties and moreover the degree and homogeneity of resin curing comparing the effectiveness of microwave and conventional processes.

Regarding vinylester resin system, optimum results are also obtained with VE-A and microwave parameters of 1 h at 60°C at 1000 W in comparison with an equivalent conventional curing cycle of 7 h at 50°C because of the low difference in T_g values (Table 9.4).

Table 9.3 Results of DSC tests of UP-C with additive 6 by different curing methods

Sample	ΔH (reference) (J/g)	ΔH (cured) (J/g)	Degree of cure (%)
Microwave curing (3.5 min at 60°C at 1000 W)	−333.7907	−30.5008	91.5
Conventional curing (50 min at 60°C)	−333.7907	−31.3659	90.6

Table 9.4 Results of T_g for vinylester (VE-A)

	Processing time	T_g (°C)
Microwave curing	1 h at 60°C at 1000 W	167
Conventional curing	7 h at 50°C	159

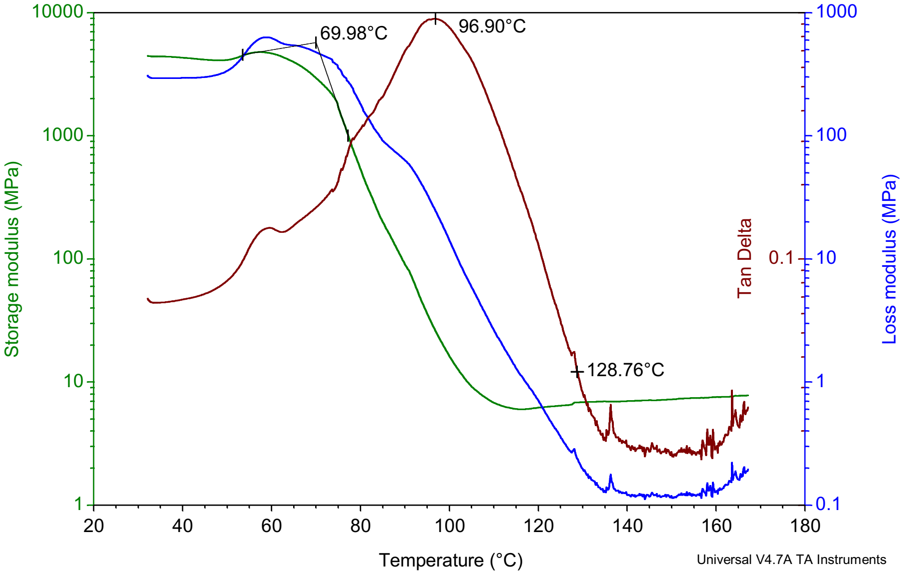


Fig. 9.9 DMA test of EP-B with microwave curing (1 h at 60°C).

In relation to epoxy resin, EP-A and EP-B have been evaluated. Both epoxy resins (EP-A and EP-B) showed time reduction with curing assisted by microwaves. In the case of fully cured epoxy resin (EP-B), the storage modulus does not indicate a residual curing; same range of T_g value is obtained with an important decrease in processing time compared to microwave curing (1 h at 60°C) with conventional curing (15 h at 60°C) (Figs 9.9 and 9.10).

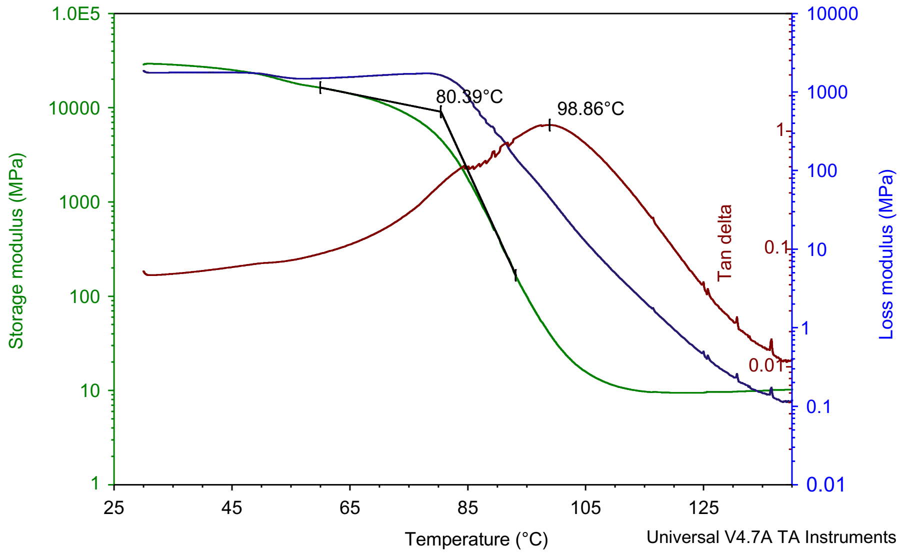


Fig. 9.10 DMA test of EP-B by conventional curing (15 h at 60°C).

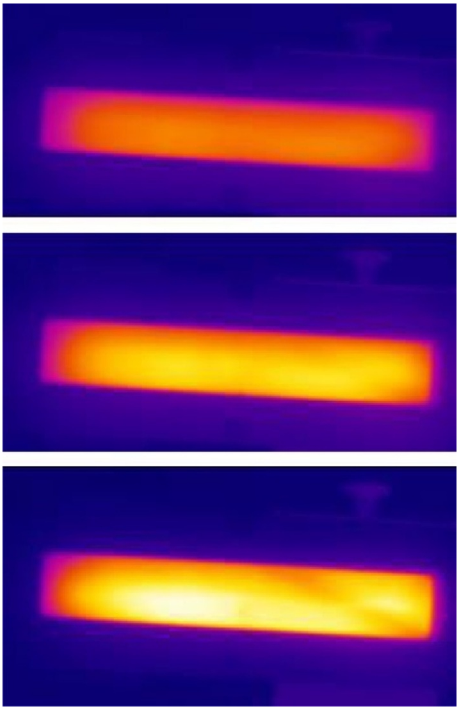


Fig. 9.11 Volumetric heating of part processed by microwave heating.

Multifunctional polyester, vinyl-ester, and epoxy resins suitable for RTM process and microwave curing have been modified, obtaining good results in terms of polymerization degree and reduction in curing time. Some conclusions can be established

- The addition of susceptors to the formulation of the UP-C polyester resin has an important effect on microwave curing, increasing the degree of cure when compared with the other additives evaluated for polyester resin.
- Comparing with conventional heating and taking into account that same extent of cure is achieved it could be concluded that an important reduction in the cycle time is obtained by microwave curing for three resin systems evaluated (polyester, vinylester, and epoxy).
- Suitable homogeneity of microwave heating effect, temperature, and curing have been reached by the innovative microwave system developed in connection with a temperature control system, helping by the simulation software for the microwave field.

9.2.10 Advantages of MW curing vs conventional curing

When samples prepared by microwave curing vs conventional curing are compared, more remarkable differences are: volumetric heating, fast and controllable, and electromagnetic energy aimed at the product (Fig. 9.11).

Conventional curing is focused on the heating of material exterior, so heat is transferred to interior by conduction (and convection in liquids and gas).

Conductive heating velocity (and convective) is controlled by different factors. Differences between surface temperatures and internal temperature of material, and the capacity of the material to conduct the heat are some of these highlighted factors.

In order to increase the index of heating in conventional curing, surface temperature is increased. Problems are caused by this temperature variation which could be solved by the use of electromagnetic heating.

Heating by electromagnetic radiation has the capacity to maintain a stable process which promotes a better quality. When electromagnetic energy is applied in a material, a portion is reflected by the material surface, other portion is transmitted by the material and remaining portion is absorbed by the material.

9.2.11 Applications

An innovative microwave-assisted curing (MAC) technology for thermoset materials with improved flexibility and more time efficiency than current curing technologies adapted to the RTM and RTM-Light industries for composites production has been developed. Different specific composite innovations have been performed in this development:

1. A scalable microwave system adapted to RTM (Fig. 9.12) has been developed for homogenous heating and therefore curing of composite parts. Only the combination of the developed resins and the microwave system with a temperature control ensured a homogenous processing of the part
2. RTM moulds adapted to MAC-RTM technology (Fig. 9.13)
3. A curing control and sensor system to guarantee a cost-efficient, controlled, and reproducible curing process (Fig. 9.14)
4. Polyester and epoxy systems adapted to microwave curing with an important reduction in time curing, especially in the case of epoxy resins

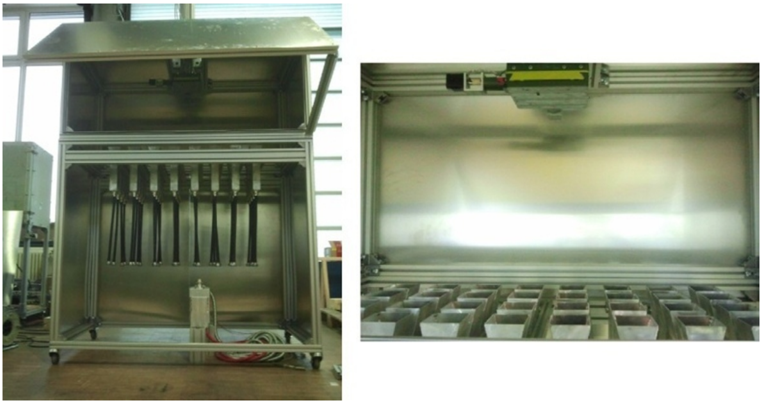


Fig. 9.12 Design and building of microwave antenna structures.

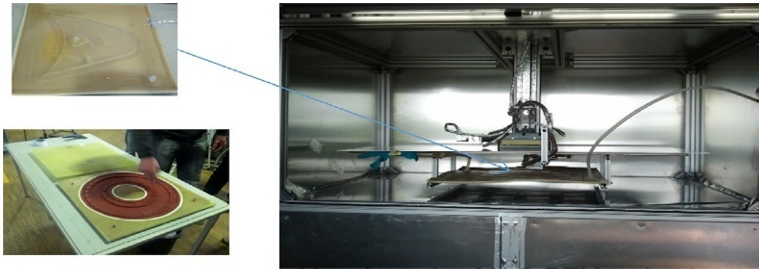
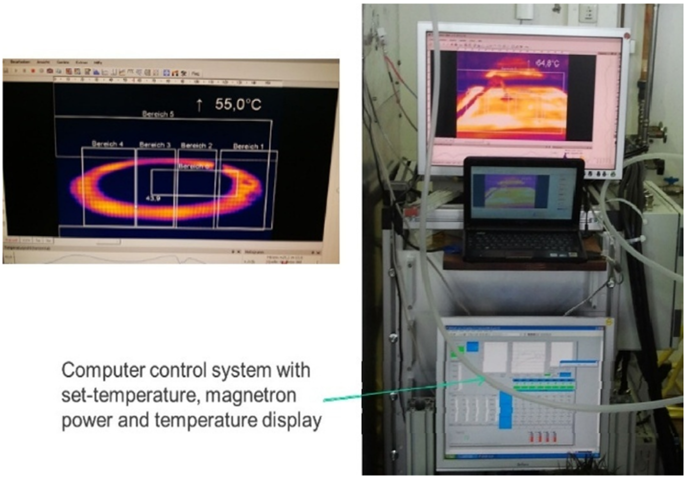


Fig. 9.13 RTM moulds adapted to MAC-RTM technology.



Computer control system with set-temperature, magnetron power and temperature display

Fig. 9.14 Computer control system adapted to microwave technology.

The developments in the MAC-RTM technology have allowed the adaptation of the RTM and RTM-light processes for medium volume components production with the following advantages:

- Fast and homogenous heating
- Reducing the production cycle time by 40%
- Achieve the cross-link (polymerization level) to nearly 100% with an important reduction of time
- Mechanical properties of composites produced using both technologies, microwave and conventional heating, are comparable

9.3 EB curing

9.3.1 Description of the EB curing process

EB curing is a nonthermal process, in which high-energy electrons from an accelerator are used to initiate polymerization and cross-linking of a resin by ionization and excitation of the resins [33]. The EB curing of composite materials reinforced with fibre

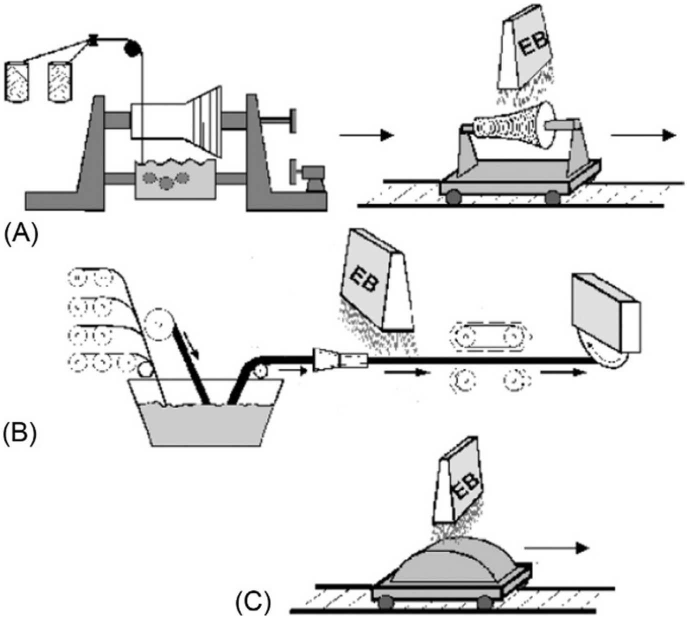


Fig. 9.15 Composite manufacturing processes suitable for EB curing: (A) filament winding, (B) pultrusion, and (C) prepreg layup with vacuum bag [31].

is a technique to fabricate aerospace components and land vehicles. As a curing technique, it must be combined with a moulding process like prepreg layup with vacuum bag, infusion, pultrusion, etc.

The basic concepts about the EB curing of composites are shown in Figs 9.15 and 9.16 [34].

9.3.2 Reaction mechanism

The EBs of high energy generate ionic species, free radicals, and molecules in excited states capable of initiating and keeping the polymerization reaction. Fig. 9.17 shows a scheme of the pathways for induction of the polymerization by EB irradiation. Depending on the chemistry of the resin system that is irradiated, two general mechanisms can initiate the polymerization process: free radical initiation or cationic initiation.

