13 Wood/Nonwood Thermoplastic Composites

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Composites made from wood, other biomass resources and polymers have existed for a long time but the nature of many of these composites has changed in recent decades. Wood-thermoset composites date to the early 1900s. "Thermosets" or thermosetting polymers are plastics that, once cured, cannot be remelted by heating. These include cured resins such as epoxies and phenolics, plastics used as wood adhesives with which the forest products industry is traditionally most familiar (see Chapter 9). For example, an early commercial composite marketed under the trade name Bakelite was composed of phenol—formaldehyde and wood flour. Its first commercial use was reportedly as a gearshift knob for Rolls Royce in 1916 (Gordon 1988). "Thermoplastics" are plastics that can be repeatedly melted, such as polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC). Thermoplastics are used to make many diverse commercial products such as milk jugs, grocery bags, and siding for homes. In contrast to the wood—thermoset composites, wood—thermoplastic composites have seen large growth in recent decades. Wood—thermoplastic composites

are now most often simply referred to as wood-plastic composites (WPCs) with the common understanding that plastic refers to a thermoplastic.

While wood is the most used filler in WPCs, other biomass resources have also been used both in PE and PP. More recently, biomass resources have been used in bioplastics such as polylactic acid. This chapter will review all of these thermoplastic materials.

13.1 WOOD THERMOPLASTICS

The performance of a WPC largely depends on its constituent materials, how they are assembled, and how they interact. Therefore, to adequately understand (WPCs), we must first understand the advantages and limitations of its main constituents.

The plastics industry often uses fillers and reinforcements to modify the performance of plastic. Fillers (e.g., talc and calcium carbonate) are typically equidimensional and do not generally improve properties such as strength but can provide other benefits such as reduced cost, increased stiffness, and reduced thermal expansion, for example. Reinforcements (e.g., glass and carbon fibers) are fibrous, having one dimension much longer than the other, and are well-bonded to the plastic matrix (Carley 1993). Reinforcements markedly improve strength by transferring applied stress to the stronger reinforcing fiber. Wood-derived materials can be used as both a filler or a reinforcement.

There are a number of reasons that manufacturers use wood as a filler or reinforcement in plastics. As with many other fillers and reinforcements, wood is added to modify mechanical performance. However, wood has lower density than inorganic fillers, which can lead to benefits such as fuel savings when composites made with it are used in transportation and packaging applications. With changing consumer perceptions, some manufacturers have used the natural look of composites made with wood as a marketing tool. Others add wood to increase bio-based material content. Though not specifically added to plastics to impart biodegradability, wood can be used as a filler or reinforcement in biodegradable polymers where its biodegradability is an attribute rather than the detriment it is sometimes considered in more durable composites.

The wood used in WPCs is most often in particulate form (e.g., wood flour) or very short fibers or fiber bundles, rather than long individual wood fibers (i.e., it is used as a filler). A wide range of wood flour contents in WPCs are used depending on the processing method used, required performance, and economics. Extruded WPCs (e.g., deckboards) typically contain approximately 50-60% wood but injection molded WPCs usually contain less so that the melt viscosity is not too high. The relatively high bulk density and free-flowing nature of wood flour compared with wood fibers or other natural fibers, as well as its low cost, familiarity, and availability, is attractive to WPC manufacturers and users. Common species used include pine, maple, and oak but others are used as well. Typical particle sizes are roughly 2-0.2 mm (10-70 mesh), although there are exceptions. WPC manufacturers obtain wood flour either directly from forest products companies such as lumber mills and furniture, millwork, or window and door manufacturers that produce it as a by-product or buy it from companies that specialize in wood flour production.

Wood fibers are an order of magnitude stronger than the wood from which they derive (Rowell 1992). In a WPC, this higher strength, as well as their higher aspect ratio compared to wood flour can improve the efficiency of stress transfer from the plastic to the stronger wood fiber when well bonded to the plastic. This leads to improved mechanical performance. Because of the potential for improved mechanical properties, there has been a continuing interest in the use of individual wood, pulp, or paper fibers rather than wood flour as reinforcement in WPC. Though lower in mechanical performance than glass, the balance of properties that wood fibers yield, along with other advantages such as lower density, aesthetics, and low abrasiveness during processing offer advantages in some applications. Fiber preparation methods have a large effect on reinforcing ability. For example, high quality pulp fibers are more effective than lower cost, thermomechanical pulp fibers and can offer other benefits such as a lighter color. Processing difficulties, such as feeding and metering low-bulk-density fibers, have limited their use in WPCs. While there have

been some developments in densification, handling, and processing of these fibers (e.g., Jacobson et al. 2002), these approaches usually add cost. Wood-derived fibers also have to compete on economics and performance with other natural fibers such as flax, depending on regional availability. Natural variability in wood and other natural fibers is typically greater than with inorganic fibers and is also a consideration.

Wood and other plant-derived flours and fibers are unusual fillers/reinforcements in that they are compressible. The high pressures during plastics processing can collapse the hollow fibers or fill them with low molecular weight additives and polymers. The degree of collapsing or filling will depend on such variables as particle size, processing method, and polymer/additive viscosity, but wood densities in WPCs that approach wood cell wall density can be found in high-pressure processes such as injection molding. Consequently, adding wood to commodity plastics such as PP, PE, and polystyrene increases their density. However, even these higher densities are considerably lower than those of common inorganic fillers and reinforcements such as talc, calcium carbonate, or glass fibers. This density advantage is important in applications where weight is important such as in automotive or packaging applications.

Wood's low thermal stability limits the plastics used in WPCs to those that can be processed at low temperatures, typically lower than about 200°C, although high purity cellulose pulps with higher thermal stability have been added to plastics (e.g., some nylons) that are processed at higher temperatures than most commodity thermoplastics (Caulfield et al. 2001). The thermal expansion of wood is less than that of the commodity plastics commonly used as matrices and adding wood can reduce part shrinkage and warping due to wide temperature changes during processing.

Wood's hygroscopicity must be considered both in composite fabrication and product performance. Wood usually contains at least 4% moisture when delivered, which is much higher than most thermoplastics. This moisture must be removed before or during processing with thermoplastics. Though moisture could potentially be used as a foaming agent to reduce density, this approach is difficult to control and is not used commercially. Even compounded material (i.e., blended pellets of wood, plastic, and additives) often needs to be dried prior to further processing, especially if high weight percentages of wood flour are used. The hygroscopicity of wood flour can also affect the performance of WPC products. If the composite is not formulated and processed correctly for exterior applications, moisture sorption can lead to mold or fungal attack and volume changes due to moisture sorption, especially repeated moisture cycling, can lead to loss of adhesion between the wood and plastic components or matrix cracking.

13.1.1 THERMOPLASTIC MATRIX MATERIALS

Much of how a polymer processes and performs is determined by its molecular structure, which is developed during the polymerization process. The number-average molecular weights of many commercial synthetic polymers are typically about 10,000-100,000 (Billmeyer 1984). Table 13.1 shows the basic chemical structural units of several common synthetic. Polymers can contain one type of monomer (homopolymer) or multiple monomers (copolymers, terpolymers, etc.). Tacticity is important in the arrangement of repeat units in polymers with asymmetrical repeat units. For example, PP contains a methyl group (CH_3) attached to a carbon chain (Table 13.1) that can be attached to one side of the chain (isotactic), alternating sides of the chain (syndiotactic), or lack a consistent arrangement (atactic). Polymers can have a few branches, such as high density polyethylene, HDPE or long branches, such as low-density polyethylene, LDPE.

Polymers are often categorized by their behavior, which is influenced by their molecular organization. Unlike thermosets, thermoplastic polymers can be repeatedly softened by heating. When cooled, they harden as motion of the long molecules is restricted. If the polymer molecules remain disordered as they are cooled from the melt, they are considered amorphous thermoplastics and the temperature at which the polymer molecules cease to rotate and slip past one another is called its glass transition temperature (T_g). Below its glass transition, amorphous plastics (or amorphous

TABLE 13.1
Structural Units for Selected Polymers with Approximate Glass Transition (T_g) and Melting (T_m) Temperatures

Structural Unit	Polymer	T_g (°C)	T_m (°C)
$-CH_2-CH_2-$	Polyethylene (PE)	−125	135
$-CH_2-CH(CH_3)-$	Polypropylene (PP)	−20	170
$-CH_2-CH(C_6H_5)-$	Polystyrene (PS)	100	—
$-CH_2-CH(Cl)-$	Polyvinylchloride (PVC)	80	—
$-C(=O)-C_6H_4-C(=O)-O-CH_2-CH_2-O-$	Polyethylene-terephthalate (PET)	75	280

Source: Condensed from Osswald, T.A. and G. Menges. *1996. Materials Science of Polymers for Engineers.* Carl Hanser Verlag, New York.

regions of semicrystalline plastics) become glassy, stiff, and sometimes brittle. Polystyrene is an amorphous thermoplastic, for example.

Some thermoplastics form regions of highly ordered and repetitive molecular arrangements on cooling. In these semicrystalline plastics much, though not all, of its molecular structure is in an ordered state. A crystallinity of 40-80% is typical for common semicrystalline plastics such as PP and PE but depends on molecular architecture as well as processing history. In addition to a glass transition temperature (T_g), semicrystalline plastics have crystalline melting points (T_m), above which temperature the crystal order disappears and flow is greatly enhanced. This ability of plastics to flow is a great advantage in processing complex shapes.

Though molecular architecture such as tacticity, polymer branching, and molecular weight are important parameters affecting crystallization rates and crystal structure, processing also plays a large role and affects characteristics such as molecular orientation and crystallinity that also influence performance. The presence of fillers, reinforcements, and additives can influence crystallization processes. For example, Figure 13.1 shows a PP melt that is slowly being cooled and whose crystallization is being partially nucleated by a cellulose fiber.

The properties of thermoplastics are often highly dependent on the temperature at which they are measured and the speed at which they are tested. Plastics are viscoelastic, behaving as it were a combination of a viscous liquid and an elastic solid. Most plastics have higher moduli when stress is rapidly applied versus when it is applied slowly. Also, some plastics have a much greater tendency than wood to sag over time (i.e., creep) when bearing sustained loads, an important consideration in structural applications.

Typical room temperature properties of plastics commonly used in WPCs are summarized in Table 13.2. These values are provided to give a general indication of the properties. However, the exact performance of these plastics are difficult to summarize since various grades are produced, whose performance has been tailored by controlling polymerization and additive content. PVC in particular often contains a considerable amount of additives such as heat stabilizers and plasticizers resulting in a wide range of processability and performance. However, some general comments can be made.

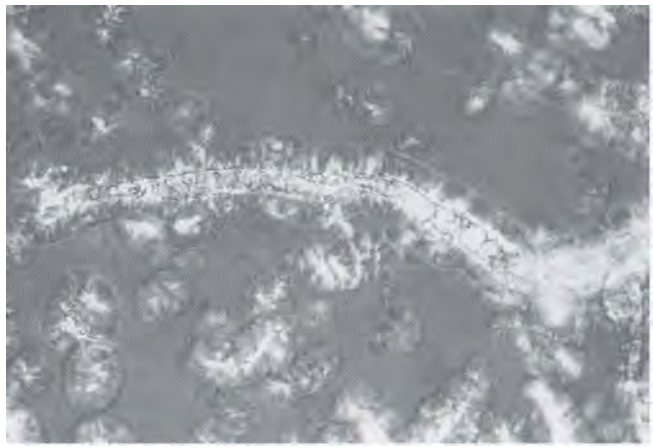

FIGURE 13.1 Cellulose fiber crystallizing a PP melt.

PE, PP, and PVC are the most common plastics used in WPCs. Though they tend to have considerably lower mechanical performance than the so-called engineering plastics, these commodity plastics have reasonably good mechanical performance for many applications, low price, and tend to have lower melting or softening temperatures. Generally WPCs are processed at temperatures lower than about 200°C to avoid significant degradation of the wood. The large use of PE is due, in part, to that fact that much of the early WPCs were developed as an outlet for recycled film as well as the low cost and availability of recycled sources of PE. They absorb little moisture and can act as effective moisture barriers. This is important since moisture sorption in WPCs can negatively affect the performance of the composite.