The polymerization of acrylic/methacrylic systems, maleic or fumaric polyester resins, maleimides and tiolenic systems is carried out through radical mechanisms without initiators.

The polymerization of nitroethylene takes place through anionic mechanisms, and the epoxy materials polymerize through cationic mechanisms using an appropriate photoinitiator under EB radiation.

The most promising among these systems for composites applications are free radical cured systems based on acrylate and methacrylate functionality, and cationically cured epoxies catalysed using diaryliodonium or triarylsulfonium salts.

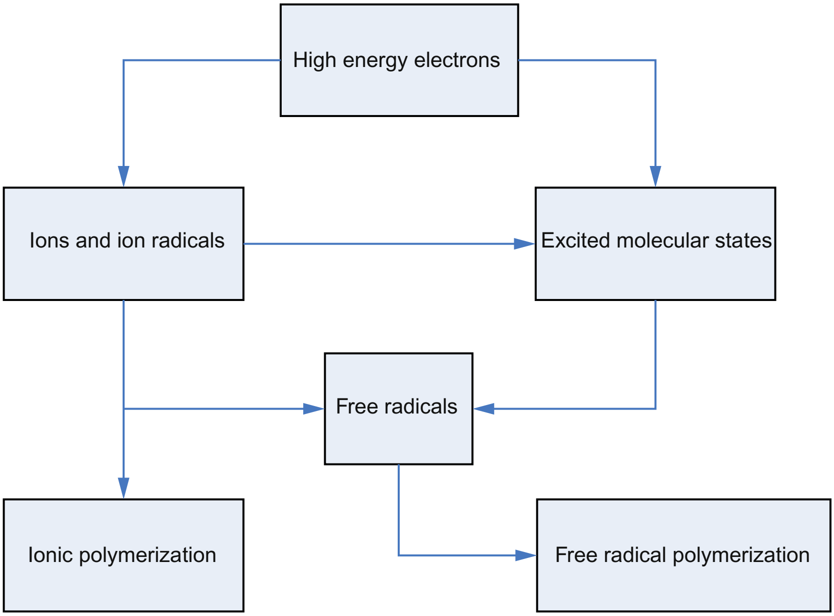


Fig. 9.16 The EB radiation over the EB curable resins and adhesives generates ions, free radicals, and excited molecular states that initiate and keep the polymerization reaction [31].

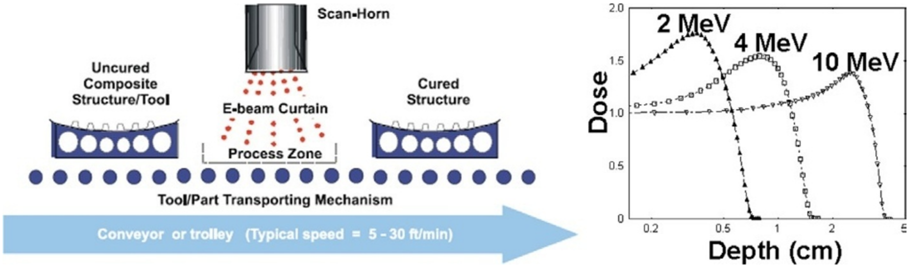


Fig. 9.17 The high energy electron beam is produced in the accelerator (sometimes known as EB gun), transported through the air and deeply introduced in the material. The penetration depth is proportional to the energy, measured in mega electronvolts (MeV). The dose is a measure of the deposited energy. The typical dose for curing composite or adhesives lies within the range of 50–200 kGy [31].

9.3.3 EB curing materials

Using this curing technique, the necessary time to cross-link the polymer is reduced in comparison with the conventional thermal curing, since the rate of cross-linking is very high. The cross-linking density is more closely associated with the absorbed radiation than the temperature achieved in the thermal curing process [35].

The main benefits of the EB curing are listed below [30,31]:

- The curing happens at temperatures near room temperature, which implies the use of low cost tools like wood, plaster, or foam.
- The curing at low temperatures can reduce the residual thermal stresses.
- The operations of bonding and curing using EB adhesives lead to the fabrication of wide integrated structures.
- In comparison with the thermal curing, the EB curing reduces the most toxic portion of the system and has low emission of volatile components by elimination of cross-linker.
- The EB curable resins are more stable and thus have longer shelf life. Without exposure to high temperature, radiation, or excessive light, these materials do not auto cure significantly, so they can be easily stored. Normally, they are composed of a single component and they are solvent-free products.
- For large parts that are impossible or inconvenient to fit in an autoclave, the EB process is the alternative. Moreover, there are EB systems that are portable.
- The EB curing can reduce between 10% and 40% of the production costs for manufacturing a variety of aerospace parts in comparison with the conventional curing. The capital costs of the EB curing systems (mainly the electron accelerator and the shielding device of some radiations) are similar to those of the large autoclaves.
- As no photoinitiators are needed in comparison with UV curing, pigments or other additives do not interfere with the curing.

9.3.4 Equipment for EB radiation generation

The high energy electrons are generated by charging a tungsten filament at a high negative potential and then, are directed by magnets in a curtain through a metal window to the resins to be cured. After the interaction of electrons with material, primary electrons and backscattered electrons are generated and they do not cause chemical reactions. Secondary electrons have less energy and are slow enough to cause ionization and radical formation. The high energy electrons cause excitation and create radicals in the resins as well as their ionization into radical cations and secondary electrons that start the polymerization reaction.

High radiation dose of EB curing causes both health and safety concerns, so it is important to apply a low dose radiation in industrial scale. EB dose can be decreased with the addition of a suitable additive to the curing formulation without sacrificing the mechanical properties of the final product [30].

9.3.5 Common limitations of EB process

Despite the benefits mentioned previously, the higher capital costs of the EB, the need to use inert atmospheres, and the need for shielding to protect workers from the EB are some of the limitations that present this curing process.

On the other hand, although the EB curing and bonding of composites is an active area of research, this technology has not been widely used in the industry. This is partially due to the conservative nature of the aerospace and automotive industry.

Different reasons explain why the composites and adhesives that can be EB cured do not reach the expected characteristics in the aerospace systems:

- The resin chemistry (either free radical or methacrylated and cationic epoxy-based) produces different polymer structures than heat-curable systems.
- Reduction of the fibre-matrix interface due to the incompatibility between the EB curable resins and the surface of the fibres.
- There are different current limitations of the EB curable resins and composites. The epoxy systems cured by a cationic mechanism generally do not exhibit good fracture toughness and other typical properties of composites like the compression resistance, which are very sensitive to the resin performance. Moreover, the interlaminar resistance is much lower, not only due to the low fracture toughness but also due to the poor interfacial resistance between the surfaces of carbon fibres, which have been optimized for the thermal curing of the epoxy-amine systems, and not for the EB cured epoxy systems and acrylate/methacrylate composites.

Thus, research and development is currently being carried out in order to overcome these limitations.

9.3.6 Applications

In the electronics industry, the EB curing process is utilized to cross-link insulators of cables and wires, to produce pipelines of low shrinkage with heat, and to make polymeric devices like resettable fuses for the electronics sector (automotive and laptop industry). Also, it has been used in the industry of inks and coatings, to sterilize medical products, to increase the resistance of the shopping plastic bags, and to cross-link the rubber in tyres. The resins and adhesives that can be cured by EB radiation can be used in the aerospace and automotive industry through free radical or cationic polymerization. The aerospace programmes have adopted cationic resins due to their high temperature of use and low contraction. Free radical resins and adhesives have the advantage of a quicker curing in comparison with cationics and they are not inhibited by nucleophilic (alkaline) materials that are above the fibres or surfaces.

9.4 Opportunities, trends, and current developments in the field of alternative curing techniques applied to bio-based resins and composites

A comparison of different alternative curing methods vs conventional curing [36] is detailed in order to review the opportunities of these techniques applied to bio-based resins and composites. Advantages (Table 9.5) and disadvantages (Table 9.6) of different techniques have been specified.

Table 9.5 Benefits of alternative curing vs conventional curing

UV curing	Microwaves curing	E-Beam curing	Catalytic curing
The curing time is reduced from hours to minutes, so significantly increases the production rate. Sometimes, it increases from 2 to 8 times more than the rate of curing with methyl ethyl ketone peroxide (MEKP)	Increase in the production rate (with a factor between 2 and 5) due to the reduction in the curing time	The curing process is developed at room temperature, so low cost tools can be used	The production rate is limited by temperature and the resin composition
Less number of rejects or unusable parts	Reduction in wastes and rejects	Reduction in wastes and rejects	Higher risk of obtaining rejects
High reduction of volatile organic compounds (VOCs). This provides a safer, faster, and more efficient process	Reduction in styrene emissions	Reduction in solvents and volatile compounds	The problem associated to the emissions is related to the values collected in the current legislation
Improvement in flexibility and process control because it is a single-component system that cures when it is previously planned	The heating of the part is volumetric, so the polymerization grade is improved	The EB curable resins and additives present long time of use and can be stored at room temperature	The control disappears when the catalyser is added
A more consistent and controlled curing is provided	Higher hardening of the polymeric materials	The low temperature curing can reduce the residual thermal stresses	The curing depends on humidity and temperature
The physical properties are the same as those obtained by thermal curing	Minimizes the thermal gradients of curing, so the microcracks and stresses due to contraction/dilatation are reduced. Improvement in the product uniformity	The physical properties are the same as those obtained by the thermal curing	The physical properties are the same as those obtained by the UV curing
Low energy consumption because it is not necessary to heat the system	–	EB curing can reduce between 10% and 40% of costs in the production of a great variety of aerospace parts	High energy consumption due to the oven costs
The photosensitive resins are thermally stable, so they have a long pot life	The resins cured by microwaves are stable until the radiation is applied	–	The catalysed resins depend on temperature, so they have low pot life

Table 9.6 Drawbacks of alternative curing methods

UV curing	Microwaves curing	E-Beam curing
It is not possible to do the curing in the presence of carbon and kevlar fibres	Possible inadequacies of microwave curing additives, pigments, and fillers, which can produce a high exothermicity in the reaction	The chemistry of the EB curable resin produces different polymeric structures compared with the systems cured at room temperature
Difficulty in curing of highly pigmented systems	Increase in energy consumption due to the use of microwave radiation	Low interlaminar resistance due to the incompatibility between EB curing resins and the surface finish of the fibre
The UV technology has a limited application in closed mould curing techniques	Impossibility of the use of metallic moulds or the inclusion of metallic inserts	
UV curing cannot be used in honeycomb core sandwich panels		

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Recent innovations in biocomposite products

10

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10.1 Introduction

Composite materials have come to the fore a few decades back because of their superior specific mechanical properties, as a result of the increasing demand of consumers and industries for high performing materials and structures. However, the combination of the fibres with the aggregating material or matrix highly increases the complexity of the design process and usually leads to challenges in the composites engineering and, correspondingly, more conservative solutions for a given application. While the success of these materials is obvious, recently, a general consensus all around the world has been reached regarding the negative influence of the human being on global warming and the environment. The best way to save the environment is to use renewable and nontoxic natural materials, and all efforts should be undertaken to make them competitive. Actually, the environmental consciousness all around the world has led to the research and development of a next generation of materials, products, and processes [1]. Under this scope, it is necessary to develop materials that are concurrently available from nature, cheap and biodegradable. This awareness triggered the interest in more sustainable materials that can be processed with lower energy consumption, as are natural fibre composites. As a result, natural fibre composites are under large investigation efforts because of their potential as an alternative for synthetic fibres. This century in particular has witnessed major improvements in sustainable technology and biocomposites, and the interest in these issues is still increasing. Recycling of natural fibre composites and natural fibre reinforcement from waste materials are other steps for saving resources and the environment. Because of these issues, biocomposites are gaining industrial interest in a world focused on environmental outcomes.

The use of these materials dates back to civilization itself and, for many centuries, natural fibres have been used as raw material. Natural fibres were initially used around 3000 years ago with clay in Egypt, and have been used ever since. Recently, it is clear that renewed incentives for their use are clearly emerging. Thus, scientists and engineers have become more interested in the study of natural fibres and their composites. The replacement of conventional materials and synthetic composites with natural fibre composites can thus be a reality, contributing to the creation of a sustainable economy. On the other hand, the concerns on the availability of petrochemicals in the future can also trigger the use of natural fibre composites by the induced pressure from the global market. Because of this, natural polymers are also gaining ground as matrix materials and are taking their market share. It should,

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however, be noticed that biodegradability is not the sole attribute of natural materials: some synthetic materials can be biodegradable, while some natural materials may not be. Obviously, an ideal natural fibre composite is fully biodegradable under controlled conditions and is composed only of short-cycle renewable plants. Due to large research efforts in the fields of fibre extraction and chemical treatments, fibre-matrix adhesion and processing conditions, natural fibre composites are expected to be a viable replacement for glass composites in many applications at a lower price. By treating the fibres with coupling agents, engineering the orientation of the natural fibre components, devising extraction techniques to increase the fibre length, and by combining with the best possible matrix, very interesting characteristics are achievable. Other advantages include the large availability, renewability, flexibility during processing, low cost, low density and, because of this, high specific strength and stiffness. Compared with synthetic fibres, energy requirements for processing are much lower, and energy recovery is also possible. Kim et al. [2] showed that natural fibre composites have a higher energy absorption rate under impact loadings than glass-reinforced composites. These achievements and the superior environmental performance are important drivers for the growing use of natural fibre composites in the near future, and make these materials attractive to industrial companies. Despite all of these advantages, some features still prevent a more widespread use of these materials, such as the strength prediction during structural loading, uncertainties about the long-term performance, moisture absorption, lower fire resistance, lower mechanical properties and durability, limited processing temperatures, larger scatter in the cost and properties than synthetic composites, and some difficulties in the use of well-known fabrication processes [3]. However, it is expected that many useful information previously gathered for synthetic composites can be applied to these materials. In fact, many efforts are being made to address the mentioned limitations, with attention to surface treatments for the fibres and interfacial improvement with the matrix. Natural fibre composites with thermoplastic matrix (e.g. polyethylene (PE), polypropylene (PP), or polyvinyl chloride (PVC)) are also a recent solution. There is equal potential for biodegradable polymers to replace synthetic ones in the near future, at least in applications that do not require a long life span, and these matrices have seen recently an important increase in industrial applications. Regarding the production volumes, the main products are starch-based plastics, poly(lactic acid) (PLA), and microbially produced polymers or polyhydroxyalkanoates (PHA) [4]. As a result of intensive research and development, these materials became competitors with conventional engineering materials in some fields of applications, with new compositions and emerging manufacturing processes. The research interest in natural fibre composites has been consistent over the last 2 decades, but this has not yet translated into a large range of industrial applications.

In the industry, several companies are increasingly interested in using materials that weigh less, are durable and ecologically efficient, and present interesting mechanical properties. Under this scope, natural fibres are highly valued since they come at low cost, are recyclable, biodegradable, can be easily processed and have a very low density. Because of this, the reinforcement with natural fibres is considered to increase significantly in the next years. According to the technical report of Lucintel [5], the global market for natural fibre composites has reached 289.3 million USD in 2010, with compound annual growth rate (CAGR) of 15% from 2005. In terms of applications, the global market for natural fibres is mainly divided into two: wood and nonwood fibres. Wood fibres are typically used in the construction industry, and North America is the region where this application is more widespread. On the other hand, nonwood natural fibre applications thrive in Europe with a tremendous growth mainly in the automotive industry, by using thermoplastic and thermoset-based natural fibre composites. This is because of advantages such as raw material renewability, environmental friendliness, good sound insulation properties, and fuel saving, on account of the smaller component weight. This usage was made possible by large investments and development in using compression moulding as the adopted process in the European automotive industry. Automotive applications include door interior panels, package trays, trunk liners, and seat backs. More specific examples are interior vehicle parts such as door trim panels made of natural fibre reinforced polypropylene composites, or exterior parts, e.g. engine or transmission covers, with polyester reinforced with natural fibres [6]. This change was triggered by the European Union End-of-Life Vehicle Directive (2000), stipulating that 80 wt% of a waste vehicle should be reused or recycled. On account of this directive, the use of these materials has been increasing in the last years. For vehicle applications, using thermoplastic matrices give some advantages over thermoset matrices with increased design possibilities, since fabrication by injection moulding and extrusion become feasible, in addition to the possibility of recycling. In civil engineering also, natural fibre composites can play an important role because of the reduced weight and lower cost compared to the carbon or glass-based composites. Natural fibre fabrics are easier to handle, with advantages on column wrapping for posterior cure with temperature, and are acoustic insulators. However, according to Dittenber and GangaRao [3], the major benefit of using natural fibre composites in construction is ecological, since these materials enable fabricating large and biodegradable structures only with natural resources and with a reduced amount of embodied energy. Extruded natural fibre composites are used for decking applications in the United States because of the generous thicknesses of the plates which overcome limitations in the mechanical properties. Regarding the global usage of natural fibres, Europe is the largest consumer, and Asia is becoming a big market for natural fibres because of the increasing demand in both China and India. In the near future, a fragmentation of the natural fibres' market is expected because of emerging economies [5]. Bio-based plastics are also following this increasing trend of natural fibre composites, with past growth rates of 38% between 2003 and 2007 (worldwide), reaching 48% in Europe alone. The fabrication capacity of bio-based plastics increased from 0.36 million ton (2003) to 2.33 million ton in 2013, and is expected to increase further to 3.45 million ton by 2020 [7]. Global markets now and in the future should be very competitive, striving to get the best possible materials, and those companies that show innovation in this area will perform best. On account of their potential, natural materials can play a very important role in the near future for the success of industries.

10.2 Biocomposites

Biocomposites can be made of natural fibres with synthetic resins, natural resins with synthetic fibres, or both natural components. These materials have been used for decades, with application in aircrafts since the 1940s [8]. Nowadays, the use of these materials extends to the constructions industry, vehicle parts, and household applications and others. Natural fibre composites have a number of interesting characteristics, such as the lower environmental impact, CO_2 neutrality, and lower CO_2 emissions than synthetic fibre composites when composted or incinerated. Additionally, they weigh less and are cheaper. Studies for their use as load bearing components are also encouraging [9]. One of the differences to synthetic composites is the large property variation, because of the following reasons: dissimilar testing protocols, moisture conditions, physical properties, cell dimensions, chemical composition, microfibrillar angle, structure, defects, scatter in the mechanical properties of the fibres, and fibre-matrix interaction. The tendency for moisture absorption of natural fibres is also a major issue, as it highly influences the mechanical properties of the composites. There is a clear relation between the moisture content of the natural fibres and the noncrystalline regions and voids. This issue was studied in detail in the work of Rowell [10]. The equilibrium moisture content of the fibres for a specific air humidity (i.e. the real moisture content of the fibres after exposure to a given amount of humidity) also has a major effect on the composite properties. For example, at the same air relative humidity of 65%, abaca fibres have a moisture content of around 15%, compared to 7% of flax. The transcrystallinity at the interface of natural fibres also affects the composite strength. Some surface treatments like stearic acid treatment can induce this effect. These issues were addressed by Zafeiropoulos et al. [11] for flax/isotactic PP with, dew-retted, duralin-treated and stearic acid-treated fibres, showing more than 100% improvement of the interfacial shear strength for the treated fibres.

In general, modification of the fibres' surface can improve adhesion to the matrix. On the other hand, a weak interface reduces the efficiency of the stress transfer between the fibres and matrix, leading to premature damage in the composites and lower strength. The treatment methods are basically divided into physical and chemical. The former method changes the fibres' structural and surface properties and promotes the mechanical bonding with the matrix, although it does not change the chemical composition. Stretching, calendaring, and thermotreatment are examples of physical methods applicable to natural fibres. The corona treatment is an example of physical process for surface activation by changing the surface energy of the fibres [12]. Another possibility is the plasma treatment, which induces different surface modifications depending on the gas, by modification of the surface energy and creation of surface cross-links [13]. Chemical treatments act by improving the adhesion with a third material between the fibres and matrix. This material promotes the compatibility between the fibres with hydrophilic behaviour and the hydrophobic matrix. One chemical method is the silane treatment, which improves the fibre-matrix compatibility at the interface promoting adhesion [14]. The largely used alkaline treatment or mercerization disrupts the hydrogen bonding in the fibres structure and thus it increases the fibres anchorage [15].

Table 10.1 **Mechanical properties of hemp-reinforced natural fibre composites and different resins**

Matrix	Tensile strength (MPa)		Young's modulus (GPa)		Source
	Resin	Composite	Resin	Composite	
PLA	47.5–51	75–85 (30% hemp fibres)	3.5–5	8–11 (30% hemp fibres)	[19]
PP	22.8–35.46	28.1–45.33 (40% hemp fibres)	1.07–1.1	3.5–3.72 (40% hemp fibres)	[20]
Polystyrene	34.1 ± 0.68	40.4 ± 0.65 (22.5% hemp fibres)	–	–	[21]
Epoxy	25	60 ± 5 (30% hemp fibres)	0.7	3.6 ± 0.4 (30% hemp fibres)	[22]
Polyester	12.5 ± 2.5	60 ± 5 (35% hemp fibres)	1.1 ± 0.2	1.75 ± 0.5 (35% hemp fibres)	[23]
Unsaturated polyester	25 ± 5	65 ± 2.5 (30% hemp fibres)	1.5 ± 1	8.75 ± 1.25 (30% hemp fibres)	[24]

The acetylation treatment turns the surface of natural fibres more hydrophobic by coating the OH groups of fibres [16]. Other possibility to improve the strength of natural fibre composites is the maleated coupling. The application of the maleic anhydride acts on the surface but also improves the interfacial bonding [17]. Finally, the enzyme treatment is environmentally friendly and cost effective, and acts by promoting reactions on the fibre surface that improve adhesion [18]. Table 10.1 gives, as an example, the mechanical properties of natural fibre composites with hemp fibres and different matrices [19–24]. The main conclusion to draw here is that, notwithstanding the matrix material, the addition of the natural fibres highly improves the strength and stiffness of the resulting material. It is also visible that, due to the chemical reactions between the hydroxyl groups on the fibres' surface and the thermoplastic resin, composites with thermoplastic resins excel compared with those with thermoset resins. Table 10.2 compares the mechanical properties of different natural fibre composites as a function of the fibre loading [25–28]. Overall, the introduction of the reinforcement in the polymer significantly improves the Young's modulus which increases as the fibre content is increased. The tensile strength of the composites increases as well, except for the results of the palm leaf fibres/PP composite. In general, the strength improvements are more modest. The impact strength increased for the ramie fibres/PP composite, while for the other composite systems there is no available data.

A merit comparison between glass and natural fibre composites (in average) is shown in Fig. 10.1. Price can be similar between both composites, but glass composites excel in mechanical performance while having a significant recyclability penalty. Thus, if natural fibres are to replace glass fibres for a given application, this will have to occur in a way that the mechanical properties are safeguarded. Natural fibre

Table 10.2 **Mechanical properties of natural fibre composites with different resin and matrix combinations**

	Fibre content (wt%)	Young's modulus (MPa)	Tensile strength (MPa)	Impact strength (kJ/m^2)	Source
Ramie fibres/PP	0	1300	35	2.8	[25]
	10	1400	42	3.0	
	20	1600	51	4.2	
	30	2250	66	4.7	
Palm truck fibres/ high density PE	0	475	17.5	–	[26]
	20	750	17	–	
	30	975	18	–	
	40	1500	20	–	
Palm leaf fibres/PP	0	800	27.5	–	[27]
	7	700	23.5	–	
	15	650	21	–	
	28	675	17	–	
Pineapple leaf fibres/polycarbonate	0	1100	67.5	–	[28]
	5	1150	67	–	
	10	1450	66	–	
	20	2000	71	–	

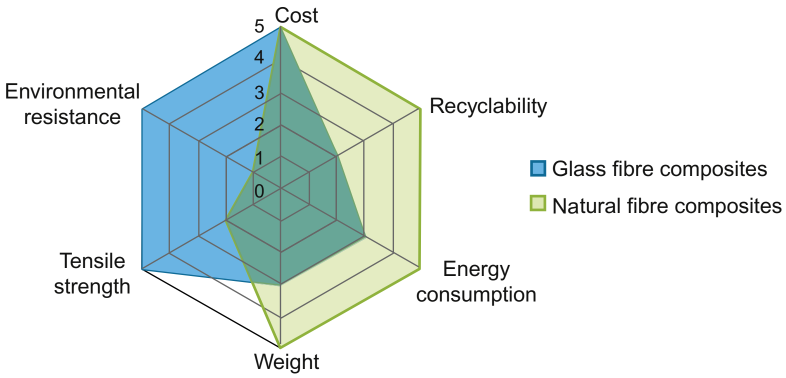

Fig. 10.1 Merit comparison between glass and natural fibre composites (in average).

composites do not match glass fibres composites in mechanical properties although they have superior specific strength and stiffness. Because of this, natural fibres are more suited to provide stiffness in applications that are not under moisture or any adverse environmental conditions. Addressing the issues of moisture, improved performance of natural fibre composites is possible, as previously mentioned, but this will require new approaches. It is well known that metal parts or structures cannot be replaced by synthetic fibre composites without any design modifications, because of the intrinsic differences in the properties and fabrication processes. In a similar context, the replacement of glass by natural fibre composites requires new designs and solutions to obtain the best performance. The immediate applications of natural fibre composites are restricted to limited performance parts, where these materials can really excel because of the biocharacteristics and eventually also cost advantage (or at least nondisadvantage). Examples are selected components for the automotive industry with low strength requirements, such as panels and trims, which also improve the biocredentials of the vehicles. Apart from this, any component whose performance demands are within the reach of natural fibre composites can potentially be fabricated from these materials. Examples are wood parts, since the consumer demands for water and moisture absorption for wood components are usually low. Replacement of unreinforced plastics is also a chance for development, and the use of low-cost plant fillers is ongoing in the electronics industry. The replacement of the fillers by fibres can give significant performance improvements. At the moment, there are still many challenges to be overcome for natural fibre composites to be able to be applied in current glass fibre composite applications (to be discussed in a subsequent section). Nonetheless, the eventual success of such replacement surely relies on the ongoing and future research and development of new designs that favour the mechanical properties of these materials.

10.3 Benefits and applications of natural fibre composites

In the last few decades, natural fibres and natural fibre composites have received attention from researchers in several industries, such as in civil construction, automotive, and biomedical [29]. Natural fibre composites have raised much attention and research efforts, mostly based on three factors: lowering of costs, weight reduction, and sustainability. The mechanical behaviour of lignocellulosic fibres (nonwood or plant) and their composites, either with bio or synthetic materials as matrix, have been studied extensively by the scientific community, in parallel to industrial use in vehicles and in construction. Actually, natural fibres of flax, hemp, sisal, or jute can replace glass or other kinds of synthetic fibres in epoxy, polyester, PVC, PE, or PP matrices, with the following benefits:

- Lower costs because of reduced cost of raw materials, smaller cycle times, lower weights, and reduction in the fuel consumption (vehicle parts);
- Identical mechanical properties to glass-reinforced parts, with fabrication advantages as smaller tool wear, good sound insulation, and geometrical stability; and
- Eco-friendliness, renewability of the raw materials, recyclability, nontoxicity, and CO_2 neutrality.