Though PE and PP are largely impervious to moisture, they are susceptible to degradation by UV radiation, and the use of light stabilizing additives is common in exterior applications. The thermal expansion and contraction of PE and PP are significant and they tend to creep (or sag over time), especially under load or at high temperatures, limiting their structural performance. However thermal expansion and creep can be reduced with fillers and reinforcements.

Polyvinyl chloride is also used in WPCs. PVC can be much stiffer than PE or PP and, with appropriate additives, have been commonly used in exterior applications such as siding. However,

TABLE 13.2
Typical Room Temperature Properties of Common Polymers

Polymer	Density (g/cm^3)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation at Break (%)	Water Absorption in 24 h (%)	Coefficient of Thermal Expansion ($K^{-1} \times 10^6$)
Low-density polyethylene	0.91-0.93	8-23	0.2-0.5	300-1000	<0.01	250
High-density polyethylene	0.94-0.96	18-35	0.7-1.4	100-1000	<0.01	200
Polypropylene	0.90-0.92	21-37	1.1-1.3	20-800	0.01-0.03	150
Rigid polyvinyl chloride	1.4-1.6	50-75	1.0-3.5	10-50	3-18	70-80

Source: Condensed from Osswald, T.A. and G. Menges. 1996. *Materials Science of Polymers for Engineers.* Carl Hamer Verlag, New York.

complexities in formulating and processing as well as patent issues have limited broader use in WPCs in North America. Also, the negative perceptions of chlorinated plastics such as PVC have also limited their use in some parts of the world such as Japan.

Different grades of a particular plastic have been tailored for a specific application and processing method. For example, a bottle grade of HDPE has high molecular weight to provide the toughness needed for a bottle application and high melt strength necessary for the melt blowing process. An injection molding grade might have a lower molecular weight yielding lower melt viscosity and good flow properties.

13.1.2 ADDITIVES

The term "additive" refers to a broad class of materials added to affect the processing and performance of polymers. Once additives such as stabilizers, plasticizers, etc. are incorporated into a polymer, it is usually referred to as a "plastic" (Carley 1993). Additives are only added in as small amounts as necessary since they are often expensive and can have detrimental effects on properties other than those for which they are added. Though the plastics themselves contain additives, more are often added during the processing of WPCs to overcome the limitations of the constituent materials, improve their interaction, or improve the processing or the performance of the end product. It is difficult to fully describe all of the additives used in WPC production because of the variety of additives, the proprietary nature of the formulations used, and the range of WPC applications. However, several of the major additive types used in WPCs are briefly described below.

Adding wood increases the viscosity of plastics, especially at high loadings such as those used in exterior building applications (e.g., extruded deckboards). Additionally, composite melts at these high wood contents have low strength and can stick and tear (especially at the edges) as it exits the extruder die (Figure 13.2a). Adding lubricants can reduce the viscosity of the composite melt, increase output, and lubricate the interface between the composite melt and the die to prevent edge-tearing (Figure 13.2b). Lubricants for WPCs are usually added at about 1-5% by weight and are made from materials such as metal stearates, aliphatic carboxylic acid salts, mono and diamides and modified fatty acid esters (Anonymous 2002). However, they can negatively impact some mechanical properties and interfere with other additives such as coupling agents if not chosen carefully.

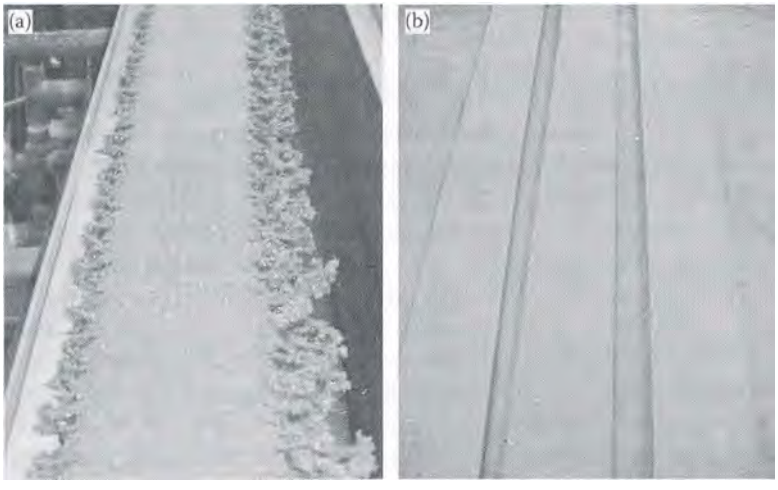

FIGURE 13.2 Extruded WPC: (a) without lubricant showing edge tearing and (b) with lubricant.

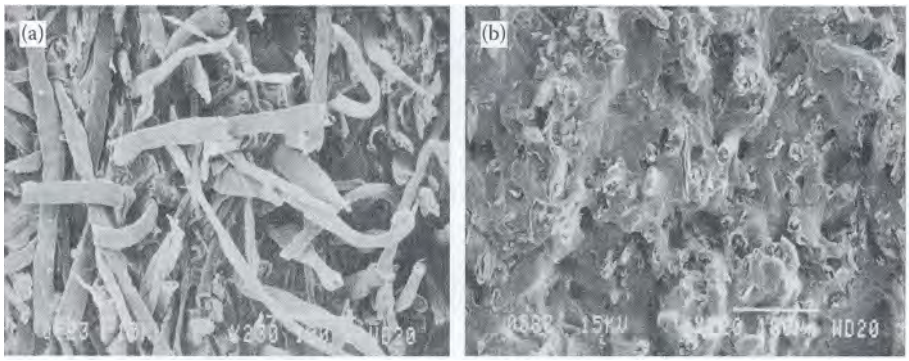

FIGURE 13.3 PP with 40% by weight of pulp fibers (a) without and (b) with a MAPP coupling agent.

The chemical incompatibility of the wood and many plastics, especially nonpolar plastics such as PP and PE can be problematic. For example, if wood fiber is used to reinforce plastic, a coupling agent is necessary to improve the adhesion between the wood and plastic so that applied stress can be transferred to the stronger fibers. Many different coupling agents have been investigated for use in WPCs and are reviewed elsewhere (Lu et al. 2000). However, one common coupling agent is maleic anhydride grafted polypropylene, often simply referred to as maleated polypropylene (MAPP). With MAPP, the anhydride portion of the molecule reacts with the wood's hydroxyl groups to form an ester bond and the long polymer chain incorporates itself into the bulk PP or PE network, thereby bonding the two together (see next section for mechanism). Figure 13.3 shows the effect of MAPP on the fracture surfaces of a composite of PP and 40% by weight of pulp fibers. Without MAPP the fibers were pulled out of the PP as the specimen failed. When 3% of a MAPP was added, the adhesion between PP and the pulp fibers was improved sufficiently that the fibers were broken during composite failure. Coupling agents can improve properties such as strength and unnotched Izod impact energy and can also decrease moisture sorption.

Adding wood to most plastics increases its density because of partial or complete collapse of wood fibers due to the high pressures during processing or filling of the lumen with low molecular weight additives and polymers. These densities are also well above those of solid wood. Additives have been used to decrease density. One approach uses foaming agents that react and evolve gas at critical temperatures (i.e., chemical foaming). Another approach uses special processing equipment that can inject nitrogen or carbon dioxide in a supercritical state that creates a very fine cell (i.e., microcellular) structure that has some advantages in performance Other additives such as hollow glass spheres or heat-expandable polymer microspheres have also been investigated to reduce WPC density (Guo et al. 2008).

A variety of additives have been used to improve the durability of WPCs, particularly in exterior applications. Moisture sorption can be reduced with some additives. For example, a common secondary effect of adding coupling agents such as MAPP is reduced moisture sorption. Colorants and light stabilizers can improve resistance to color fade and UV degradation. Biocides such as zinc borate are sometimes added to WPCs to improve fungal resistance. Flame retardants have also been investigated for certain applications.

13.1.3 PROCESSING

Although there are a wide variety of methods for preparing WPCs, all involve melting the plastic, mixing in the wood and additives, and forming a product. "Compounding" is the feeding and dispersing of fillers and additives in the molten polymer. Many options are available for compounding, using either batch or continuous mixers. The compounded material can be immediately pressed or shaped into an end product or formed into pellets for future processing. Some product manufacturing

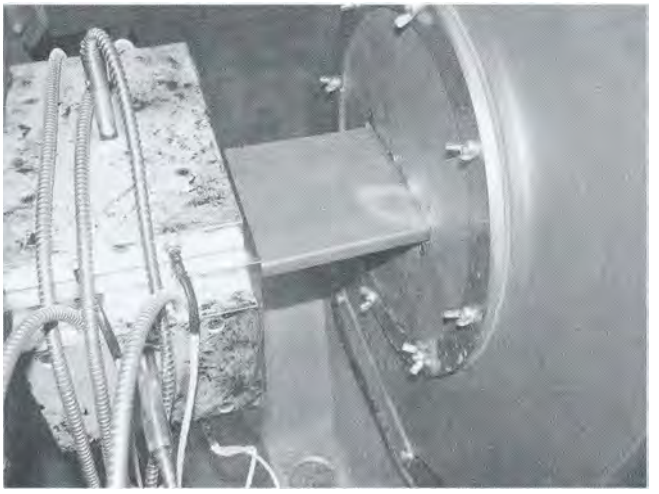

FIGURE 13.4 WPC exiting the extruder die (left) and entering cooling tank (right).

options for WPCs force molten material through a die (sheet or profile extrusion), into a cold mold (injection molding), between calenders (calendering), or between mold halves (thermoforming and compression molding) (Youngquist 1999). Combining the compounding and product manufacturing steps is called in-line processing.

The majority of WPCs are manufactured by profile extrusion, in which molten composite material is forced through a die to make a continuous profile of the desired shape (Figure 13.4). Extrusion lends itself to processing the high viscosity of the molten WPC blends and to shaping the long, continuous profiles common to building materials. These profiles can be a simple solid shape, or highly engineered and hollow.

Although extrusion is by far the most common processing method for WPCs, the processors use a variety of extruder types and processing strategies (Mapleston 2001a). Some processors run compounded pellets through single-screw extruders to form the final shape. Others compound and extrude final shapes in one step using twin-screw extruders. Some processors use several extruders in tandem, one for compounding and the other for profiling (Mapleston 2001a). Moisture can be removed from the wood component before processing, during a separate compounding step (or in the first extruder in a tandem process), or by using the first part of an extruder as a dryer in some in-line process. Equipment has been developed for many aspects of WPC processing, including materials handling, drying and feeding systems, extruder design, die design, and downstream equipment (i.e., equipment needed after extrusion, such as cooling tanks, pullers, and cut-off saws). Equipment manufacturers have partnered to develop complete processing lines specifically for WPCs. Some manufacturers are licensing new extrusion technologies that are very different from conventional extrusion processing (Mapleston 2001a,b).

Compounders specializing in wood and other natural fibers mixed with thermoplastics have fueled growth in several markets. These compounders supply preblended, free-flowing pellets of high bulk density that can be reheated and formed into products by a variety of processing methods. The pellets are advantageous to manufacturers who do not typically do their own compounding or do not wish to compound in-line (e.g., most single-screw profilers or injection molding companies).

Other processing technologies such as injection molding, thermoforming, and compression molding are also used to produce WPCs. These alternative processing methods have advantages when processing of a continuous piece is not desired or a more complicated shape is needed. Composite formulations must be adjusted to meet processing requirements (e.g., the low viscosity needed for injection molding can limit wood content).

13.1.4 PERFORMANCE

The wide variety of WPC formulations and markets makes it difficult to discuss the performance of these composites. Performance depends on the inherent properties of the constituent materials, interactions between these materials, additives used, processing, product design, and service environment. Because formulations can vary greatly and are proprietary, performance data should be obtained directly from the manufacturer or supplier. However, some generalizations regarding performance can be made.

13.1.5 MECHANICAL PROPERTIES

Wood flour is often added to thermoplastics as a low cost filler to alter mechanical performance, such as the stiffness and heat deflection temperature without increasing density excessively. Tensile and flexural strengths are, at best, maintained and more often decreased in the absence of a coupling agent. Adding wood fiber (rather than wood flour) and a coupling agent can improve strength properties and somewhat mitigate losses in other properties such as unnotched Izod impact energy.