Many literature exist on the use of natural fibre composites in automotive applications, mainly for vehicle interior parts [1,30,31], either with thermoplastic or thermoset matrices. The selected materials for these applications shall meet requirements of minimum strength and strain to failure, impact and flexural properties, sound insulation, fire resistance, processing characteristics (dwell time and temperature), odour, dimensional stability, and energy absorption under crash conditions. Bledzki and Gassan [32] reported an application of jute, coffee bag wastes, and PP bags in Brazilian trucks trim parts after recycling. Saxena et al. [30] concluded that using natural fibre composites in vehicle applications as trim parts, panels, shelves, and brake shoes can give an advantage of 10% in weight, fabrication process energy savings of 80%, and overall reduction of the parts cost of 10%. Moreover, around 6000 natural fibre composite parts could be introduced in vehicles with this potential advantage. In locomotives, components like the gear casing, doors and side panels, interior furnishing and seating, luggage racks, berths, chair backings, modular toilets, and roof panels made of natural fibre composites can also bring benefits in terms of weight, cost, corrosion resistance, and weight reduction driven fuel consumption savings. For civil engineering applications, natural fibre composites from bast fibres are in general the best, while flax gives the best balance between strength and stiffness to cost and weight. Jute reinforced composites are very common, but their strength and stiffness does not match flax. Because of the specific stiffness advantages over glass composites, natural fibre composites are an excellent solution for reinforcement of existing infrastructures. In general, the development of natural fibre composites, which are biodegradable, to replace synthetic materials like glass-reinforced composites without compromising their distinctive characteristics is currently and will continue to be a big challenge.

Natural animal fibre composites are scarcely used in industrial or other applications. Animal fibres, like wool or spider silk, are made of proteins and find useful applications in some bioengineering and medical applications. Wool is the most used animal fibre, although it suffers from low fracture resistance, which is its biggest limitation. A major application of wool fibres is the fabrication of rock wool fabrics or panels, used in the construction industry on account of the good fire resistance and sound absorption. Silk fibres are characterized by their stability even when exposed to varying environment conditions, have a low weight and their composites are very tough and impact resistant. Some applications of these fibres were reported in automotive, aerospace, and sport equipment industries [6]. Feathers meet application in cement-bonded feather boards, which are resistant to decay and termite attacks due to the keratin. These feather boards can be employed in panelling, ceilings, and insulation, although not as structural components. Animal feather composites can compete with conventional materials in a few specific applications.

There is also a history of application of mineral fibres or asbestos in corrugated panels (e.g. roofing compounds), gaskets, pipeline wrapping, sheets, rods, shaped mouldings, and thermal and/or electrical insulation. Fabrics of mineral fibres also find application in parts that involve friction, such as brake or clutch pads, because they are durable to friction, and heat and oil resistant. Mineral fibres can be fabricated with bio or synthetic matrices to produce a large variety of products. Chrysotile with rubber matrix finds application in packings, gaskets, and heavy-duty insulation parts as compressed boards. More specific applications include reinforcement agents in coatings and adhesives. Mineral fibres have a significant limitation, related to health hazards, including lung, eye, and skin diseases, which causes numerous deaths under working conditions. Because of this and environmental concerns, these fibres are being less used.

10.4 Potential of natural fibre composites and drivers for change

Recent advances in natural fibre composite technology enabled the development of materials of attractive performance and sustainability. Up to now, these materials were applied mostly in vehicle products and some construction applications, with the previously mentioned advantages. If these new materials are to be generalized to other sectors of industry, as for example household products or goods, there are basic inherent properties that they must accomplish: performance for the desired function, usability, reliability, and durability. The discussion is divided into three main areas of actuation: mechanical properties, environment, and cost effectiveness.

10.4.1 Mechanical properties

Currently, natural fibre-related technology is being improved to provide better mechanical characteristics of the bio-based components. With this large effort, it will be possible for biocomposites to exploit other fields of application that are not currently in use. But for this to happen, the knowledge of the materials, fabrication processes, and design methods must reach a much higher degree of confidence. These issues, together with proper standardization for these materials can give them a distinctive edge over conventional materials. At the moment, large efforts are being made to make biocomposites a solution for load-bearing parts in construction. In fact, some authors tested the use of cellular plates and beams as structural parts in the construction industry (house building) made from hemp, jute, and flax fibres in polyester resin [33]. The components were experimentally tested, and the results showed that the cellular arrangement of the natural-fibres can improve the mechanical properties of the composites just enough to compete with other engineering materials (e.g. glass fibre composites or common construction materials) and make them viable to load-bearing applications. This line of research is to be followed in the future to make civil construction a strong application of natural fibre composites. Applications in other sectors of industry rely on additional improvements. However, from the current state-of-the-art, some limitations of these materials still need to be addressed for them to be considered competitive against synthetic composites. It was previously mentioned that natural composites are a cost-effective solution compared to other materials, but it is also true that if a 100% biological and recyclable solution is needed, costs increase and this also needs further research efforts. Moreover, ecological superiority over synthetic composites is not yet fully true because of the fabrication techniques that consume large amounts of energy. Other feature to be improved is the resistance to moisture and temperature, and here a long path exists, knowing that there are limits to the materials themselves. For example, currently it is possible to make a part fully biodegradable with the proper choice of biomatrix, although biodegradation would be high. Also, significant improvements in some key aspects of biomaterials like large nonlinearity/relaxation, long-term performance, and small impact resistance can occur by improving the processing of the fibres and composite fabrication. It can be concluded that new frontiers will emerge for these materials when the following characteristics are met with a significant degree of comparison with the other materials: durability, dimensional stability, environmental, and fire resistance [7].

One of the materials-related fields that has endured major enhancements recently is that of nanotechnology. Common natural fibres contain a small amount of nanocrystalline cellulose. The artificial fabrication of natural fibres with this structure could produce fibres with 10% of carbon nanotubes strength, but costing up to 1000× less [7]. Research on this field mainly uses wood pulp to produce nano cellulose, but other nonlignocellulosic products can be used with this purpose: hemp [34], wheat [35], or flax [36]. Some authors [9] obtained cellulose nanofibres with a mixed chemical/mechanical technique and combined them with a starch polymer. Preparation of the nanofibres enabled cleaning the fibres surface of hemicelluloses, lignin, and pectin, and also the defibrillation of nanofibres from the initial fibre bundles. It is also possible to fabricate microfibrillated cellulose from wheat and soy by the processes of cryocrushing, disintegration, and fibrillation, giving fibres with diameters between 30 and 40 nm [37]. Many other works used similar techniques to produce these nano materials from soy, root crops, wood, seaweed, cotton, hemp, cereals, and sea squirts. Composites made with these nanofibres experience a major improvement in the tensile strength and stiffness. Nanotechnology can also be used differently, to improve natural fibre composites by application of coatings, diminish the effects of biodegradation, or improve the fire resistance of the materials. With the recent efforts under way, it is a matter of time until nano concepts would give natural fibre composites the performance, durability, value, service-life, and utility that makes them more competitive, while maintaining their ecological features.

10.4.2 Environment

Natural fibre composites fit in the concepts of sustainable economy, since synthetic materials are replaced by bio-based and renewable ones. These materials also have the potential to be more cost effective for identical structural characteristics, and provide opportunity to produce or grow the fibre plants in controlled facilities or farms. Compared to synthetic resins and fibres (or even conventional materials) these materials can potentially replace, the carbon footprint that will be tremendously reduced. Synthetic fibres and resins are posing difficulties in their disposal for decades, accounting for up to 20% of the total landfill space, depending on the country. This is a strong motivation for the replacement of synthetic composites, since landfill capacity is scarce and overcrowded. In terms of saving the environment, it is more urgent to replace the matrix than the fibres by natural equivalents, since petroleum-based resins take hundreds of years to degrade [38]. Recycling is an opportunity, although recycled petroleum-based resins lose some characteristics by incorporation of external substances, which affects the adhesion between fibres and matrix. On the other hand, PLA can be reconverted without affecting its performance. Natural fibre composites benefit the environment in three ways compared to synthetic fibre composites: (1) less pollution during fabrication, (2) lower fuel consumption and CO_2 emissions during transport to the constructions sites (if applicable) and (3) absence or significant reduction of the disposal and energy-consuming disposal efforts. However, the CO_2 advantage arising from the fibres processing is highly variable, such that accounting for the environment advantage of natural fibre composites is not the easiest of tasks [39].

10.4.3 Cost effectiveness

The price of materials is a major issue for the assessment of natural fibre composites' position in the market and overall potential. Specifically for the case of civil construction, the cost of raw materials has a share between 60% and 75% of the total costs and thus, the proper choice of materials is the major issue to act on [3]. On the other hand, the choice for these materials also relies on the environmental issues, like disposability of the materials, lack of raw materials for synthetic fibres and matrices, and public opinion. Some countries even have specific laws on the use of recycled or natural materials [38]. Mohanty et al. [40] predict a sustained yearly increase of natural fibres and bioresins up to 60% for construction and up to 30% for vehicles. Satyanarayana et al. [41] presented slightly smaller numbers, between 10% and 22% overall. Because of this, it is likely that worldwide production of natural fibres and bioresins will have difficulties to meet the industry expectations very soon. This opens a window of opportunity for regions other than United States and Europe to bet on these materials and India, for instance, is nowadays a large producer. However, the costs of the biomatrix materials are still too high to compete with the synthetic plastics. Fabrication processes should be kept as simple as possible, to reduce costs and pollution. Surface treatments are equally required for the composites to be able to compete with established materials in the industry, and these should be improved to allow natural fibre composites to match or at least to approach the mechanical properties of synthetic fibre composites [40]. It was shown previously that a large price variation exists on natural fibres, because of different reasons, and a good route is to choose natural fibres that satisfy the desired properties but will also always be cost-effective, disregarding these variations. Since natural fibres and bioresins are under intense research, unlike synthetic composites that are established in the market, room for improvement exists. Once the cost lowers to acceptable levels, the use of these materials is likely to become widespread in many fields of industry. Currently, a consensus does not exist regarding the future of natural fibre composites, with the remaining doubt if these materials will ever be able to replace synthetic fibres in many applications.

10.5 Innovations in biocomposite products

Green composites have high potential to have a significant environmental impact, since carbon can be sequestered in these products for a long time, while also providing weight savings and vibration damping [42]. However, in high structural applications such as those in the automotive and construction industries green composites are not the best solution because of issues like variability in the mechanical properties and low durability. Some problems also appear in replacing glass composites due to inferior strength properties and degradation by water, which excludes applications

Table 10.3 **Potential applications of green composites deriving from their specific properties [42]**

Material properties	Potential applications
Excellent weight specific stiffness, good weight specific strength	Weight critical vehicles/products (transport, mobile electronics, sport equipment
Variable fibre properties	Nonsafety critical/low required reliability applications
Renewable resource low embodied energy biodegradable	Short life-span product (disposable and high obsolescence rate products)
Nontoxic	Children's toys, consumer handled items, hobbyist built items
Biocompatible	Medical devices and implants
Low cost	Competitive consumer products
High water absorption	Dry use products
Poor durability	Short life-span products, limited exposure to harsh environments

such as boats, kayaks, piping, and tanks. Even if the component geometries and fabrication methods that are currently established for glass composites could be adapted to take advantage of the good specific stiffness of natural fibre composites, some issues would still have to be accounted for the high property variation and reduced durability of these materials. In view of the reported characteristics of natural fibre composites, Table 10.3 proposes potential applications of green composites deriving from their specific properties. Numerous applications and innovations of natural fibre composites have been proposed in recent years in distinct fields such as automotive parts, structural components, construction industry, and packaging applications [43]. Natural fibre composites also find applications in fields such as electronic, aerospace, sports and recreation equipment, and machinery and others [44]. However, the two main applications of natural fibre composites are undoubtedly automotive components (in Europe) and construction industry (in the United States). Disregarding the application, Europe consumes the highest amount of natural fibre composites, although the demand in Asia is increasing swiftly because of the Chinese and Indian markets [45]. Future markets are expected to be highly competitive and companies with innovative ideas can succeed and gain market share. The implementation of these green materials was made possible in these different competitive fields because of attractive properties such as the good specific strength, biodegradability, moderate static and fatigue strength, low production cost, resistance to corrosion, availability, and renewability [46]. It is preferable to use fully natural composites, i.e., natural fibres and matrices, but biodegradable polymer matrices are much more expensive than synthetic thermoplastics, even though their costs significantly reduced recently because of the increase in the production. The most typical synthetic thermoplastic polymers to be combined with natural fibres are PE, PP, and PVC. As for thermoset polymers, the choice can be unsaturated polyester, epoxy, vinylester, and phenolic resins [47].

Some of the most relevant state-of-the-art applications of natural fibre composites are described in the next sections, dividing the recent developments into structural applications, automotive industry, marine applications, packaging and other short life items, medical uses, and sporting equipment.

10.5.1 Structural applications

Natural fibre composites are highly relevant for the sustainability of the construction industry, providing sustainable, safe, cheap, and light materials. These products can currently be found in various applications, such as fibre/cement composites, fencing, decking, siding, door, window, bridge, and others. Natural fibre composite applications can be found in industries such as aerospace, construction, and sports. However, due to environmental degradation issues, in civil engineering applications, the applications are limited to indoor noncritical load bearing components [48]. In the construction industry, the advantage of using biocomposites is based on issues such as specific stiffness, weight, and biodegradability [49]. The concept of Green Buildings relies on the use of biocomposites in their constructions, which can be categorized into two types: structural parts, for example bridges and roof structures, and nonstructural parts, such as windows, exterior parts, panels, and door frames [50]. An example regarding nonstructural parts are the façade panels developed by NetComposites [51] within the scope of a collaborative project of 13 partners aiming to reduce the embodied energy in building components by at least 50%. The façade panel is 4 m high and 2.3 m wide (Fig. 10.2) and it is composed of two biocomposite outer shells of flax/bioresin and a central layer of insulating material. The BIOSTRUCT project [52] was dedicated to develop new wood-based and cellulose-based natural fibre reinforced products, with either natural or synthetic matrices, and to synthesize novel biomatrices to be used in the constructions industry and other fields of application. Operations such as chemical modification and pretreatment of the fibres, insertion of functionalities into the fibres (e.g. flame retardancy), and development of new synthesis routes for biopolymers were undertaken. Fibre reinforced cement composites (or just fibre-cement composites) were developed by James Hardie in

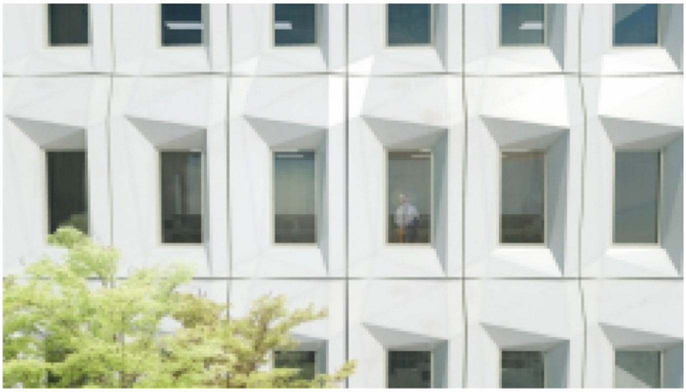

Fig. 10.2 Biocomposite façade for buildings [51].

the 1980s, and were applied to the construction of residential buildings. Currently, these biocomposites find applications in exterior and interior of a building such as siding, roofing, external cladding, internal lining, floors, walls, building boards, bricks, bracing, fencing etc. Fibre-cement composites are equally employed in dams, bridge decks, and road building. Cellulose fibres are typically used as reinforcement in fibre-cement composites, together with additives such as fly ash, slag, and silica fume to provide products with particular characteristics, namely increasing the durability or diminishing the chemical interactions between cement and the biofibres. Hempcrete is another biocomposite for building construction [53], made of chopped hemp shiv as reinforcement and a matrix of natural lime and cement. Hemp is a renewable biomaterial and lime is an abundant quarried material. The resulting composite is an extremely light insulating material that weighs about a seventh or an eighth of concrete and that floats on water (Fig. 10.3) [47]. Possible applications of hempcrete with regard to its insulation abilities are timber frame infill, insulation and, with the addition of aggregate, as floor slabs. Applied to buildings, this material controls the temperature and humidity, possibly cancelling the necessity of cooling, with the respective cost advantage.

Fig. 10.3 Applications of Hempcrete in the construction industry [53].

Particle boards made of green composites can also be applied as construction materials. For example, bagasse fibres are used in the United States to make particle boards, fibre boards, and composition panels. Other eligible types of fibres for this application are ryegrass straw fibres, hulls, sunflower, and soybean stalks [54]. Cereal straw is also used to produce flame retardant (due to the silica content), resilient, resistant to earthquakes, and low density panels. Rice straw is another alternative to produce boards; however, when compared to wood fibres, the resulting fibre boards have a lower quality because of impurities and nonfibrous elements in its composition [47]. Wood fibres can be used to form wood-reinforced composites in the form of constant cross-section long structural elements used as dock surface boards, deck, picnic tables, landscape timbers, and industrial flooring. Other elements for particle boards derived from waste fibres are beech fibres, hemp, tobacco, vines, cotton, raspberry, maize, or sunflower stalks, and good results were already reported with hemp and tobacco fibres [54]. Nowadays, many companies are dedicated to the commercialization of green composites for building construction, fencing, roofing, decking. BCOMP [55] sells sustainable materials like flax fabrics, green core products for sandwich plates, and natural reinforcements to different industries. Composites Evolution [56] is dedicated to the fabrication of biodegradable resins and fibre reinforcements made from natural recycled feedstocks. This company made available ecopregs with jute and flax fibre reinforcements, and polyfurfuryl alcohol (PFA) resin as fire resistant natural materials (Fig. 10.4). PFA is a thermosetting bioresin derived from crop waste and is similar in nature to a phenolic resin. These products perform similarly to phenolic resin-based prepregs, but increasing health and

Fig. 10.4 Biotex fabric, PFA ecopreg and biocomposite products [56].

safety, while reducing the environmental impact. The prepreg fabrication can be carried out by vacuum-bag, autoclave, or in a press moulding, and the resulting products find application in the aerospace, transportation, furniture, and construction industries in components such as door modules, cabinets, turbine blades, and acoustic guitars.

The feasibility of using natural composites reinforced by sisal fibres was showed by Van de Weyenberg et al. [57] regarding thin walled elements to be applied as structural elements in buildings, permanent formwork, tanks, facades, roof bars, and strengthening elements. Other authors [58] considered bamboo fibres as reinforcement in concrete, and also sisal and coir-reinforced natural composites in roof elements to replace asbestos. Plain and corrugated sheets and boards made of natural fibre composites weigh less than conventional materials and are viable for roofing, ceiling, and walling in domestic buildings [59]. Table 10.4 provides a summary of applications of natural fibre composites in structural elements.

Table 10.4 **Application of natural fibre composites in structural applications [60–64]**

Fibre	Application in building, construction, and others
Hemp fibre	Construction products, textiles, cordage, geotextiles, paper & packaging, furniture, electrical, manufacture bank notes, and manufacture of pipes
Oil palm fibre	Building materials such as windows, door frames, structural insulated panel building systems, siding, fencing, roofing, decking, and other building materials
Wood fibre	Window frame, panels, door shutters, decking, railing systems, and fencing
Flax fibre	Window frame, panels, decking, railing systems, fencing, tennis racket, bicycle frame, fork, seat post, snowboarding, and laptop cases
Rice husk fibre	Building materials such as building panels, bricks, window frame, panels, decking, railing systems, and fencing
Bagasse fibre	Window frame, panels, decking, railing systems, and fencing
Sisal fibre	In construction industry such as panels, doors, shutting plate, and roofing sheets; also, manufacturing of paper and pulp
Stalk fibre	Building panel, furniture panels, bricks, and constructing drains and pipelines
Kenaf fibre	Packing material, mobile cases, bags, insulations, clothing-grade cloth, soilless potting mixes, animal bedding, and material that absorbs oil and liquids
Cotton fibre	Furniture industry, textile and yarn, goods, and cordage
Coir fibre	Building panels, flush door shutters, roofing sheets, storage tank, packing material, helmets and postboxes, mirror casing, paper weights, projector cover, voltage stabilizer cover, a filling material for the seat upholstery, brushes and brooms, ropes and yarns for nets, bags, and mats, as well as padding for mattresses, seat cushions
Ramie fibre	Use in products as industrial sewing thread, packing materials, fishing nets, and filter cloths. It is also made into fabrics for household furnishings (upholstery, canvas) and clothing, paper manufacture.
Jute fibre	Building panels, roofing sheets, door frames, door shutters, transport, packaging, geotextiles, and chip boards

10.5.2 Automotive industry

Natural fibre composites reinforced by kenaf, hemp, flax, jute, and sisal have been used by car manufacturers, giving advantages of weight reduction, cost reduction, lower carbon footprint, and less dependence on petroleum products [47]. Despite this fact, exterior and load bearing applications in vehicles are limited by factors like uniform fibre properties, strong adhesion between fibre and matrix, flame retardancy, ultraviolet (UV) resistance and, most importantly, moisture resistance [65]. The property variations from one year to another (or harvest to harvest) are other major concerns that limit the use of these materials as automotive components.

A large effort is currently being made by automotive manufacturers to replace components made of traditional materials by natural fibre composites, namely with regard to interior parts such as seat backs, parcel shelves, boot linens, front and rear door linens, truck linens, and door-trim panels [66]. Apart from these applications, reinforcement of natural fibres in polymers was already applied for outer body components such as front aesthetic panels in passenger trucks [67]. Different automotive companies such as Audi, BMW, Ford, Opel, Volkswagen, and Mercedes use cellulose fibre-reinforced biocomposites in several interior parts, shown in Fig. 10.5 for an example, the Mercedes Class E. The Mercedes Class A model utilizes coconut fibres rubber latex composites for the seat construction and door panels made of flax-sisal fibre mat reinforced epoxy [69]. The Audi car manufacturer currently uses a flax/sisal mat reinforced polyurethane biocomposite for the door trim panels [70]. The Ford Mondeo also included biocomposites in interior parts: kenaf fibres in different components such as the door panels (kenaf reinforced PP composites) and flax in floor trays [71]. The Vectra model of Opel uses package trays and door panel inserts made of reinforced kenaf/flax hybrid biocomposites. Different Audi Group models use cellulose fibre reinforced biocomposites to produce the seatbacks, door panels, and boot-lid finish panels. The BMW series 7 has around 24 kg of natural/renewable materials in its construction, considering flax and sisal for the interior door lining panels, cotton

Fig. 10.5 Use of cellulose fibre-reinforced biocomposites in several interior parts in a Mercedes-Benz car [68].

for sound insulation, wool for the upholstery, and wood for the seatbacks. The replacement of glass-reinforced composites is a solution presented by Daimler-Benz, namely using sisal, jute, coconut, hemp, and flax together with a polypropylene matrix. With this purpose, dashboards, centre armrest consoles, seat shells, and seatbacks were designed [44]. The CARBIO project [72], involving car manufacturer Jaguar. Land Rover, developed a hybrid carbon/flax composite for car roof that excels in the weight, cost, environmental impact, noise, vibration, and harshness compared to the full carbon components. A 50/50 carbon/flax composite composed of Biotex flax supplied by Composites Evolution and SHD Composites material prepreg resin with the same bending stiffness of the full carbon fibre component reduced the cost by 15%, the weight by 7%, and increased the vibration damping by 58%. As shown in Table 10.5, automotive companies like Toyota, Proton, Volvo and others have several biocomposite car parts.

Table 10.5 **Application of natural fibre composites in the automotive industry [1,70,71,73]**

Manufacturer	Model	Application
Rover	2000 and others	Rear storage shelf/panel, and insulations
Opel	Vectra, Astra, Zafira	Door panels, pillar cover panel, headliner panel, and instrumental panel
Volkswagen	Passat Variant, Golf, A4, Bora	Seat back, door panel, boot-lid finish panel, and boot-liner
Audi	A2, A3,A4, A4 Avant, A6,A8, Roadstar, Coupe	Boot-liner, spare tyre-lining, side and back door panel, seat back, and hat rack
Daimler Chrysler	A, C, E, and S class, EvoBus (exterior)	Pillar cover panel, door panels, car windshield/car dashboard, and business table
BMW 3	5 and 7 series and other	Pilot Seat back, headliner panel, boot-lining, door panels, noise insulation panels, and moulded foot well linings
Peugeot	406	Front and rear door panels, seat backs, and parcel shelf
Fiat	Punto, Brava,Marea	Door panel
General Motors	Cadillac De Ville, Chevrolet Trail Blazer	Seat backs, cargo area floor mat
Toyota	ES3	Pillar garnish and other interior parts
Saturn	L300	Package trays and door panel
Volvo	V70, C70	Seat padding, natural foams, and cargo floor tray
Ford	Mondeo CD 162, Focus	Floor trays, door inserts, door panels, B-pillar, and boot-liner
Saab	9S	Door panels
Renault	Clio, Twingo	Rear parcel shelf

Table 10.5 Continued

Manufacturer	Model	Application
Toyota	Raum, Brevis, Harrier, Celsior,	Floormats, spare tyre cover, door panels, and seat backs
Mitsubishi		Cargo area floor, door panels, and instrumental panel
Mercedes Benz	C, S, E, and A classes	Door panels (flax/sisal/wood fibres with epoxy resin/UP matrix), glove box (cotton fibres/wood moulded, flax/sisal), instrument panel support, insulation (cotton fibre), moulding rod/apertures, seat backrest panel (cotton fibre), trunk panel (cotton with PP/PET fibres), and seat surface/backrest (coconut fibre/natural rubber)
	Trucks	Internal engine cover, engine insulation, sun visor, interior insulation, bumper, wheel box, and roof cover
Citroen	C5	Interior door panelling
Lotus	Eco Elise (July 2008)	Body panels, spoiler, seats, and interior carpets
Rover	2000 and others	Insulation, rear storage shelf/panel
Opel	Corsa, Astra, Vectra, Zafira	Headliner panel, interior door panels, pillar cover panel, and instrument panel

10.5.3 Marine applications

The naval industry is naturally associated to glass-reinforced composites (typically with polyester matrices), but end-of-life disposal of these components is extremely difficult. The replacement of these parts by natural fibre composites should thus provide a viable alternative with low environmental impact. On the other hand, natural fibre composites do not behave well in water or even humid environments since, when subjected to these conditions, they degrade by water absorption resulting hydrolysis, causing swelling, matrix cracking, and fibre/matrix debonding [74]. Thus, these parts are highly prone to lose their mechanical characteristics in these environments, especially if in direct contact with water. However, despite these challenges, some biocomposites are appearing as products in marine industries. The adhesives' manufacturer Huntsman Advanced Materials was pioneer in building racing boat including 50% of natural flax fibres in the composite structure [75]. The company Sustainable Composites produces environmentally friendly kayaks, canoes, and surf boards from natural flax fibres as reinforcement in an also natural resin (EcoComp UV-L) Fig. 10.6 [76]. Despite all of these applications, further research is definitely required to improve

Fig. 10.6 Recreational boat made of natural fibre composites [76].

the water resistance of natural fibre composites such that their application can be further extended to products which can perform well in marine environments [47].

10.5.4 Packaging and other short life items

An important feature of packaging items is that these should be disposable because they have a short life-span. Typically, polymers like polyethylene, polystyrene, and polyvinyl chloride are used with these purposes, but these are harmful to the environment because of their nonbiodegradability [42]. To surpass this limitation of common plastics, biomaterials, i.e., those incorporating a biodegradable matrix, with an equivalent cost and mechanical properties can be a replacement [77]. Aqvacomp [78] is a recent biocomposite product composed of natural cellulose fibres as reinforcement material in plastic that can be applied in packaging items, with the main advantage being that the fibres can be blended with the polymer directly from the pulp production process without drying, increasing the production rate. The FLHEA project [79] developed a novel degradable biocomposite packaging material that can be processed with commercially available thermoforming lines. The resulting product increased the oxygen barrier properties by 30% and was found to be promising towards the development of a sustainable and biodegradable material that can in the near future replace currently commercialized products.

Other items than packaging that have a short life-span, a good example is consumer electronics. In these products, design and/or technological reasons can make the product obsolete in a very short period of time, although these still remain fully functional. On the other hand, these products are seldom subjected to harsh environmental conditions, which would be harmful for biocomposites. Because of this, companies like NEC have been using biocomposites (PLA/kenaf composite) in computer mother-boards since 2004 [80]. More recently, the same company commercialized a green phone considering the same natural composite and began using green composites for the outer shell of computer towers [81]. Another example of application of green composites for short-life products are toys, by providing improved renewability, low embodied energy, biodegradability, environmental credentials, and nontoxicity. Examples of these applications, apart from those deriving from wood toys, were found by Sprigwood [82], a toy manufacturer that uses composites made of recycled plastics reinforced by cellulose fibres.