Table 13.3 demonstrates some of these effects of wood on the mechanical performance of PP. Both tensile and flexural moduli increase with wood flour since wood is much stiffer than commodity thermoplastics such as PP. However, the increase in modulus with addition of wood flour comes at the expense of elongation, a drastic reduction in unnotched impact energy, and a general decrease in tensile strength. Not surprisingly, the wood fibers are more effective reinforcements than the wood flour when a coupling agent (MAPP) is added, nearly doubling the strength unfilled PP. Wood fibers are an order of magnitude stronger than the wood that they come from Rowell (1992) and their higher aspect ratio (ratio of length to diameter) results in increased stress transfer area and stress transfer efficiency (relative to wood flour) when a coupling agent is used.

13.1.6 DURABILITY

Since the majority of WPCs are used in exterior applications, durability is often important. Rather than relying on painting, staining, or chemical treatments to protect it from moisture intrusion, the durability of WPCs largely lies in the ability of the thermoplastic to at least partially encapsulate the wood and retard moisture sorption. This results in a low maintenance product, which is a common selling point for WPCs in outdoor applications. Moisture management is critical since volume

TABLE 13.3
Selected Properties of PP and Its Composites with Wood

		Tensile Properties		Flexural Properties		Izod Impact Energy	
Composite	Specific Gravity	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)	Notched (J/m)	Unnotched (J/m)
PP	0.90	28.5	1.53	38.3	1.19	20.9	656
PP + 40% wood flour	1.05	25.4	3.87	44.2	3.03	22.2	73
PP + 40% wood flour + MAPP	1.05	32.3	4.10	53.1	3.08	21.2	78
PP + 40% wood fiber	1.03	28.2	4.20	47.9	3.25	23.2	91
PP + 40% wood fiber + MAPP	1.03	52.3	4.23	72.4	3.22	21.6	162

Source: Condensed from Stark, N.M. and R.E. Rowlands. 2003. *Wood and Fiber Science.* 35(2), 167-174.

TABLE 13.4
Weight Gain in Aspen-Polypropylene Composites at 90% Relative Humidity after *D* days

	Weight Gain (%)					
ASPEN/PP/MAPPa	25 D	50 D	75 D	100 D	150 D	200 D
0/100/0	0	0	0	0	0.2	0.4
30/70/0	0.7	1.4	1.7	2.1	2.4	2.8
30/68/2	0.7	0.7	1.1	1.5	1.5	2.2
40/60/0	0.7	1.4	1.7	2.0	2.4	3.0
40/58/2	0.4	1.2	1.5	1.9	2.7	3.5
50/50/0	1.3	2.0	2.6	3.6	4.3	5.3
50/48/2	1.5	1.8	2.2	2.9	4.0	5.1
60/40/0	3.7	4.5	5.6	6.0	6.3	6.7
60/38/2	1.6	2.2	3.5	4.4	5.1	6.0

[a] Compositions are weight percent.

changes due to moisture sorption, especially repeated moisture cycling, can lead to warping, buckling, interfacial damage, matrix cracking, and biological attack.

Table 13.4 shows the moisture absorbed by wood fiber-PP composites that were subjected to 90% relative humidity (RH) for an extended period of time. Even after 200 days, all of the composites continued to gain weight and equilibrium was not yet reached. The higher the wood fiber content, the more moisture was picked up by the specimen. Adding MAPP helped to reduce moisture sorption. Table 13.5 shows data on a cyclic humidity test where the specimens were subjected to 30% RH for 60 days, measured and then subjected to 90% RH for an additional 60 days. This cycle was repeated four times. As with the static 90% RH tests, the specimens continued to gain weight with each 90% RH cycle. As the percentage of hydrophilic wood fiber increases in the wood-thermoplastic composites, there is a corresponding increase in moisture gain. The moisture gain is slow but continues over a very long period of time. The data also suggests that at about 50% wood, the rate and

TABLE 13.5
Weight Changes in Repeated Humidity Tests on Aspen-Polypropylene Composites Cycled between 30% and 90% Relative Humidity

	Weight Gain (%)							
ASPEN/PP/MAPPa	30%	90%	30%	90%	30%	90%	30%	90%
0/100/0	0	0	0	0	0	0.2	0	0.4
30/70/0	0.6	0.9	0.7	1.4	0.7	1.4	0.9	1.9
30/68/2	0.4	0.9	0.7	1.2	0.7	1.3	0.9	1.8
40/60/0	0.4	0.9	0.7	1.4	0.7	1.6	0.7	2.1
40/58/2	0.2	1.2	0.8	1.6	1.0	2.0	1.2	2.2
50/50/0	0.5	1.5	1.2	2.5	1.2	2.7	1.2	3.2
50/48/2	0.6	1.3	1.1	2.2	1.3	2.2	1.3	2.6
60/40/0	0.7	2.5	1.5	4.1	1.6	4.1	1.3	4.8
60/38/2	0.2	1.5	1.0	2.6	1.3	2.6	1.3	3.3

a Compositions are weight percent.

extent of moisture pickup increases. At this fiber content, there more connectivity (percolation) between the fibers and moisture can wick faster and further into the composite.

Since WPCs are not usually protected by these means, those containing no pigments usually fade to a light gray when exposed to sunlight. Photostabilizers or pigments are commonly added to help reduce this color fade when used in exterior environments. Because WPCs absorb less moisture and do so more slowly than unprotected solid wood, they have better fungal resistance and dimensional stability when exposed to moisture. For composites with high wood contents, some manufacturers incorporate additives such as zinc borate to improve fungal resistance. Mold can form on surfaces of WPCs and can be caused by moisture sorption by the wood flour or buildup of organic matter on the composite surfaces. Although mold does not reduce the structural performance of the composite, it is an aesthetic issue and WPCs usually have to be periodically cleaned. Manufacturers ensure a useful level of durability by limiting wood content, careful processing, and judicious use of additives. To further improve durability as well as stain and scratch resistance some manufacturers cover the WPC with a capstock or protective layer.

13.1.7 MARKETS AND FUTURE TRENDS

By far the greatest use of WPCs is in building products that have limited structural requirements. Customers and builders have a certain familiarity with wood in applications such as decking (Figure 13.5) and railings (the largest WPC market) and often desire an alternative that may have similar attributes. Mixing wood flour with plastic is seen as a way to use wood in these applications yet improve its durability without chemical treatment or the need for painting or staining. Although more expensive than wood, many consumers have been willing to pay for the lower maintenance required when WPCs are used. Mechanical properties such as creep resistance, stiffness, and strength are lower than those of solid wood. Hence, these composites are not currently used in applications that require considerable structural performance unless carefully formulated, designed, and tested. For example, WPCs are used for deckboards but not the substructure. Development of codes and standards for these materials are also important for their acceptance in building applications, for example. Solid, rectangular profiles are manufactured as well as more complex hollow or ribbed profiles. However, WPCs have expanded beyond decking and railing to other exterior building products including roofing (Figure 13.6), fencing, siding, and window/door profiles.

Automotive components are another market for WPCs, although plastic composites are also made with natural fibers other than wood (e.g., flax). These products take advantage of the balance

FIGURE **13.5** Examples of extruded WPCs.

FIGURE 13.6 WPC roofing tiles.

of performance and low density of natural fillers and fibers relative to their inorganic counterparts. Some components made from WPCs are interior substrates thermoformed from wood-PP sheets and injection-molded glove boxes, fixing hooks, and sound system components (Carus et al. 2008).

The development and use of WPCs varies by region. While there has been maturation of some major markets and some consolidation due, in part, to a recent slow-down of the building industry, wider acceptance of WPCs beyond North America has fueled growth in China, Japan, and southeast Asia, for example (Toloken 2010). There is increasing diversification of WPC markets beyond building components and automotive components as well. Flooring, benches, shelving, chairs, and other furniture components are currently produced in Europe, for example, Anonymous (2011).

The future of WPCs is very difficult to predict and depends on many factors including the economy, legislation, societal trends, and the technological advancements of WPCs and competing materials. A continued increase in familiarity and acceptance of WPCs by consumers, designers, and manufacturers as well as a desire for more sustainably sourced materials will likely continue to increase demand. As the use of biopolymers increases, wood and other plant-derived materials are a logical consideration for fillers and reinforcements.

Research and development efforts will likely have a large influence on the future of WPCs as well. Through better understanding of material behavior and more rigorous testing and engineering, WPCs are being used in more structural applications such as deckboards, chocks, and whales of naval piers and pedestrian bridges, for example (Wolcott et al. 2009). Advanced processing techniques such as reactive extrusion to produce cross-linked WPCs (Bengtsson et al. 2005), microcellular processing to produced lighter WPCs with a fine (microcellular) foam structure (Guo et al. 2008), and co-injection or co-extrusion techniques that uses multiple materials to their best advantage (Stark and Matuana 2009) are just a few examples of new approaches to processing that are being investigated.

Many different materials are also being investigated for use in WPCs. For example, use of wood with higher performing plastics (e.g., the so-called "engineering polymers" such as nylon, Caulfield et al. 2001) or new nano-scale additives such as nano-sized titanium dioxide (Stark and Matuana 2009) may greatly improve performance. Although somewhat beyond what is typically considered WPCs, wood-derived materials such as carbon fibers from lignin (Kadla et al. 2002), and nanofibrillated cellulose (Siró and Plackett 2010) are being investigated as reinforcements in high-performance polymer composites. If the remaining technical and economic hurdles can be overcome and these reinforcements are accepted by industry, these new composites may look and perform very differently from previous generations of composites from plastics and wood.

13.2 NONWOOD FIBERS IN THERMOPLASTIC COMPOSITES

13.2.1 AGRICULTURAL FIBERS

While wood fiber and flour are used the most in wood plastic composites, there are many other natural fibers that can and have been used to make these composites (Rowell et al. 1997). Chapter 18 presents a table of the world inventory of wood and agricultural biomass and it can be seen that collectively, the nonwood biomass inventory is as large as that of wood. In some countries, wood is very scarce and is not used as a building material. These countries must resort to nonwood sources of fiber and flour in order the produce composites.

There has been a lot of research done on agricultural fibers in thermoplastic composites (Sanadi et al. 1994a,b, 1996, Rowell et al. 1999). Some of this research was on kenaf due to a large USDA research project in the 1990s to promote the growing of kenaf in the United States. Table 13.6 shows the physical properties of kenaf at two different levels and jute in polypropylene composites compared to pure PP, glass, mica and calcium carbonate filled PP (Sanadi et al. 1995a,b, 1996). The fibers and fillers were blended in a kinetic mixer with PP and a coupling or compatibilizing agent (maleic anhydride grafted polypropylene, MAPP) and discharges at 190°C. There are many different types of MAPP's differing in molecular weight and the degree of maleic anhydride substitution. One used most often had a number average molecular weight of 20,000, a weight average molecular weight of 40,000 and about had 6% by weight of maleic anhydride in the polymer. Specimens were injected molded and tested according to ASTM standards.