10.5.5 Medical uses

The hydrophilic nature of biocomposites is a major advantage with regard to medical applications, because it eases the compatibility with the living cell tissue. Apart from this, natural fibre composites also exceed synthetic composites in the biocompatibility and biodegradability [42]. According to Lv et al. [83] and Cheung et al. [84], the use of biocomposites in medical applications has several benefits: higher specific strength and toughness, possibility to improve biodegradation kinetics and cell permeability, capability to integrate growth factors or nutrients in the composite cells and shapability. Tissue engineering is particularly attractive because natural fibre composites can act as a cellular matrix with whom living cells find support and growth, and examples exist in the regeneration of articular cartilage by poly(-lactic-co-glycolic acid) (PLGA)/collagen composites [85]. Actually, this material is nontoxic since its biodegradability can be improved by the monomer ratio and its by-products are naturally present in the human body [86]. The use of cellulose for biomedical purposes is also possible, namely the combination of bacterially sourced cellulose into a PLA matrix, or cellulose/chitosan biocomposites [87]. Microbial cellulose (a pure form of cellulose) based composites has recently been used for the development of tissue engineered constructs due to its unique nanostructure that closely resembles the structure of native extracellular matrices [88,89]. Different approaches are found in the literature concerning the use of composites with microbial cellulose for medical applications (Table 10.6) [47].

Table 10.6 Application of natural fibre composites for biomedical applications [47]

Biocomposite	Reinforcement type	Applications
Poly(3-hydroxubutyrate-co-4-hydroxubutyrate)/cellulose	Microbial cellulose fibres	Tissue engineering
Nanocrystalline cellulose (NCC)/polyvinyl alcohol (PVA)	Commercially available rod-shaped nanocrystalline cellulose (NCC)	Tissue regeneration
Cellulose/PVA	Microbial	Tissue regeneration
All-cellulose composite	Commercial cellulose nanowhiskers	Small grafts
All-cellulose composite	Norway spruce cellulose fibres	Ligament or tendon substitute

10.5.6 Sporting equipment

It is known that some issues exist regarding the applicability of natural fibre composites in high responsibility applications because of issues like limited strength or strength reduction when formed into a composite. On the other hand, the good specific strength of these materials, especially the specific stiffness, makes them viable for applications that benefit from reduced overall weight, while component failure due to material variations or environmental degradation would not be so critical regarding injury or economic loss, as it is the case of sports equipment [42]. Despite this advantage, the use of natural fibre composites in sporting goods generally involves combining natural with synthetic fibres (hybrid composites) or also considering synthetic and, thus, nonrenewable matrices, which cancels the biodegradability advantage of these materials. Some examples of application are snowboards made of flax-reinforced biocomposites [90], tennis rackets reinforced by 25% flax and 75% carbon fibres [91], and bicycle frames reinforced with 80% flax and 20% carbon fibres [92]. The common choice of flax in these applications is related to the improved vibration damping capabilities compared to glass or carbon fibres providing, for instance, higher navigability to the snowboards, more gaming comfort in rackets and also more comfort by shock absorbing in riding bikes. Composites Evolution [93] developed carbon/flax hybrid materials at a lower cost than full carbon components to be applied in the sporting goods sector. Three products are available to harness the benefits of flax: hybrid woven yarn fabrics, hybrid spread tow fabrics, and a layered hybrid approach (Fig. 10.7). These products provide a synergistic combination between the two fibre types to attain tuneable performance, superior vibration damping, and improved aesthetics at a lower cost than full carbon components.

Fig. 10.7 Carbon/flax fabrics from composites evolution [93].

10.6 Challenges in the use of natural fibre composites

It is a general consensus amongst natural fibre composite researchers that significant challenges exist regarding their use as load-bearing components. In the beginning, since the mechanical strength was not so valued, these materials were limited in application to nonstructural parts. Other limitations were the environmental degradation (especially to moisture) and low resistance to impact. Research in fabrication processes, fibre-matrix compatibility and others has shown that these limitations could be overcome. Moreover, recent indicators show that there is room for significant improvements by application of coatings, fibre surface treatment technology, new resins, and incorporation of additives. Many other challenges exist, listed in the following [3].

Hydrophilicity: The biggest challenge is perhaps the hydrophilic nature of natural fibres, which makes them prone to water absorption and, in consequence, with poor adhesion to hydrophobic polymer matrices. Many reported cases exist showing failure of natural fibre composites under water or moisture exposure, namely by delamination and fibre swelling. Natural matrices are also more sensitive to water absorption than petroleum-based ones. The behaviour when immersed in water is even worse, and this was checked by Singh and Gupta [94], finding a strength reduction in sisal-reinforced composites up to 31% larger by immersion in water than by exposure to 95% of relative humidity.

Durability: Durability and behaviour prediction over long periods of time are two major concerns with natural fibre composites, especially under adverse environments/moisture. From an extensive literature review, a major gap of knowledge is undoubtedly the fatigue behaviour of these materials, and this definitely needs addressing before these materials go under usage for load-bearing components.

The strength and stiffness of natural fibre composites usually falls between 100–200 MPa and 1–4 GPa, respectively, which is markedly low for structural parts and needs to be addressed conveniently.

Variability in fibre properties: The inconsistencies in the fibre properties, already discussed in terms of origin, is a major setback of natural fibre composites if they are going to be used as structural parts, because of the associated design uncertainties.

Fire resistance: The fire resistance is another point requiring improvement. Strength and stiffness of natural fibre composites can be significantly depreciated at temperatures of 120ºC. Currently, very few of these materials pass civil construction fire resistance tests.

Thermal stability: Processing difficulties and limitations are also present in the fabrication of these materials. The maximum operating temperature is around 180ºC [95], which brings some restrictions on the chosen matrix and fabrication methods. Regarding the bioresins, they are not usually processed at very high temperatures, which is a good indicator as it makes the process feasible with respect to degradation of the fibres.

10.7 Possible solutions to implement

Based on the current state-of-the-art, overcoming the water absorption limitation should involve one of the two procedures: fibre or matrix modification. Fibre modification usually involves the process of alkalization, which reduces the cellulose capacity to bond hydrogen and in turn cancels bonding of open hydroxyl groups with water molecules. This process concurrently eliminates hemicellulose, which helps to turn the fibres less hydrophilic. Issues to account for in a proper treatment are the alkali concentration, the exposure time, water washing need after the treatment under penalty of fibre degradation over time, and production of waste products. Other alternative seems to be the Duralin steam process [39]. This treatment promotes the creation of aldehyde and phenolic functionalities and promotes a significant reduction of moisture uptake in water environments, and also diffusion in the material. This process has some advantages: increase of the fibre strength, ductility, and resistance to fungi, and dimensional stability. Matrix modification is not so used as treatment, because resins are typically hydrophobic and are not very prone to absorb moisture. Despite this fact, some soy-based resins can be affected by moisture and thus, solutions exist to overcome this limitation: additives and coatings. One solution for additives was proposed by Kumar and Zhang [96], which treated the soy proteins by immersion in benzilic acid, allowing the improvement of strength and moisture resistance, while keeping the matrix fully biodegradable. Oppositely, the use of coatings can also be effective if the coating material is chosen correctly and well applied. A coating example is a natural lignin-based coating [97].

The durability and behaviour prediction concerns can be overcome by the development or application/modification of damage models applied to materials such as synthetic composites and respective validation. Moreover, investigations already exist on durability under wet conditions. One of the main considerations is the growth of bacteria. Singh et al. [98] tested natural fibre composites of jute-reinforced phenolic resin after water exposure and detected hyphae fungi. Singh and Gupta [99] showed that prolonged ultraviolet exposure leads to matrix cracking and fibrillation, accompanied by strength reductions of over 50%. To reduce these effects, polyurethane coating was applied with success. The use of coatings and fibre treatments as bleaching or using silanes seems to be a field to be explored, with some good preliminary results [100].

A possibility to overcome the limitation in strength and stiffness, without improvements in the materials, is by taking advantage of design (e.g. sandwich solutions). Other modifications to improve mechanical properties and also the durability involve adhesion or wetting, and the use of hybrid solutions, even though this last one cancels or reduces the bioadvantage. Regarding the fibres/matrix adhesion many treatments exist to change the fibres surface and improve wetting. The most straightforward way to increase adhesion is fibre drying before mixing with the matrix to minimize bonding of H_2O molecules to the fibres surface. Adhesion can be improved by additives, coupling agents or alkalization. Additives can be applied to fibres (e.g. calcium chloride or sodium carbonate nanoparticles) or matrices (e.g. maleated polyolefins). Malkapuram et al. [101] used maleated polyolefins to improve adhesion. Others [102] mixed soy protein concentrate powder and microbamboo fibrils with good results. Coupling agents are compatibilizers between fibres and matrix that improve the bond by the removal of weak boundary layers and creation of a cross-linked region. Covalent bonds are then created between the fibres and matrix [101]. The use of silane coupling agents is very common between synthetic fibres and bioresins; between both biocomponents it is not so common, although trialkoxysilanes have been used [100]. Maleated propylene is highly effective in terms of mechanical properties and is easy to apply, giving stiffness and strength improvements of over 100% [103]. Careful examinations of the fracture surfaces showed a drastic reduction of fibre pull-out after treatment, with the fibre fracture coinciding with the macro cracks of the material. Other coupling agents are stearic acid, isocyanates, and triazine. Finally, alkalization or the alkali treatment reduces the absorption and modifies the fibres surface, which results in the improvement of mechanical properties. This treatment promotes the removal of cementitious materials and increase of the surface roughness. The main improvements are the tensile and flexural mechanical properties, although with a reduction of the impact strength. This treatment removes the nonstructural components of the fibres, which increases their specific properties. Some authors [104] found an improvement of mechanical properties by up to 50%. Chang et al. [105] tested the combination between ultrasonic and alkali treatments, resulting in extraction of low molecular constituents and depolymerization of macromolecules. Improvements due to the use of the alkali treatment alone were found. Hybridization, or combination of natural with glass fibres, also constitutes a possible way to improve the mechanical properties. Some studies are available on this solution that reported improvements of strength and reduction of moisture absorption [106]. This is however a residual solution, since most of the bioadvantages vanish. Combination of natural and synthetic matrices is also possible to allow an increase of mechanical properties, but with the same inconvenience.

To overcome the variability in the fibre properties, quality assurance protocols are needed so that the differences in properties between different batches are within tolerable limits [39]. Variability of cost and availability also exist. Some natural fibres cost actually vary with the climatic conditions. Other scenario is an eventual poor season for a particular plant, which make the respective fibres less available and with a higher cost. To reduce these problems to a minimum, the most relevant plants should be cultivated in several regions around the globe.

Regarding the fire resistance of natural fibre composites, the flammability is higher for fibres constituted mainly by cellulose, compared to those with a higher content of hemicellulose [107]. Fire resistance is also increased with the following factors: silica or ash in the fibre composition, fibre structure with higher crystallinity and small polymerization. Amongst synthetic resins to use with natural fibres, phenolic resins are probably the best choice due to their high compatibility with the natural fibres and for their high inherent fire resistance property. Otherwise, coatings and/or additives can also be used. Coatings of ceramics, intumescents, ablatives or glass, or chemical additives are possible solutions. The most effective coatings for natural fibre composites are intumescents, which act by forming a cellular surface when heated that protects the base material. Fillers like tack or nanoparticles also improve the materials resistance to fire by being heat barriers [107]. A lignin coating that promoted the appearance of char was also successfully tested [97]. An integrated solution would be the combination of a cellulosic material that promotes formation of char with an intumescent coating.

The processing/fabrication limitations for natural fibre composites depend on the selected process. Hand lay-up is the simplest process and it does not require heat. However, it is limited in the wt% of natural fibres. Compression moulding, on the other hand, is the most widespread technique for natural fibre composites, achieving up to 80 wt% of fibres [41]. Other processes were tested for natural fibre composites, like resin transfer moulding (RTM), vacuum moulding, and vacuum assisted RTM. Pultrusion is widespread for glass and carbon composites, but it is new for natural fibre composites. Some authors [108] showed the feasibility of this technique, although hybrid solutions with glass fibres gave better results. It was shown that the obtained composites had good mechanical properties, although adhesion could still be improved. Others [109] tested production methods like compounding or injection moulding, but mechanical properties were limited by the fibres length and room for improvement is big.

10.8 Conclusions

Natural fibre composites have been receiving huge attention in the last few decades by the industry and researchers because of their potential in civil engineering, vehicles, packaging, and other fields. This is because of some desirable characteristics such as low cost, low density (and, thus, high specific properties), eco friendliness, processing advantages, and reduction of CO_2 emissions in the whole life cycle. Despite these facts, some limitations exist, such as low mechanical properties and toughness, property variations, sensitivity to temperature, moisture and UV radiation, and poor fire resistance. Some of these limitations lead to their typical short lives in outdoor applications. Plant fibres are the most widely used, and a huge variety is available, with distinct physical and mechanical properties. Most of the research up to now was focused on the feasibility of using these materials for industry applications, with promising results.

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Green materials for aerospace industries

11

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11.1 Introduction

Throughout the last few years of using green composites in the aerospace sector, designers and manufacturing engineers have progressed from relatively small, lightly loaded components and sections of structure such as ailerons and fairings to heavily stressed and critical items. Early manufacturing processes for lightly stressed components were small scale, involving significant elements of manual intervention in the process. They relied on the low density and high stiffness and strength of the raw materials to deliver the required performance. As the size, stress values, and criticality of the parts all increased, manual input has declined dramatically, substituted by complex, sophisticated robotic machinery. The robots have delivered consistency, freedom from defects, and increased processing speed to cope with the manufacture of wings and fuselage sections of large civil aircraft. However, the essentials of this prepreg route have remained unchanged, and there are still issues of the cost effectiveness of this route. In parallel, manufacturing researchers are pursuing lower cost options. Fibre-reinforced polymer-matrix (FRP) composites are increasingly used in high-performance aircraft and spacecraft structures, mainly based on their comparatively high specific strength and stiffness, which derive from their relatively low density. This trend is expected to continue due to the increasing demand for energy-saving aircraft and propulsion systems for space applications for which weight reductions are a key element. FRP composites are prone to damage from the initiation and propagation of delaminations (i.e. areas in which separation occurs in the polymer-matrix resin in which the fibres are embedded). Delaminations may also occur between the polymer and fibre layers in the form of fibre-matrix debonding.