Some of the earliest research on the effect of coupling agents was done using kenaf (Sandi et al. 1994b). Figure 13.7 shows the results of using a coupling agent in kenaf-PP composites. The figure

TABLE 13.6
Properties of Kenaf Polypropylene Composites

Property	Pure PP	Kenaf	Kenaf	Jute	Mica	$CaCO_3$	Glass
% filler by weight	0	40	50	50	40	40	40
% filler by volume	0	30	39	39	18	18	19
Tensile modulus, GPa	1.7	6.0	8.3	8.8	7.6	3.5	9
Specific tensile modulus, GPa	1.9	5.9	7.2	8.1	6.0	2.8	7.3
Tensile strength, MPa	33	56	65	74	39	25	110
Specific tensile strength, MPa	37	55	61	69	31	20	89
Elongation at break, %	»10	1.9	2.2	2.3	2.3	–	2.5
Flexural strength, MPa	41	82	98	97	62	48	131
Specific flexural strength, MPa	46	80	92	90	49	38	107
Flexural modulus, GPa	1.4	5.9	7.3	7.3	6.9	3.1	6.2
Specific flexural modulus, GPa	1.6	5.8	6.8	6.8	5.5	2.5	5.0
Notched Izod impact, J/m	24	28	32	43	27	32	107
Specific gravity	0.9	1.02	1.07	1.08	1.26	1.25	1.23
Water absorption, % in 24 h	0.02	–	1.05	–	0.03	0.02	0.06
Mold (linear) shrinkage, cm/cm	0.028	0.004	0.003	–	–	0.01	0.004

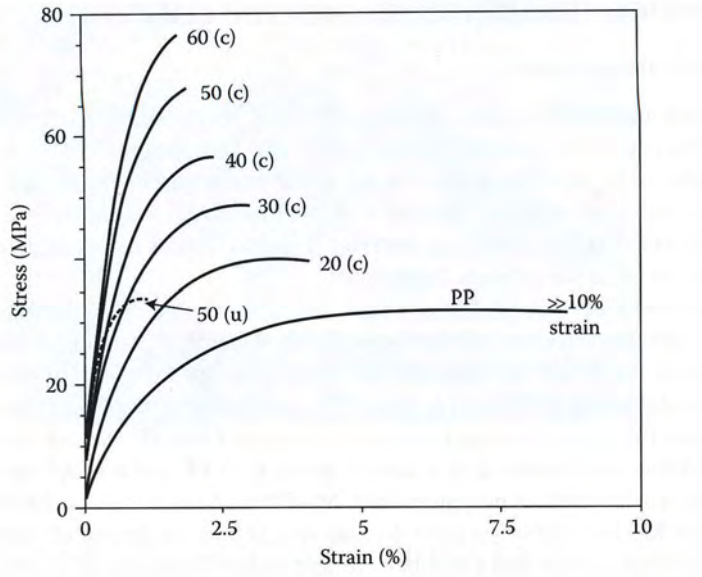

FIGURE 13.7 Stress–strain curve for kenaf-PP composites.

shows how the strength and stiffness increases as the percentage of kenaf is increased in the composite using a coupling agent.

The strength in the noncompatibilized blend is much lower as compared to the compatibilized composite.

The mechanism of compatibilization or coupling is suspected to be as follows: First, the anhydride reacts with a cell wall polymer hydroxyl group to form an ester bond the then the PP polymer attached to the anhydride intertangles into the PP or PE network in the melt (see Figures 13.8 and 13.9). Figure 13.10 shows a composite where a compatibilizer has been used. It can be seen that when the composite was broken in two pieces, the fiber shown broke rather than be pulled out of the thermoplastic matrix. There is a small gap at the base of the fiber showing that there was some slippage but the fiber broke rather than be pulled out of the matrix due to weak interfacial bonding between the fiber and the matrix.

Figures 13.11 through 13.21 show the mechanical properties of several fibers other than wood in a PP matrix (Jacobson et al. 1995a,b, 1996).

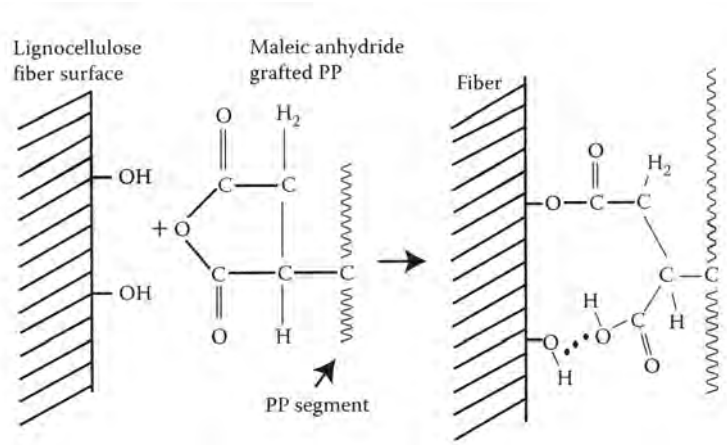

FIGURE 13.8 Reaction of maleic anhydride grafted PP with cell wall hydroxyl groups.

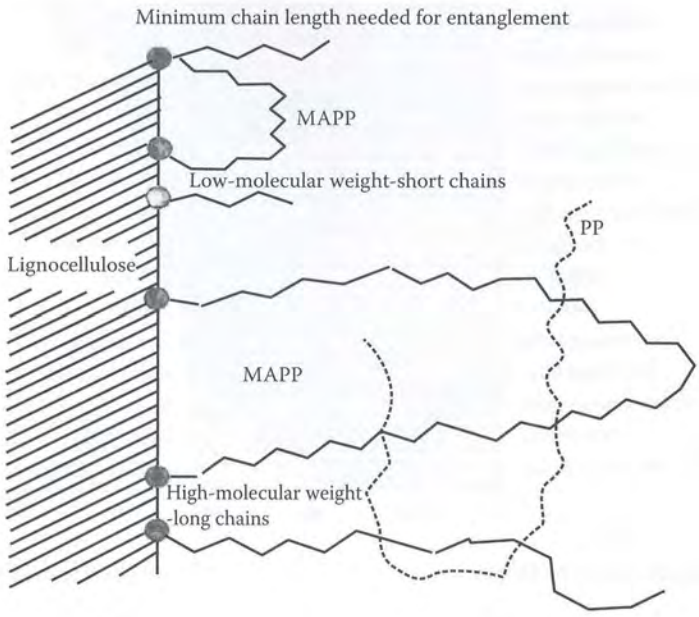

FIGURE 13.9 Entanglement of MAPP with PP.

13.2.2 OTHER FIBERS

Another option for the biomass fraction is to utilize the solids in animal manures (Rowell et al. 2008).

Animal agriculture is under increasing pressure to produce more and more meat, milk and eggs giving rise to an increasing amount of manures. In the past, manures have been viewed as a waste by-product used mainly as a fertilizer that has a value of 2-4 cents/dry pound. We need to change our view of manures from waste to asset. Destroying manures by burning or lagooning may solve the environmental problem but it does nothing to add to animal income.

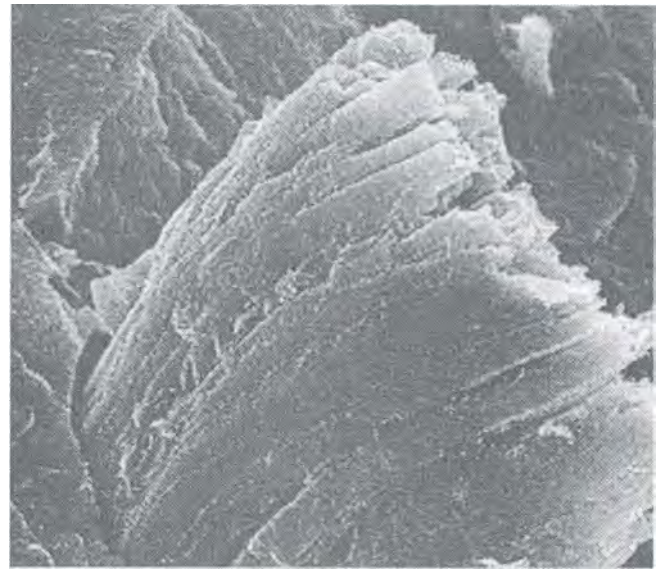

FIGURE 13.10 Fiber broken rather than pulled out of the thermoplastic matrix.

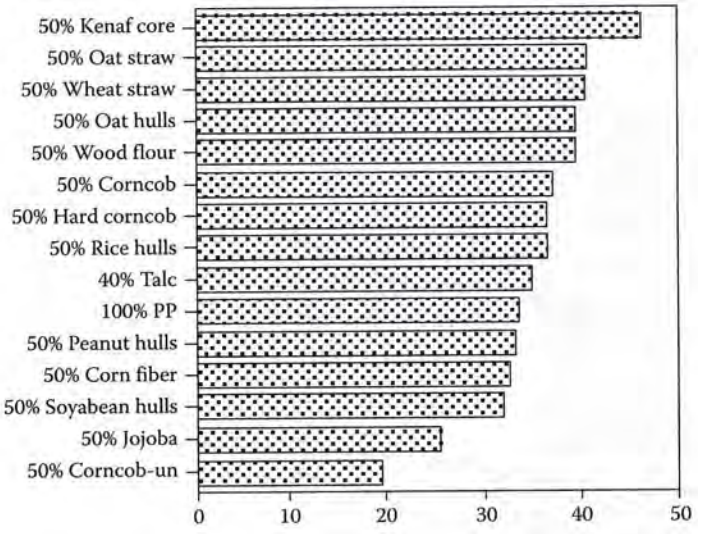

FIGURE 13.11 Tensile strength (MPa).

One of the alternatives is to use animal manures in industrial products. It is possible to use swine and cow manures and residue from a methane digester plant as reinforcing fillers in HDPE and HDPP. This is a win-win situation as it increases the value of the animal manures, decreases the cost and improves mechanical properties of the thermoplastic composites.

A 40% blend of dry dairy manure with 58% HDPE and 2% MAPE gives a composite with an MOE in bending of 2.18 GPa and MOR 34.7 MPa as compared to 40% pine flour with 58% HDPE and 2% MAPE of MOE 2.98 and MOR 33.4 MPa.

A 40% blend of dry swine manure with HDPE and 2% MAPE gives a composite with MOE in bending of 1.31 GPa and MOR of 34.7 MPa as compared to unfilled HDPE MOE of 0.75 GPa and MOR of 15.1 MPa.

A 40% blend of dry residue left after methane digestion with 58% HDPE and 2% MAPE gives a composite with and MOE of 2.21 GPa and MOR of 26.9 MPa.

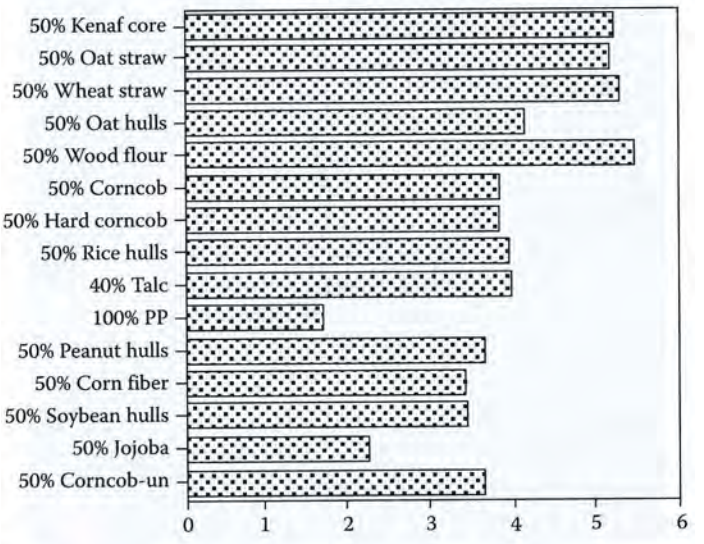

FIGURE 13.12 Tensile modulus (GPa).

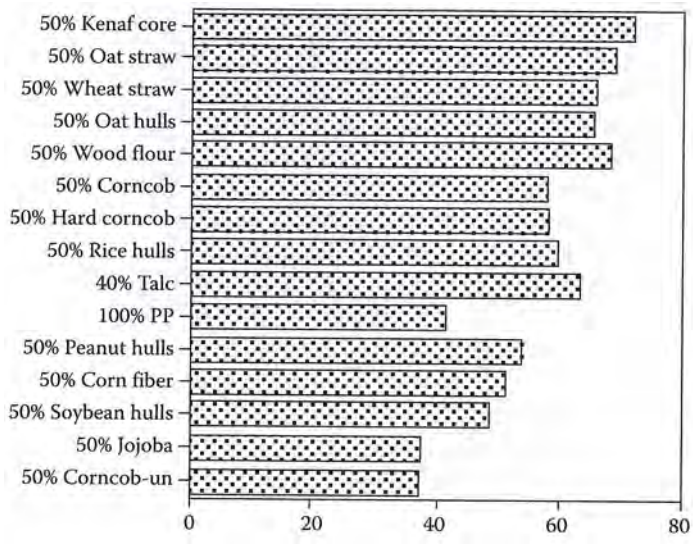

FIGURE 13.13 Flexural strength (MPa).