Polymer is a class of materials with wide variety and large number of plastics, elastomers, and adhesives.

The three main groups of polymers are called thermoplastics, thermosetting polymers (or thermosets), and elastomers. The most common use for polymers is the matrix phase of fibre composites. Polymers are the 'glue' used to hold together the high-stiffness, high-strength fibres in fibre–polymer composites. Another important application of polymers is as an adhesive for joining aircraft components.

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11.2 Polymers for aerospace application

One of the important applications of polymers is as an adhesive for joining aircraft components. It is possible to produce high strength, durable joints using polymer adhesives without the need for fasteners such as rivets and screws. Adhesives are used to join metal-to-metal, composite-to-composite, and metal-to-composite components, e.g., bond ribs, spars, and stringers to the skins of structural panels used throughout the airframe. Adhesives are also used to bond face sheets to the core of sandwich composite materials and to bond repairs to composite and metal components damaged during service. Thin layers of adhesive are used to bond together the aluminium and fibre–polymer composite sheets that produce the fibre–metal laminate called GLARE, which is used in the Airbus 380 fuselage. The use of elastomers is usually confined to nonstructural aircraft parts that require high flexibility and elasticity, such as seals and gaskets [1].

11.3 Polymers for aerospace structures

Epoxy resin is used extensively in aircraft composite structures, but cannot be safely used inside cabins because of its poor fire performance. Most epoxy resins easily ignite when exposed to fire, and release copious amounts of heat, smoke, and fumes. Federal Aviation Administration (FAA) regulations specify the maximum limits on heat release and smoke produced by cabin materials in the event of fire, and most structural-grade epoxy resins fail to meet the specifications. Phenolic resins meet the fire regulations, and most of the internal fittings, components, and furniture in passenger aircraft are made of fibreglass–phenolic composite and moulded phenolic resin.

Elastomers are not suitable for use in aircraft structures because they lack stiffness and strength, but they do have exceptionally high elasticity with elongation values between one hundred and several thousand percent. This makes elastomers suitable when low stiffness and high elasticity is required, such as aircraft tyres, seals, and gaskets. Many aircraft components that require a tight seal, such as window and door seals, use elastomers. These materials are used for their excellent elasticity; they can be easily compressed to make a tight seal without being damaged or permanently deformed. Elastomers have some cross-linking between the chains that provides a small amount of resistance to elastic stretching. The amount of cross-linking is much less than that found in the heavily cross-linked thermosets. The cross-links in elastomers are widely spaced along the coiled polymer chains. The cross-links between the elastomer chains are created in a process called vulcanisation. The most common vulcanisation process involves heating rubber with sulphur to temperatures of about 120–180°C. Without vulcanization, elastomers behave like a very soft solid under load. When vulcanization is carried too far, however, the chains are too tightly bound to one another by excessive cross-linking and the elastomer is very brittle. The cross-links also improve the wear resistance and stiffness, which is important when elastomers are to be used in aircraft tyres. These properties improve with the amount of cross-linking, but the amount of sulphur present in the elastomer should not exceed about 5% otherwise the material becomes too brittle.

11.4 Polymer nanocomposites for aerospace applications

Nanocomposites are an exciting new range of materials that can withstand many adverse conditions and have a potential to replace conventional materials existing today. These have many advantages over conventional materials used for aerospace. Many types of nanomaterial (such as carbon nanotubes (CNTs), carbon nanofibres (CNFs), SiO_2, and montmorillonite) are now available due to the establishment of well-developed manufacturing technologies, such as chemical vapour deposition, ball milling, and electrospinning. Through improvements in bulk manufacturing, fibre-reinforced polymer nanocomposites are being used in an increasing number of practical applications (e.g. in the manufacture of composite components in aerospace and microelectronics). The improvements that have been identified for high-performance structures and payloads are due to the modification of mechanical, thermal, and electrical properties. High-performance structural design criteria impose a number of restrictions on the properties of materials to be used. Lighter, thinner, stronger, and cheaper structures are important things to be kept in mind.

Nanoscale fillers such as CNTs and CNFs offer new possibilities for low-weight composites with extraordinary mechanical, electrical, and thermal properties. Taking into consideration their high axial Young's modulus, high aspect ratio, large surface area, low density, and excellent thermal and electrical properties, these fillers can be used as modifiers for the polymer matrices of fibre-reinforced polymer composites leading to advanced mechanical behaviour. However, with nanotube-reinforced polymer composites there has only been a moderate strength enhancement, which is significantly below the theoretically predicted potential. To achieve the full potential of nanotubes, there are two critical issues that have to be solved:

- The dispersion of the nanotubes in the polymer matrix
- The interfacial bonding between the nanotubes and the polymer matrix

One key area where nanocomposites can make a significant impact is in addressing interlaminar toughness in fibre-reinforced composites. The improvement of the interlaminar toughness of fibre-reinforced composites has been the focus of research for a considerable time, since it is directly related to the dynamic as well as the damage-tolerance performance of the composite. The problem has been addressed in various ways: stitching, Z-pinning, or interleaving, with a notable increase in toughness while also providing improvements in mechanical properties, such as fatigue life. Other approaches focus on tailoring the matrix or interface properties in order to provide the necessary interlaminar fracture toughness. Matrix toughening may be performed through chemical modification or, more recently, with the incorporation of fillers in the matrix [2].

CNT technology could have a dramatic breakthrough for magnetic devices, especially magnets, in space and aircraft applications. The basic electronic properties of semiconducting CNTs change when placed in a magnetic field. Nanotube band gaps are comparable with silicon and gallium arsenide, which are currently the mainstays of the computer industry because their narrow band gaps correspond with how much electricity it takes to flip a transistor from ‘on to off’.

Various studies can be found on the incorporation of CNFs in polymeric matrices giving the final mechanical and electrical properties of these materials. As in all cases where nanosized fillers are involved, the development of high-performance CNF/polymer composites requires a homogeneous dispersion of CNFs in the polymeric matrix because it is crucial to the composite's performance. Material Interface modification can also be performed by grafting, which tailors the chemical compatibility between the fibres and the matrix.

Hsiao et al. [3] explored the potential of using CNTs to reinforce the adhesives joining two composite structures. In the study, different weight fractions of MWCNT were dispersed in epoxy to produce toughened adhesives. The reinforced adhesives were used to bond the graphite fibre/epoxy composite. This experimental study showed that addition of 5 wt% MWCNT to an epoxy adhesive effectively transferred the shear load from the adhesive to the graphite fibre system in the composite laminates and improved the average shear strength of the adhesion by 46% (±6%). A significant enhancement of the bonding performance was observed as the weight fraction of CNTs was increased. As shown in Fig. 11.1, the 5 wt% MWCNT effectively transferred the load to the graphite fibres in the adherends and the resulting failure was in the graphite fibre system. On the other hand, for epoxy adhesives containing no MWCNTs (see Fig. 11.2), failure occurred at the epoxy along the bonding interface and no significant fractures of the graphite fibres were observed. Despite the promising results, the researchers concurred that further experiments involving increasing MWCNT weight fractions and more detailed scanning electron microscopy observations are required in order to understand and model the role of MWCNTs in enhancing adhesion.

Yokozeki et al. [4] investigated the damage accumulation that occurred in carbon–fibre-reinforced nanocomposite laminates under tensile loading. The nanocomposite laminates used in the study were manufactured from prepregs consisting of traditional carbon fibres and epoxy resin filled with CNTs. The thermomechanical properties of

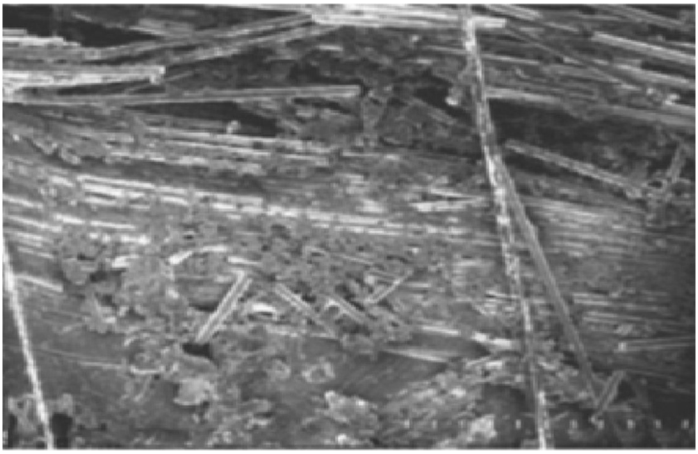

Fig. 11.1 5 wt% MWCNT effectively transferred the load to the graphite fibers in the adherents and the resulting failure was in the graphite fiber system.

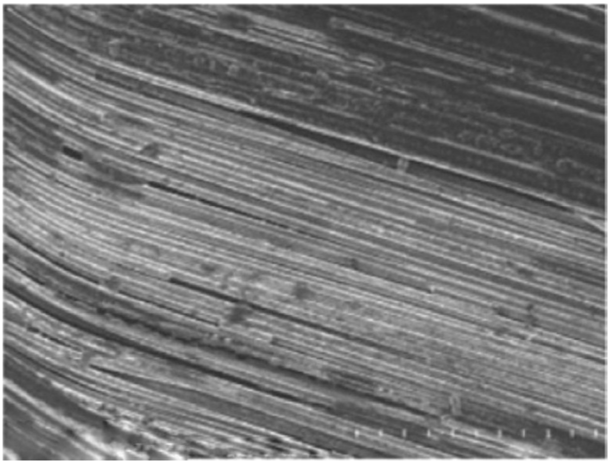

Fig. 11.2 Epoxy adhesives containing no MWCNTs, failure occurred at the epoxy along the bonding interface.

the unidirectional carbon–fibre-reinforced nanocomposite laminates were evaluated, and cross-ply laminates were subjected to tension tests to observe the damage accumulation of matrix cracks.

Park et al. [5] explored this concept by applying the electro-micromechanical technique to obtain fibre damage and the reinforcing effect of carbon nanocomposites against content. The sensitivity to fibre damage such as fibre fracture, matrix deformation, and fibre tension was highest for 2.0 vol% CNT composites. They suggested that damage sensitivity as measured by electrical resistance might be closely related to the 3D network structure, the percolation structure. For CNT composites, the mechanical properties and apparent modulus indicate that the reinforcing effect increased with CNT content. The researchers confirmed that the apparent modulus, as measured by electro-micromechanical tests, could be used to evaluate the mechanical properties of fibre-reinforced composites.

A Kireitseu et al. [6] study on the rotating fan blades of turbine engines represents another feasible aerospace or defence application. The authors considered a large rotating civil engine blade, illustrated in Fig. 11.3, which is typically hollow and

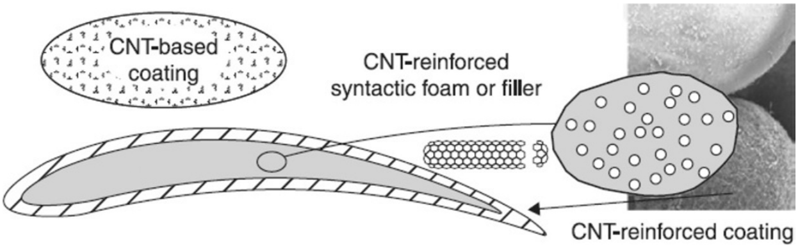

Fig. 11.3 Damping material for an aircraft engine blade.

usually has stiff rib-like metallic structures in order to increase rigidity and maintain the cross-sectional profile of the blade. They suggested a foam-filled fan where the metal structure or traditional fillers are replaced with a CNT-reinforced syntactic foam and also, with a CNT-reinforced composite layer on the top. Results of the damping behaviour and impact toughness of the composite sandwiches showed that CNT-reinforced samples have better impact strength and vibration-damping properties over a wide temperature range.

11.5 Green materials

Structural components for aircraft made from fibre polymer composites frequently comprise duroplastics shaped in prepreg and resin transfer moulding (RTM) processes. Celanese adds that the greatest disadvantage of this process is the extensive drying times required for the matrix to cure. FIBER uses prepregs that contain additional inlaid thermoplastic fibres, as well as carbon fibres, to lend structure to the window frames. These prepregs are processed to form structural inlay preforms—versions made from multiaxial fibre inlays (MAG) are used to shorten cycle times. FIBER also produced tailored fibre placement preforms (TFP) parallel for precise fibre alignment. The matrix of knit and weft fibres is formed in the subsequent consolidation in a variotherm press. In this process, the Fortron polyphenylene sulphide (PPS) fibres in the prepreg ensures homogenous matrix distribution. After consolidation, the structure inlays are sprayed with short fibre-reinforced Fortron PPS to add integral stiffening or functional elements which would be much more difficult to implement with continuous fibre-reinforced materials.

The main purpose of combining materials to create a composite is to gain a synergistic effect from the properties of both the reinforcement and matrix. For example, carbon–epoxy composite used in aircraft structures is a mixture of carbon fibres (the reinforcement phase) embedded in epoxy resin (the matrix phase). The carbon fibre reinforcement provides the composite with high stiffness and strength while the epoxy matrix gives ductility. Used on their own, carbon fibres and epoxy are unsuitable as aircraft structural materials, the fibres being too brittle and the epoxy too weak, but when combined as a composite they create a high-performance material with many excellent properties [7].