13.3 BIOPLASTICS

13.3.1 INTRODUCTION

The opportunity to manufacture plastics from renewable resources, especially from biomass, has been the subject of research and development and considerable commercial interest for a number of decades (Belgacem and Gandini 2008). Interest in these materials in academe as well as in industry has grown further in recent years for a number of key reasons. First, there is an increasing awareness of the limited nature of fossil fuels and the need to investigate renewable resources for our future energy and material needs. Second, the use of materials such as plastics obtained from biomass offers a way to reduce overall greenhouse gas (GHG) emissions and reduce carbon footprints. Third, most but not all bio-derived plastics are biodegradable or compostable and, providing

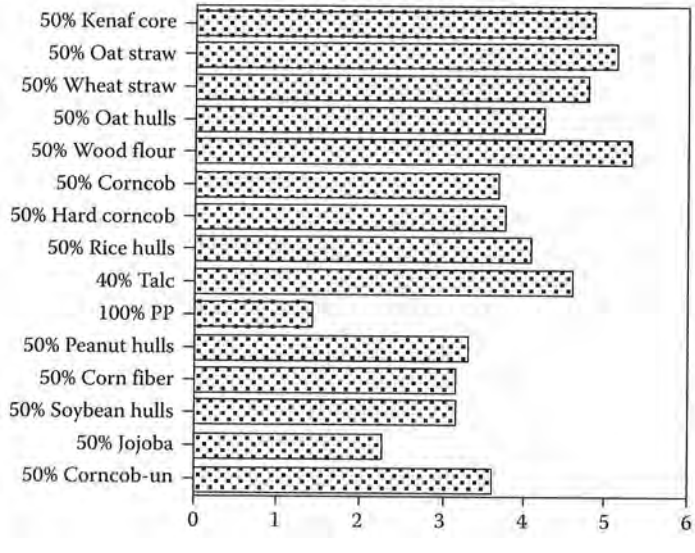

FIGURE **13.14** Flexural modulus (GPa).

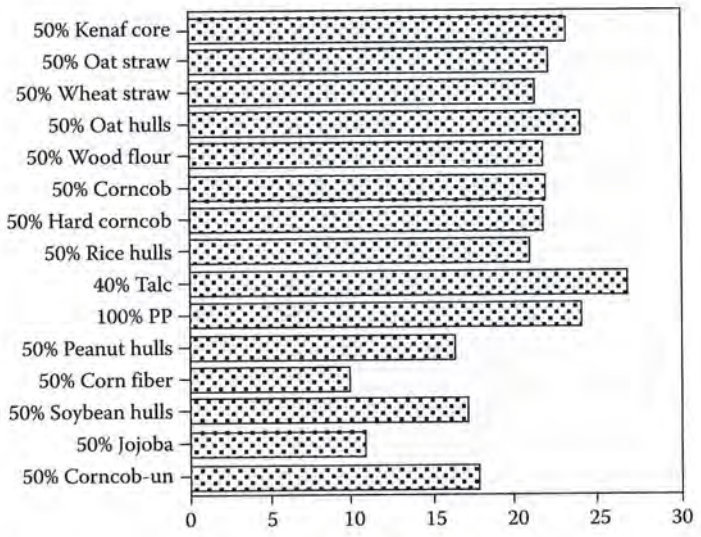

FIGURE 13.15 Notched Izod impact (J/M).

suitable materials sorting and other infrastructure can be put in place, can make a contribution to reducing the plastic waste disposal problem in land and marine environments around the world.

Bio-derived polymers can be broadly divided into three categories as illustrated in Figure 13.22. In the first category there are those polymers which can be extracted more or less directly from biomass, including starch and cellulose from plants, chitin from the shells of marine organisms and proteins or lipids derived from plant or animal sources. The second category encompasses polymers which are composed of and synthesized from bio-derived monomers, prime examples being polylactide (PLA) and related polyesters. In the third category there are polymers which are synthesized by natural or genetically modified (GM) organisms and, in this case, the best-known examples from a bioplastics perspective are the polyhydroxyalkanoates (PHAs) which are produced in-situ by certain strains of bacteria under nutrient-limited growth conditions (Figure 13.23). Celluloses synthesized by bacteria and algae as well as by tunicates, a group of oceanic filter feeders, can also be

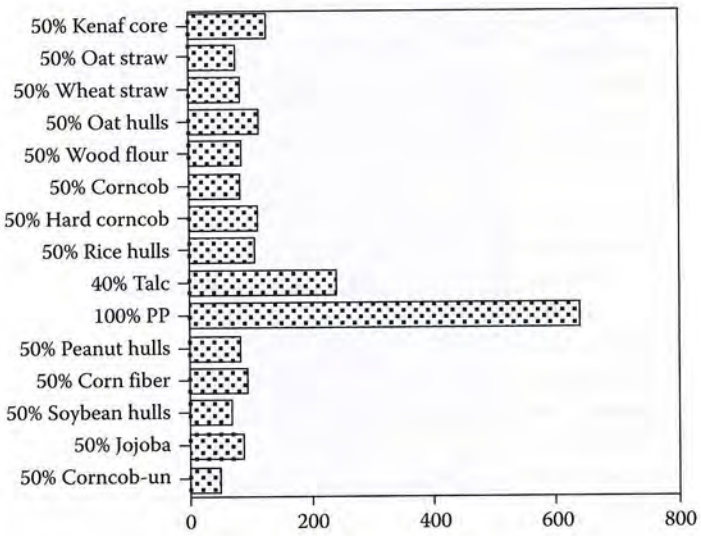

FIGURE 13.16 Unnotched Izod impact (J/M).

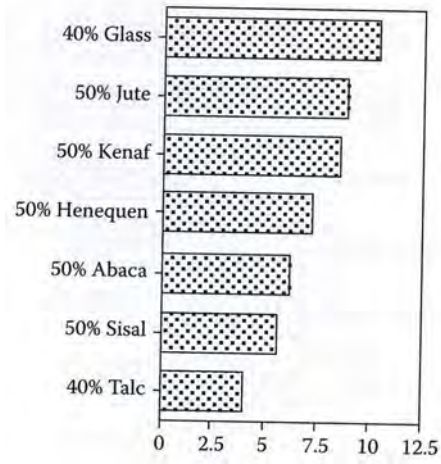

FIGURE 13.17 Tensile modulus (GPa).

included in the third category of bio-derived polymers. As far as is known, tunicates are the only members of the animal kingdom which naturally produce cellulose (Kimura and Itoh 2004).

Although there has been extensive research over the years aimed at deriving plastics or fibers for plastic reinforcement from each of the various types of biopolymer identified in Figure 13.22, significant commercial development has been limited to only a few types. Historically, derivatives of cellulose such as esters and ethers have been important commodities and some of these derivatives are the oldest thermoplastic materials prepared by man, dating back well into the nineteenth century (Belgacem and Gandini 2011). Products such as cellulose acetate and cellulose acetate butyrate (CAB) are still widely used today in the form of various films, coatings and printing inks. Of the other bio-derived polymers which have been commercialized, thermoplastic starch, PHAs and PLAs have been particularly important.

Starch is the most abundant reserve polysaccharide in plants and, as a source of bioplastics, has the advantage of being both inexpensive and biodegradable in soil or water. Starch can be plasticized by the addition of glycols, polyethers, urea or water and converted to thermoplastic starch (TPS) by the application of heat and mechanical energy during extrusion processing. Starch-based plastics have a number of limitations, including water sensitivity and poor mechanical properties

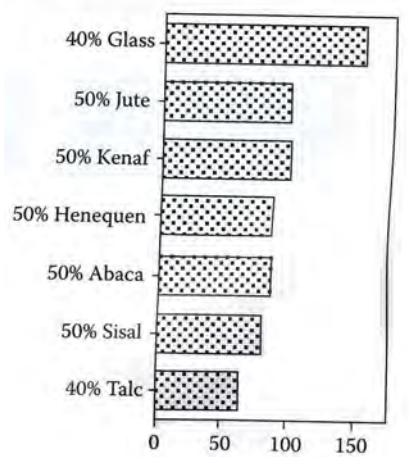

FIGURE 13.18 Flexural strength (MPa).

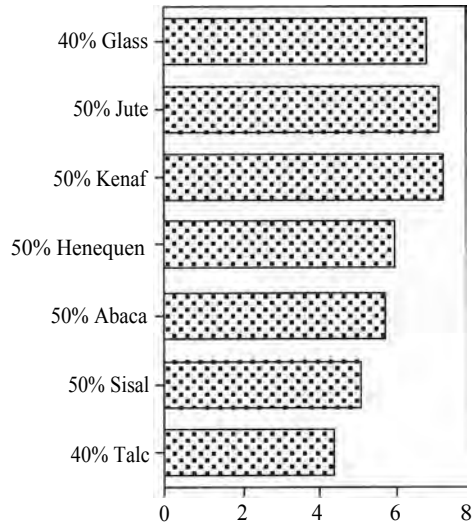

FIGURE 13.19 Flexural modulus (GPa).

and, for that reason, there have been numerous studies on the blending of plasticized starch with other biodegradable polymers to obtain inexpensive, biodegradable or compostable materials with improved properties (Vazquez et al. 2011). Such blends offer possibilities for reductions in manufacturing costs, tunable rates of degradation, and materials with properties which are a combination of those of the individual monomers. At the present time, Novamont based in Italy is one of the main suppliers of starch-based bioplastics with its Mater-Bi® range of products, which find application as agricultural mulching films and in disposable tableware. In addition, Mater-Bi products are used in biodegradable or compostable bags for shopping or waste collection, thermoformed trays for foodstuffs, transparent film for packaging of fruit and vegetables, and extruded or woven nets for food products such as potatoes and onions. There are also a variety of non-food related products based on Mater-Bi such as cotton buds, sanitary towels, nappies, and chewable items for pets.

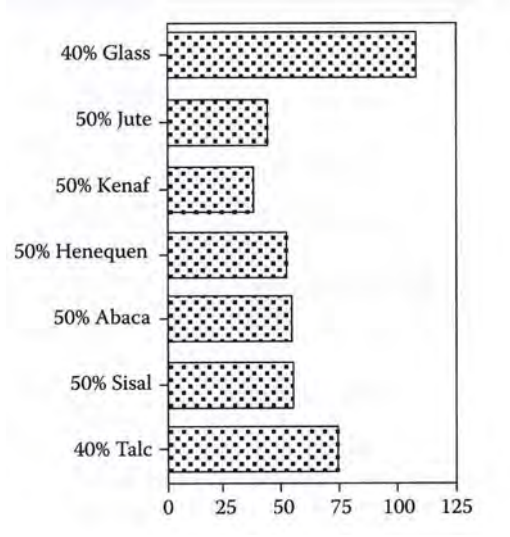

FIGURE 13.20 Notched Izod impact (J/M50

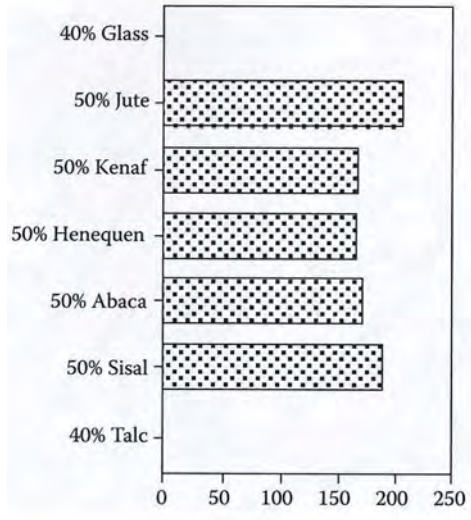

FIGURE 13.21 Unnotched Izod impact (J/M).

PHAs or, as they are otherwise known, bacterial polyesters, were first observed in detail during the 1920s in the laboratory of Maurice Lemoigne, a French microbiologist (Lemoigne 1923, 1924a, 1924b). However, it was not until the 1950s that the structure and mechanism of synthesis of the PHAs was understood and there has been considerable research and development as well as industrial interest ever since (Macrae and Wilkinson 1958, Chodak 2008, Pollet and Averous 2011). In one of the first commercial developments in the 1960s, ICI introduced Biopol®, a polyhydroxybutyrate-co-hydroxyvalerate (PHBV) copolymer, but this product was not widely adopted, probably for cost reasons, and was taken over by Zeneca BioProducts when ICI was split up in 1993. Subsequently, the technology was sold to Monsanto and then acquired by the American company Metabolix in 1998. At the time of writing, Metabolix is working with Archer Daniels Midland (ADM) in a joint venture (Telles) to manufacture PHAs under the Mirel™ trade name. This joint venture is currently establishing a plant in Iowa with a 50,000 tonnes/year capacity which will be one of the biggest, if not the biggest, such facilities worldwide. A recent survey suggests that there are more than 15 companies around the world at various stages and scales of PHA production. These companies are either raw material suppliers or are targeting application of PHAs in packaging or medicine (e.g., drug delivery).

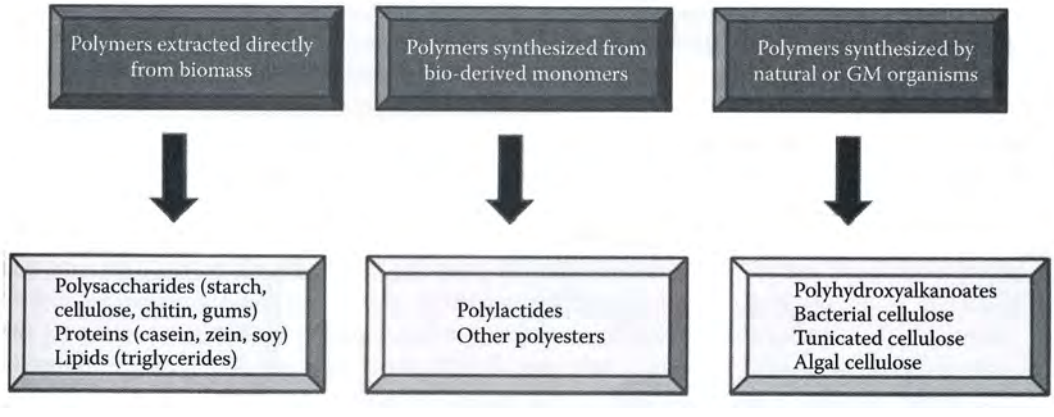

FIGURE 13.22 Biopolymer categories.

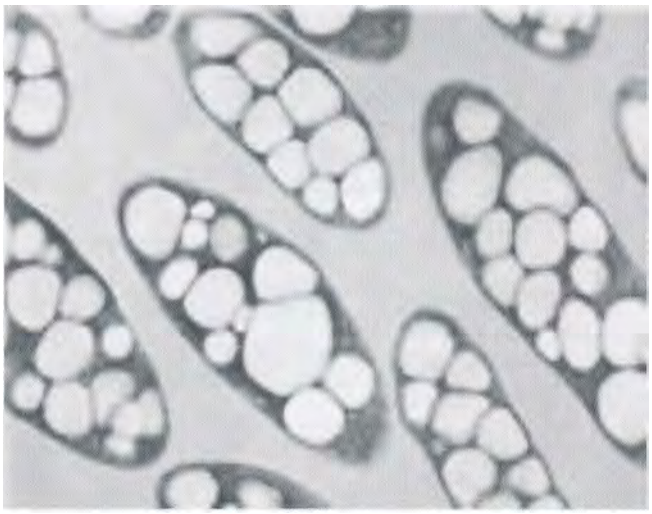

FIGURE 13.23 An optical microscopy image showing polyhydroxyalkanoate (PHA) granules produced in bacterial cells under nutrient-limited conditions.

PLA thermoplastics are at present the most advanced and widely used of the commercial bioplastics with interest driven by their potential uses in packaging, medicine, electronics, and composite materials (Auras et al. 2004, Kricheldorf 2001, Sï derg¬rd and Stolt 2002). The most widely available PLA is the L-form (Figure 13.24) which, although strictly not biodegradable in a technical sense, is compostable in the presence of high humidity and at temperatures above the glass transition (normally in the 50-60°C range). PLA is attractive for applications such as food packaging because of its processability, transparency, and other properties, which can be similar to those of polystyrene. Wider adoption of PLA in this large commodity market has, however, been hindered so far by cost factors as well as by limitations in some physical characteristics, notably thermal stability and barrier properties. Ongoing research and development and innovations which have already been introduced commercially are going some way to improving these characteristics. PLA is manufactured by companies in Europe, North America, and Asia; however, NatureWorks LLC, which was originally created out of a joint venture between Cargill and Dow, has by far the largest share of PLA production capacity. NatureWorks has a production plant in Blair, Nebraska with a capacity of 140,000 metric tonnes PLA per year under the Ingeo™ trade name. Major applications for Ingeo™ include food packaging, bottles, films, nonwovens, textiles, and tableware. A list of companies with interests in PLA research and development and manufacturing is provided in Table 13.7.

With this introduction, the next section of this chapter deals with the manufacturing and properties of PLAs as a prelude to a summary of past research and development aimed at new PLA composite materials reinforced with wood or agricultural fibers.

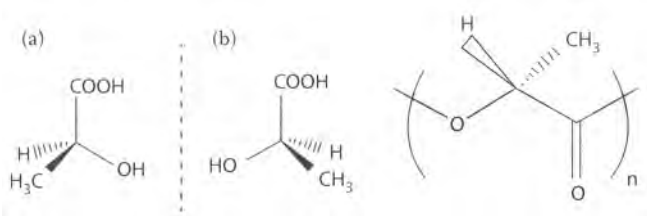

FIGURE 13.24 The enantiomeric (L- and D-) forms of lactic acid (a) and the monomer unit in polylactides (PLAs) showing the chiral carbon centre with a proton and methyl group attached (b).

TABLE 13.7
Companies Currently Manufacturing Lactic Acid-Based Polymers

Company	Location	Main Products	Trade Name
Birmingham Polymers	USA	Lactide polymers for medical applications	Lactel
Boeringer Ingelheim		Lactide polymers for medical applications	Resomer
Durect	USA	Range of lactide, glycolide and caprolactone polymers for medical applications	Lactel
FKuR	Germany	PLA blends for extrusion and injection molding	
Galactic	Belgium	Lactic acid and latates	Galacid, Galaflow, etc.
Mitsui Chemicals	Japan	PLAs for film and fiber uses	Lacea
Nature works	USA	PLA raw materials for film, fiber and other diverse applications	Ingeo
Phusis	France	Medical-grade lactide polymers	Phusiline
Purac	The Netherlands	Monomers and lactide polymers for diverse applications	Purasorb
Shimadzu Corporation	Japan	PLA raw materials	Lacty

13.3.2 PLA MANUFACTURING

The starting raw material for production of PLA is lactic acid in all cases. This naturally occurring Ŭ-hydroxy acid, which exists in two enantiomeric forms (L- and D-) (Figure 13.24) is widely used in the food, pharmaceutical, textile, leather and chemical industries. The L-form of lactic acid is found in all living organisms but the D-form is not commonly found in nature. Microbial fermentation of carbohydrates is the favored method for manufacturing lactic acid and allows the production of optically pure forms. The use of optically pure lactic acid is critically important in respect to PLA production, since even small amounts of enantiomeric impurities can cause very significant changes in polymer crystallinity and biodegradability.

The synthesis of PLA can in principle follow three routes: (1) condensation polymerization, (2) azeotropic dehydrative condensation, and (3) ring-opening polymerization from the lactide dimer. The condensation polymerization approach is the least expensive, but high-molecular weight PLA is difficult to obtain when using this method. One possibility is to introduce chain-extending agents; however, the final product may contain unreacted chain-extending agents, or residual impurities from the catalyst. Coupling or esterification-promoting agents may also be used to increase chain length, albeit with increased cost and process complexity. The second approach, involving azeotropic condensation polymerization, can be used to produce PLAs with long chain lengths and without the use of chain extenders and adjuvants. A process of this type has been commercialized by Mitsui Chemicals (Japan) in which lactic acid and a catalyst are azeotropically dehydrated in a refluxing, high boiling, aprotic solvent under reduced pressure to obtain high molecular weight PLA (Mw Ó300,000). A drawback of this approach is the need for relatively high catalyst concentrations in order to achieve acceptable reaction rates, with the result that polymer hydrolysis and degradation occur during processing. Catalyst deactivation has been proposed as one solution to this problem as residual catalyst concentrations can then be reduced to ppm levels. The third method, based on ring-opening polymerization (ROP) of lactide (Figure 13.25) is the only practical technique for producing pure high molecular weight PLA (Mw Ó100,000) and the one that has been developed most widely for industrial-scale production. ROP also has the advantage that the chemistry and therefore the properties of the final polymer can be accurately controlled and tuned to requirements. As shown in Figure 13.25, the first step in ROP is polycondensation of lactic acid, which is then followed by depolymerizaton to obtain the lactide dimer. The latter step is typically carried out by raising the reaction temperature, lowering the pressure and distilling off the resulting lactide. The

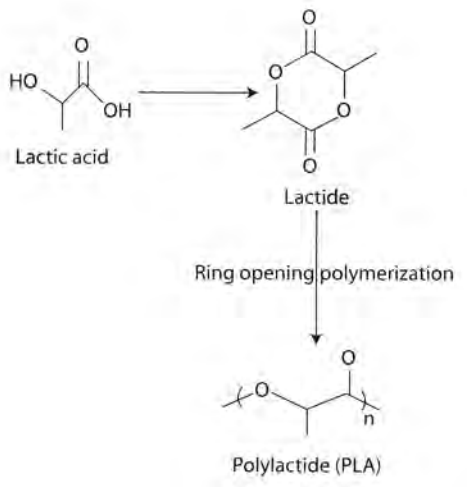

FIGURE 13.25 Schematic showing synthesis of PLA by ring-opening polymerization from the lactide dimet

use of ROP to produce PLAs has been carried out by solution polymerization, bulk polymerization, melt polymerization and suspension polymerization techniques and, depending upon which type of catalyst is used, the reaction mechamism is of ionic, coordination or free-radical type. Reports indicate that ROP of lactide can be catalyzed by many different metal compounds but tin(II) 2-ethylhexanoate (tin octanoate) is the most frequently used. Just as lactic acid is available in L- and D-forms, so lactide also has two different versions, namely D,D- and L,L- and, in addition, can be formed from one D- and one L-lactic acid molecule, yielding D,L-lactide (meso-lactide). On this basis, ROP can be used to create PLA copolymers of different stereoforms, with the various combinations having a large effect on the final product properties.

13.3.3 MELT PROCESSING OF PLAs

Melt processing is the main method used to convert PLA raw materials (i.e, granulates) into useful materials such as bottles, cups, tableware, fibers, films, and coatings, using either extrusion or injection molding or both. As with other polymers containing ester linkages, an important processing consideration is the tendency towards degradation on exposure to heat for even relatively short periods. Melt extrusion of PLAs is often linked to a second processing step (e.g., injection molding, fiber drawing, film blowing) and the properties of the final product are determined by melt processing factors including the temperature and temperature gradient, residence time, atmosphere and moisture content. The moisture level is particularly important given the hydrolytic tendency of PLAs and, as an example, the processing recommendations for NatureWorks Ingeo^{TM} 2003D extrusion grade suggest that the polymer granulate should be dried to a maximum of 250 ppm moisture as determined by the Karl Fischer method. Furthermore, processes which use longer residence times and/or higher temperatures will benefit from pre-drying of granulate to ~50 ppm water content. Typically NatureWorks supplies products in sealed bags dried to 400 ppm moisture level and the company recommends drying and re-sealing of unused material. The recommended drying conditions for Ingeo^{TM} 2003 D and other PLA granulates are shown in Table 13.8.

13.3.4 PROPERTIES OF PLAs

The physical properties of PLAs are determined by the molecular structure (e.g., stereochemistry, copolymers) as well as by the processing conditions. Methods for characterization and analysis of lactide polymers and their precursors have recently been reviewed (Inkinen et al. 2011). The key

TABLE 13.8
Typical Drying Conditions Recommended for Nature Works LLC IngeoTM PLA Granulates

Drying Parameter	Settings for Dry Pellets Received in Packaging with a Barrier Linera	Settings for Pellets with 2000 ppm Moisture Content
Residence time (h)	2	4
Air temperature (°C)	90	90
Air dew point (°C)	—40	—40
Air flow rate (m^3/h • kg resin)	1.85	1.85

a Material is dried to less than 400 ppm moisture content before shipping in foil-lined containers.

properties of PLA in relation to its use in composite materials are discussed in the following sections.