Fibre–polymer composites alongside aluminium alloys are the most used materials in aircraft structures. The use of composites in civil aircraft, military, and helicopters has increased rapidly since the 1990s, and it is now competing head-to-head with aluminium as the material of choice in many airframe structures [8,9]. The use of composites in aircraft has been led by the military, particularly with fighter aircraft and helicopters. Carbon fibre–epoxy composites have been used in the primary structures of fighter aircraft for many years, including the wings and fuselage, to minimize weight and maximize structural efficiency. The amount of composite varies between different types of fighter aircraft, and the usage has increased greatly since the 1970s. Polymer matrix composites have been used for many years in space structures, including truss elements, antennas, and parabolic reflectors. The main truss of the Hubble space telescope, for example, is made of carbon fibre–epoxy composite for lightness, high stiffness, and low coefficient of thermal expansion. As another example, the main cargo doors of the space shuttle orbiter are made of sandwich composite material and the arm of the remote manipulator system is made of carbon–fibre composite.

Polymerization reactions for most of the polymers used in aircraft involve just one type of monomer. When the polymer chain is made using just one monomer type it is known as a homopolymer. Polymers can also be produced by the polymerization of two types of monomers, which is called a copolymer. Although copolymers are not used extensively in plastic aircraft parts, they are sometimes used as elastomers in seals. When the two different monomers are distributed randomly along the chain it is called a random copolymer. Under controlled processing conditions, the two monomer types may alternate as single mer units along the chain, and this is known as a regular copolymer. If, however, a long sequence of one type of mer unit is followed by a long sequence of another type of mer unit, it is termed a block copolymer. This latter type is called a graft copolymer when the chains produced from one type of monomer are attached (or grafted) to the chain created from the other monomer.

In addition to plant oils, other renewable raw materials of interest in the design of bio-based thermosetting materials include lignin and proteins due to their vast abundance and high functionality. Lignin is the second most abundant naturally occurring macromolecule amidst cellulose and plant oils. Due to its phenolic nature, lignin has been considered as a promising substitute for phenol in phenol–formaldehyde-based resins. Thermo-chemical conversion of lignin is carried out to enhance its reactivity for reactions with formaldehyde. In nonfood applications, the use of plant proteins like soy proteins and wheat gluten may be also a promising way to produce thermosetting (bio)materials with a large range of applications. For example, plant proteins are considered to be ideal templates for biomaterials as temporary replacement implants due to their ease of processability, adhesion to various substrates, and surface-active properties. For any processing technique, the processing of proteins involves heat-treatment leading to cross-linked systems. In some cases, a suitable cross-linker is added in order to control the cross-linking density for the protein-based systems [10].

Manufacturers and engineers are always on the lookout for new materials and improved processes to use in manufacturing better products, and thus maintain their competitive edge and increase their profit margin. Wood plastic composites (WPCs) are being used in a large number of applications in automotives, constructions, marine, electronic, and aerospace (Fig. 11.4). The WPCs market is now a multibillion-dollar business. The major market identified for the application of green WPCs, the replacement of fibreglass and steels, is the automotive components. They are used as trim parts in dashboards, door panels, parcel shelves, seat cushions, backrests, and cabin linings. Plant fibres are increasingly used for thermo-acoustic insulation purposes. The use of flax fibres in car disc brakes to replace asbestos fibres is also another example. So far, there are only very few exterior parts made from plant fibre composites [11].

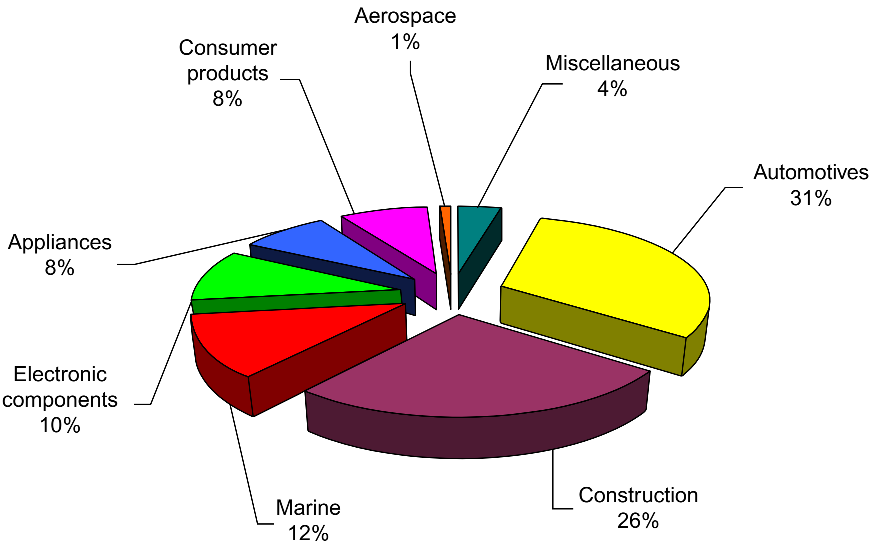

Fig. 11.4 Applications of wood plastic composites.

11.6 Fibre-reinforced materials for aerospace application

High strength, high modulus carbon fibres are about 5–6 mm in diameter and consist of small crystallites of ‘turbostratic’ graphite, one of the allotropic forms of carbon. The graphite structure consists of hexagonal layers, in which the bonding is covalent and strong ($w > 525$ kJ/mol) and there are weak van der Waal forces (<10 kJ/mol) between the layers. This means that the basic crystal units are highly anisotropic; the inplane Young's modulus parallel to the a-axis is approximately 1000 GPa and the Young's modulus parallel to the c-axis normal to the basal planes is only 30 GPa [12].

A serious problem of plant fibres is their strong polar character, which creates incompatibility with most polymer matrices. Surface treatments are potentially able to overcome the problem of incompatibility. Chemical treatments can increase the interface adhesion between the fibre and matrix, and decrease the water absorption of fibres.

One advantage of designing with FRP composites is that the layup (i.e. the number of plies (fibre layers) and the relative orientation of the fibres in each ply) can be chosen according to the strength and/or stiffness requirements for the specific application. This frequently results in so-called multidirectional layups. Another solution is the use of so-called three-dimensional (3D) reinforcements (e.g. braided or woven) but also preparing composites by stitching, tufting, or inserting pins in the through thickness direction. The standard test methods published so far, however, are mainly intended by their scope for unidirectionally reinforced FRP laminates (i.e. composites with essentially all fibres aligned in one direction only).

The Faserinstitut Bremen e.V. (FIBRE) has developed a cost-effective and efficient process to manufacture lightweight aerospace components that use a continuous fibre-reinforced structural inlay based on Fortron PPS from Celanese Corporation. In a pilot project, FIBRE worked with AIRBUS Operations GmbH, KARL MAYER MALIMO Textilmaschinenfabrik GmbH, Krauss–Maffei Technologies GmbH, Ferdinand Stükerjürgen GmbH, and TU Chemnitz to produce aircraft window frames successfully using a thermoform and injection moulding process. Shorter cycle times were possible, resulting in an increase in productivity. Structural components for aircraft made from fibre polymer composites frequently comprise duroplastics shaped in prepreg and RTM processes. Celanese adds that the greatest disadvantage of this process is the extensive drying times required for the matrix to cure. ‘From a production point of view there is actually a great deal in favour of thermoplastic materials like Fortron PPS, which are often more economical’, said Peter Radden, Fortron PPS specialist. ‘Fortron PPS is more dimensionally stable, chemical and temperature resistant, and has a long tradition in aircraft construction where it is often the material of choice in structural components’. FIBRE uses prepregs that contain additional inlaid thermoplastic fibres, as well as carbon fibres, to lend structure to the window frames. These prepregs are processed to form structural inlay preforms—versions made from MAG are used to shorten cycle times. FIBRE also produced TFP parallel for precise fibre alignment. The matrix of knit and weft fibres is formed in the subsequent consolidation in a variotherm press. In this process, the Fortron PPS fibres in the prepreg ensure homogenous matrix distribution. After consolidation, the structure inlays are sprayed with short fibre-reinforced Fortron PPS to add integral stiffening or functional elements, which would be much more difficult to implement with continuous fibre-reinforced materials. The combination of thermoforming and injection moulding makes the process more cost-effective and allows for higher production volumes in a shorter time.

11.7 Applications in aircraft construction

In the pioneering days of flight, aircraft structures were composite, being fabricated largely of wood (natural composite), wire, and fabric. Aluminium alloys took over in the 1930s and have dominated the industry since then. Wooden structures did however, persist until World War II, and the de Havilland Mosquito aircraft (DH98) constructed of a plywood-balsa-plywood sandwich laminate probably represents the high point of engineering design with wood. The DH91 Albatross airliner in 1937 was moulded as a ply-balsa-ply sandwich construction, and the Spitfire fuselage in 1940 was designed and built of Gordon Aerolite material that was a phenolic resin incorporating untwisted flax fibres that could be regarded as the precursor of modern fibre-reinforced plastics. Current civil aircraft applications have concentrated on replacing the secondary structure with fibrous composites where the reinforcement media have been carbon, glass, Kevlar, or hybrids of these. The matrix material, a thermosetting epoxy system, is either a 125°C or 180°C curing system with the latter becoming dominant because of its greater tolerance to environmental degradation [13,14].

Composites have been used in Bell helicopters (Dallas Fort Worth, Texas) since the 1980s following their advanced composites airframe programme when they were, in order to detect low velocity impact damage in multidirectional laminates, employed the fundamental antisymmetric A0 Lamb mode at frequencies of

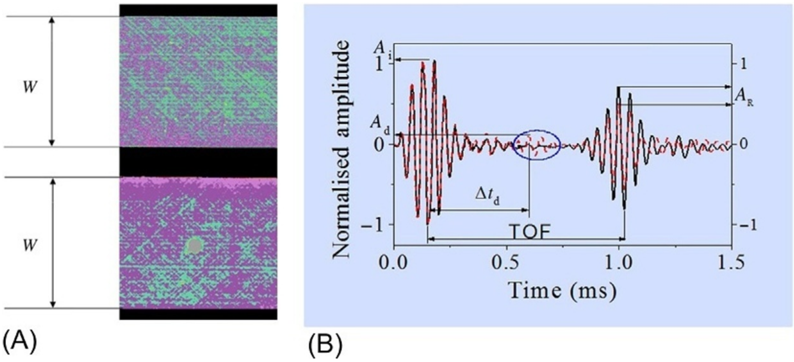

Fig. 11.5 (A) An ultrasonic C-scan image (across the width, *W*) of undamaged and 2J impact damaged laminate and (B) response of pristine and damaged composite plate [14].

15–20 kHz; Fig. 11.5 illustrates an ultrasonic C-scan image of the undamaged and damaged configuration together with time-of-flight method used to detect the location of damage; its location was calculated with an error of just 2.3% from the actual position [15]. Some success, but further research and development in this area, is required, especially on repair [16,17] and structural health monitoring of repaired configurations [18,19].

Another topic of interest in the context of aerospace applications of FRP composites is the testing of nonstandard specimen geometries that differ from the typical straight beam-type specimens defined in the standards.

Glass fibre-reinforced polymer shells have been developed by, for example, Refs. [19–21]. Hojo and Aoki [22] explored the effects of specimen thickness in mode I delamination resistance measurements (a double cantilever beam specimen). They manufactured laminates with a nominal thickness of 8 mm, effectively 8.9 mm thick CFRP epoxy (T800/3631) and 8.3 mm thick CFRP PEEK (AS4/PEEK) laminates, and then milled specimens with 3–5 mm thickness in addition to the 8 mm thick specimens. Initiation values determined from 6 to 8 mm long precracks (prepared manually by wedging) did not show any thickness dependence for both types of laminates. Propagation values for thicker specimens were slightly higher than those for thin specimens. However, there was a difference between values for CFRP epoxy for specimens prepared from two different plates, which was attributed to differences in fibre orientation. This is again an example of how processing and manufacturing may play important roles in delamination resistance performance.

A safety concern with using polymers and polymer composites in aircraft is fire. Most polymers are flammable and release large amounts of heat, smoke, and fumes when they burn. It is often necessary to use flame-retardant additives in polymers to achieve the fire resistant standards specified by safety regulators such as the FAA. Many types of additives are used to improve the flammability resistance of polymers, with the most common containing halogenated or phosphorus compounds. Flame-retardant additives are either discrete particles within the polymer or are chemically incorporated into the polymer chain structure.

11.8 Conclusion

A good engineering design should not only meet the performance specifications required of the composite structure, but it should do so at the lowest cost feasible for that structure. Traditional design focuses on meeting performance requirements and uses quality control measures to accept or reject the manufactured part. Materials development for improvement of performance, specifically of damage and delamination resistance of FRP composites, has received and still receives significant attention. Fibre-reinforced composites are a type of engineered material, which exhibits high strength/weight and modulus/weight ratios compared with some metallic materials. In the last two decades, studies have shown potential improvement in properties and performance of FRP materials in which nanoscale and microscale particles have been incorporated.

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WOODHEAD PUBLISHING SERIES IN COMPOSITES SCIENCE AND ENGINEERING

Biocomposites developed from renewable resources have received significant interest in recent years due to increased awareness of a more environmentally sustainable society. Although biocomposites have emerged as an alternative to glass fibre composites in many applications, they have been mostly perceived as low-performance materials. Significant technological advancements are required in terms of their supply, consistency, and manufacturability to improve their performance and reliability. This book presents a comprehensive review of various aspects of biocomposites from the existing literature and discusses the drawbacks associated with such products. The chapters in this book have described:

- Different cellulose based reinforcement types: plant derived and man-made;
- Biomatrices- thermoplastic biopolymers and thermosetting bioresins; their comparison with equivalent synthetic counterparts in regard to their processing and performance;
- Forensic identification techniques of bast fibres;
- Fibre matrix interface and environmental degradation behaviour;
- In-situ compatibilization and reactive extrusion of biocomposites and their rapid manufacturing possibilities;
- Recent innovations in biocomposites and their possible use in aerospace sector.

This book includes contributions from renowned experts in biocomposite field. The novelty of this book lies in the fact that it has focussed on identifying the current barriers associated with such materials and discussed the future direction. This book is a technical guide for students, engineers, and scientists in industries and academia, who will find interesting ideas for future research to develop next generation of biocomposite materials and processes for high performance applications.

Dipa Ray is Lecturer at University of Edinburgh, United Kingdom. Her main research interests are polymer composites with a special focus on biofibres, biopolymers and biocomposites. She has been the author of more than 65 papers in peer-reviewed international journals, over 30 conference proceedings and has written 12 chapters in books.

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