13.3.4.1 Thermal Properties

As mentioned earlier, the limited thermal stability of PLA is of concern when melt processing. Thermal degradation of PLA is a complex process, reported to have first-order kinetics, and involves both radical and nonradical reactions (St clergard and Stolt 2002). Racemization, the process by which an enantiomerically pure form is converted into a mixture of L- and D-forms, can also take place at high temperatures. Thermal degradation of PLA is accelerated by high amounts of reactive end groups (i.e., low molecular weight) and high polydispersity (Mw/Mn), as well as by the presence of residual catalyst, lactide or lactic acid, moisture and various impurities. PLA stereocomplexes based on 50:50 blends of L- and D-PLA were first reported by Ikada et al. (1987), who also discovered that the melting point of the stereocomplex is about 50°C higher than that of either the pure L- or pure D-forms. PLA stereocomplexes have also been shown to have higher thermal resistance. For example, this approach was recently used to produce a cup which could withstand boiling oil (US Patent 2008207840 2008). The T_g of PLA increases with increasing polymer molecular weight up to a threshold value and usually lies in the 50-80°C range, although lower values have been reported for oligomers or low molecular weight polymers. The melting point of PLA typically lies in the 170-180°C range and, like the T_g, increases as the molecular weight increases up to a specific threshold.

PLA exists in semi-crystalline or amorphous states depending upon stereochemistry, composition, and thermal history. As with other polymers, the solid state structure of PLA influences its mechanical characteristics, electrical and solvent resistance, and biodegradation properties and the polymer may therefore be modified in order to tune these properties for particular needs. As an example in the field of food packaging, higher crystallinity generally means higher gas barrier properties, which is desirable for some of these packaging applications. Differential scanning calorimetry (DSC) is a very useful method for analyzing thermal transitions and crystallinity in PLA and, as an example, the second heating curve in the DSC thermogram for PLA with 5% clay nanofiller is shown in Figure 13.26. It is not uncommon to observe multiple melting point behavior in the DSC of PLAs, which may be due to the presence of crystallites of different morphologies and dimensions in the initial sample but can also arise from formation of imperfect crystals as a result of annealing during the DSC scan (Sarasua et al. 1998).

13.3.4.2 Hydrolytic Stability

Hydrolysis of PLA, leading to molecular fragmentation, is influenced by a variety of factors, including chemical structure, molar mass and its distribution, purity, morphology, specimen shape and history, and the environmental conditions. The mechanism of PLA hydrolysis involves random attack at the ester linkages as well as chain-end scission in the presence of water. Amorphous parts of the polymer generally exhibit faster water uptake than the crystalline regions and therefore

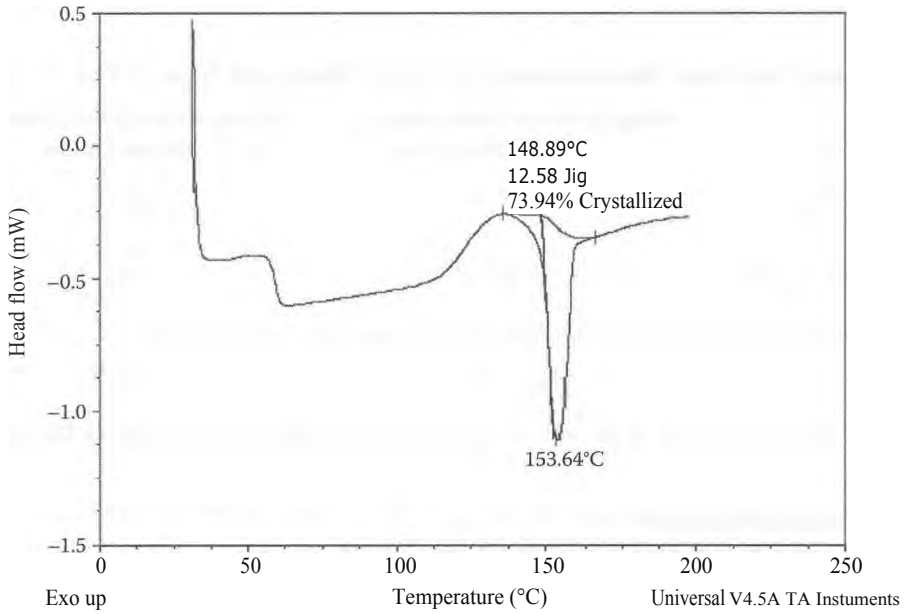

FIGURE 13.26 Second heating curve in the DSC thermogram of PLA with 5% clay nanofiller, showing the glass transition in the 50-60°C range, a pre-melting exotherm and a peak melting temparture close to 153°C.

will be the first to undergo hydrolysis. This being the case, the polymer chains in the remaining nondegraded material will have more space and greater mobility with consequent reorganization and increased crystallinity. This provides an explanation for the greater opacity of PLA test films when subjected to hydrolytic conditions over a short period of time. After the initial phase, crystalline regions of PLA are also hydrolyzed, which produces increased mass loss and eventually complete resorption of the material. It has been suggested that hydrolysis takes place more rapidly in the core of PLA materials due to autocatalysis in the presence of compounds with carboxylic end groups, which are unable to permeate the outer shell of the material (Li et al. 1990). Meanwhile, degradation products in the surface layer are continuously dissolved in the surrounding aqueous medium. As would be expected, hydrolytic degradation of PLA is accelerated at higher temperatures.

13.3.4.3 Biodegradability

The biodegradation of aliphatic biopolyesters has been extensively reported in the literature (Amass et al. 1998, Sødergård and Stolt 2002, Zhang and Sun 2005). Biodegradation of PLA occurs when the polymer is hydrolyzed at or above the T_g in a composting environment. When the oligomeric breakdown products reach a threshold molecular weight, microorganisms start to digest these lower molecular weight compounds, releasing carbon dioxide and water (Figure 13.27). Specific factors which will influence the rate of biodegradation of articles made from PLA include chemical structure, molar mass and molar mass distribution. At a higher level, the influence of the T_g, T_m, crystallinity and modulus will also be important. Material surface area and surface hydrophilicity or hydrophobicity may also play a role. In general, as the molar mass and T_m increase, the rate of biodegradation decreases. The biodegradation of PLA also depends upon the environment to which it is exposed. For example, tests in soil have shown that it can take a long time for degradation to start. For instance, in one study, PLA films showed no degradation after six weeks of soil burial. On the other hand, in a composting environment at 50-60°C PLA can be substantially degraded to smaller molecules within 45-60 days.

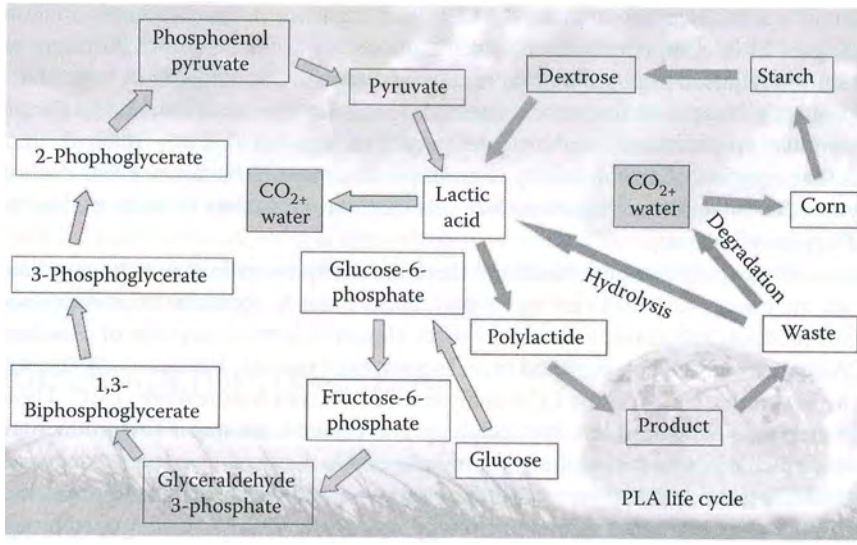

FIGURE 13.27 Schematic showing the pathways for synthesis of lactic acid in nature and the cycles for production and breakdown of PLA.

13.3.4.4 Mechanical Properties

The mechanical properties of PLA can be varied to a large extent, providing materials which range in character from soft and elastic to stiff and strong, as a complex function of parameters such as polymer structure, molecular weight, crystallinity, formulation and processing. It has been reported that semi-crystalline PLA has a tensile strength of 50-60 MPa, tensile modulus of 3 GPa and an elongation at break of 4%(Sødergård and Stolt 2002). In terms of dependence on molar mass, significant changes in tensile strength and modulus have been observed when the molar mass is raised from 50 to 100 kDa; however, further increases in molar mass to 300 kDa appear not to have such a significant effect. Fiber spinning has been used as a way to increase the tensile strength and modulus of L-PLA and its blends or copolymers with D-PLA or polycaprolactone (PCL), a synthetic biodegradable polyester. Solution spinning processes may offer an advantage in this respect since melt spinning is often associated with very significant thermal degradation of PLAs (Penning et al. 1993). As a result, the L-PLA fiber modulus increases from a range of 7-9 GPa when using melt spinning to a range of 10-16 GPa when solution spinning is used (SodergArd and Stolt 2002).

Brittle, high modulus PLAs can be modified by copolymerization with polymers having lower T_g values. For example, after copolymerization with ε-caprolactone, products are obtained which exhibit lower tensile strength, increased elongation at break and higher impact strength (Grijpma et al 1992, 1991, Hiljanen-Vainio et al. 1997).

13.3.5 SUSTAINABILITY

PLA as a raw material for products in packaging, electronics and automotive, medicine and the broad field of composite materials offers the advantages of compostability, biocompatibility, and nontoxicity and can, in principle, be manufactured starting from a wide range of different biomass residues (Sodergaard and Inkinen 2011). As a bioplastic, it therefore fits well with the cradle-to-cradle principle espoused by McDonough and Braungart (2002). In the commodity packaging field, PLA has attracted considerable interest and is already used in some countries for certain types of food packaging. Wider adoption in this sector is feasible as and when the price of PLA comes down relative to that of synthetic petroleum-derived plastics and when certain technical properties are improved, notably the heat distortion temperature and gas barrier properties. In the

electronics and automotive sectors there have been significant developments in commercial manufacturing of PLA components for electronic goods, in which case natural fibers have been used to obtain the required strength and thermal properties. In medicine, PLA and related lactide polymers have long been used for suture materials, bone fracture fixation, sheets for preventing adhesion, blood vessel prostheses, and drug delivery (Letchford et al. 2011). In terms of commodity products, the question of sustainability is an important issue to be defined and evaluated. Life cycle analysis (LCA) techniques are therefore relevant and a number of such studies have been applied to PLA-based plastics.

LCA represents a discipline unto itself and there are many complexities to be considered when evaluating all the energy and material inputs and outputs, not to mention other issues such as the particular end-products and manufacturing location. However, a brief overview of conclusions from various LCA studies on PLAs is presented here. In a series of reports, Vink et al. (2003, 2004, 2007, 2010) have reviewed studies involving LCA analyses of PLA from NatureWorks LLC. These authors emphasized the value of using LCA methodology and pointed out that PLA production systems generally outperformed those for synthetic thermoplastics in the two key impact categories of fossil fuel use and GHG emissions. The possibility for continued improvement in the processing systems for PLA as part of an overall cost reduction strategy was also noted. With continued process development, very significant reductions in CO_2 emissions and fossil energy use for PLA manufactured in 2006 relative to data from 2003 were reported. The values of 0.27 kg CO_2 eq./kg emitted and 27.2 MJ/kg fossil energy used compare favorably with data for commercial thermoplastics published by Plastics Europe (Figure 13.28). In a study on biodegradable food packaging published in 2004, PLA was compared with polypropylene (PP) for the specific application of thermoformed yoghurt cups. The authors concluded in this case that the use of PLA was a more energy-efficient option; however, the differences were considered marginal when uncertainties in the various estimates were taken into account. Furthermore, uncertainties concerning PLA biodegradation in landfills complicated the GHG emission estimates. More recently, Uihlein et al. (2008) compared PLA with polystyrene for production of drinking cups and concluded that life-cycle assessments did not unequivocally support decision-making either for or against the use of materials from renewable

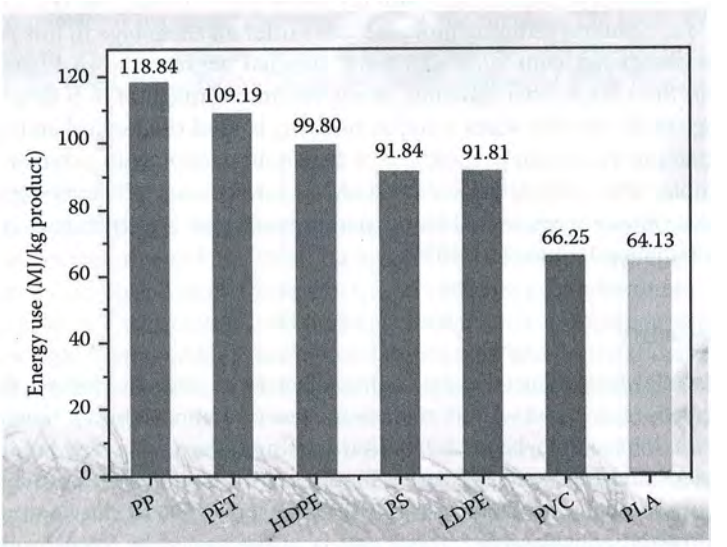

FIGURE 13.28 A comparison of energy used for production of PLA with comparable values for a range or commodity thermoplastics. (Data from: http://www.plasticseurope.org, The contribution of plastic products to resource efficiency—Final report (2005), p. 46.)

resources. The substantial further reductions in GHG emissions and fossil energy utilization in PLA manufacturing by NatureWorks are detailed in the most recent report by Vink et al. (2010).

The assessment of PLA production and the use of PLA-based products from a sustainability perspective using LCA methodologies is likely to continue developing in parallel with the evolution of commercial PLA manufacturing. Similarly, PLA use in combination with natural fiber reinforcements in biocomposites or nano-biocomposites will also be increasingly evaluated as these new materials are adopted more widely in industry. In this respect, there will be a need to ensure the basic requirements for LCA, such as data transparency, uncertainties, sensitivity analysis for key data and methodological choices are all taken into consideration if, as seems probable, sustainability assessments become increasingly relevant in the future.

13.4 POLYLACTIDE FIBER COMPOSITES

Wood or other bio-fiber composites using PLA as matrix material have been widely studied the last decade. The mechanical performance of this type of composites can, as with PLA alone, be varied to a large extent. Apart from the inherent properties of the constituents used, variation depending on the manufacturing method is also to expect. Moisture can, if present during processing hydrolyze the PLA, it is therefore of outmost importance to keep both the fibers and the PLA dry before processing. The properties of the composites can also be controlled by cooling rates and annealing steps after processing. Table 13.9 demonstrates mechanical performance of a variety of injection molded wood/agro fiber PLA composites. The addition of fibers to PLA gives a higher Young's modulus, the tensile strength is also possible to improve by the addition of fibers but Table 13.9 shows that the resulting strength reported in some studies could also be lower compared to neat PLA. The notched impact strength is increased or similar when fibers are added to the PLA, the unnotched impact strength is decreased except for a study with man-made cellulose where the unnotched impact strength is increased almost 4 times when the fiber was added to composite (Ganster et al. 2006).

The biological durability of these composites has mainly been studied regarding the ability to degrade the composite at the easiest way after end of use. In order to degrade the material it is needed for the PLA to be hydrolyzed and composting is the most preferred disposal route (Mathew et al. 2005). Mathew et al. (2005) also studied the biodegradability in a 58°C, 60% relative humidity of PLA composites with 25% microcrystalline cellulose, wood flour and wood fiber. Initially the neat PLA started to degrade first, after 75 days all samples shoved a rapid increase in degradation, where the PLA with wood flour was the most rapid. For the in-use biological durability there is not many studies performed, Table 13.10 demonstrates resulting weight losses from a 10 week soil block test (ASTM D1413), there the composites first are subjected to a preconditioning step by water soaking for 2 weeks followed by 10 weeks of exposure to a brown rot fungus. The mass losses obtained from these types of laboratory tests normally are very low for WPCs, this is due to the slow moisture transport and relative short duration of the test, therefore it could be valuable to combine durability tests with mechanical tests before and after decay testing. Tables 13.11 and 13.12 present strength and stiffness properties of the PLA fiber composites before and after soil block testing. There it is seen that the losses in strength and stiffness is similar for both sterile and fungus soil, so the brown rot fungus used had no effect on the mechanical properties of the composites. However, the strength and stiffness of the PLA unmodified fiber composite show dramatically lower values after decay testing, this would be related to the moisture induced movements which causes cracks and destroyed interfaces between the fiber and the PLA. Figure 13.29 shows scanning electron micrographs of the surface of a PLA unmodified composite after water soaking and after a decay test in soil, the water soaking does not create visible cracks but after decay testing there are surface cracks formed over the entire surfaces. The PLA acetylated fiber composite show almost no loss in mechanical properties after decay testing, so dimensional stabilization by acetylation proved to be a good route to ensure a long term performance of these PLA composites.

TABLE 13.9
Comparison of the Mechanical Properties of Some Injection Molded PLA Wood/Agro Fiber Composites

			Tensile Strength		Young's Modulus		Unnotched Charpy Impact Strength		Notched Impact Strength		
Fiber	PLA Polymer	Fiber Wt%	Neat PLA (MPa)	Composite (MPa)	Neat PLA (GPa)	Composite (GPa)	Neat PLA (kJ/m^2)	Composite (kJ/m^2)	Neat PLA	Composite	Source
Abaca fibers	PLA 4042D, Nature Works	30	63	74	3.4	8.0			2.2[a]	5.3[a]	Bledzki et al. (2009)
Cellulose fibers	POLLAIT	25	50	45	3.6	6.0					Mathew et al. (2005)
Cellulose nanofibers	ESUN, Shenzhen Bright China Co	5	59	71	2.9	3.6					Jonoobi et al. (2010)
Flax	PLA 6202D, Nature Works	10	44	43	3.1	3.9	16.1	10.0			Bax and Müssig (2008)
Flax	PLA 6202D, Nature Works	20	44	49	3.1	5.1	16.1	10.5			Bax and Müssig (2008)
Flax	PLA 6202D, Nature Works	30	44	54	3.1	6.3	16.1	11.1			Bax and Müssig (2008)
Hemp	PLA 4042D, Nature Works	10		52	3.5	4.1					Sawpan et al. (2007)
Hemp	PLA 4042D, Nature Works	20	51	60	3.5	5.5					Sawpan et al. (2007)
Hemp	PLA 4042D, Nature Works	30	51	66	3.5	7.0					Sawpan et al. (2007)
Kenaf fiber	Biomer l.. 9000	30	61	53	3.3	5.5	76	52	7.4[a]	12.2[a]	García et al. (2008)
Kenaf fiber	LACTY 7.4a0, Shimadzu	30	47	36	1.4	1.9					Pan et al. (2007)
Man-made cellulose fibers	PLA 2002D, Nature Works	25	71	108	2.8	4.2	14.4	69.0	2.8[a]	8.4[a]	Ganster et al. (2006)
Man-made cellulose fibers	PLA 4042D, Nature Works	30	63	92	3.4	5.8			2.2[a]	7.9[a]	Bledzki et al. (2009)

Microcrystalline cellulose	POLLAIT	25	50	36	3.6	5.0					Mathew et 23.9b.4a)
Rice husk fiber	Biomer L 9000	30	61	36	3.3	4.5	76	36	7.4[a]	6.8[a]	García et al. (2008)
Silkworm silk fibers	Eask Link Degradable Materials Ltd.	5	65	62	1.8	2.5					Cheung et al. (2008)
Sugar beet pulp	PLA, Dow Cargill	45	70	30	1.9	2.6					Finkenstadt et al. (2007)
Wood flour	PLA 3001D, Nature Works	10	56	53	0.6	2.0					Pilla et al. (2009)
Wood flour	Biomer L 9000	20	63	66	2.7	4.8			25.7[b]	23.9[b]	Huda et al. (2006)
Wood flour	PLA 3001D, Nature Works	20	56	56	0.6	2.7					Pilla et al. (2009)
Wood flour	POLLAIT	25	50	45	3.6	6.3					Mathew et al. (2005)
Wood flour	Biomer L 9000	30	63	63	2.7	5.3			25.7[b]	23.2[b]	Huda et al. (2006)
Wood flour	Biomer L 9000	40	63	59	2.7	6.3			25.7[b]	21.9[b]	Huda et al. (2006)
Wood flour	PLA 7000D, Nature Works	50	69	55	3.6	8.3					Sykacek et al. (2009)

[a] Charpy (kJ/m^2).
[b] Izod (J/m).

TABLE 13.10
Mass Loss of PLA Fiber Composite after Soil Block Test

Matrix	Wood	Wt% wood	Mass Loss %
PLA 4042D, Nature Works		0	0.1
PLA 4042D, Nature Works	Unmodified fiber	50	1.6
PLA 4042D, Nature Works	Acetylated fiber	50	0.2

TABLE 13.11
Strength of the PLA Fiber Composites before and after Soil Block Test

					After Soil Block Test	
Matrix	Wood	Wt% wood	Reference (MPa)	After Water Soaking (MPa)	Sterile Soil (MPa)	Fungus Soil (MPa)
PLA 4042D, Nature Works	–	0	103	102	94	95
PLA 4042D, Nature Works	Unmodified fiber	50	102	72	59	55
PLA 4042D, Nature Works	Acetylated fiber	50	94	89	89	92

TABLE 13.12
Stiffness of the PLA Fiber Composites before and after Soil Block Test

					After Soil Block Test	
Matrix	Wood	Wt% wood	Reference (GPa)	After Water Soaking (GPa)	Sterile Soil (GPa)	Fungus Soil (GPa)
PLA 4042D, Nature Works	–	0	3.17	4.02	3.72	3.80
PLA 4042D, Nature Works	Unmodified fiber	50	7.00		4.00	3.67
PLA 4042D, Nature Works	Acetylated fiber	50	6.37	7.17	6.88	6.83

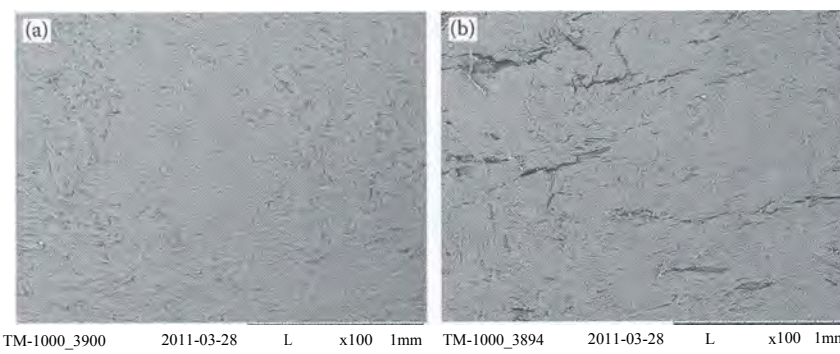

FIGURE 13.29 PLA-unmodified fiber, (a) subjected to preconditioning with moisture, (b) after testing in compost soil.

REFERENCES

Amass, W., A. Amass, and B. Tighe. 1998. A review of biodegradable polymers: Uses, current developments in the synthesis and characterization of biodegradable polyesters, blends of biodegradable polymers and recent advances in biodegradation studies. *Polym Int* 47,89-144.

Anonymous. 2002. Want to improve your plastic composite? Struktol knew you wood." Technical brochure, Struktol Company of America, Stow OH.

Anonymous. 2011. *iBIB2011: International Business Directory for Innovative Bio-Based Plastics and Composites.* DominikVogt ed., nova-Institute GmbH. Huerth, Germany and Polymedia Publisher GmbH, Moenchengladbach, Germany.

Auras, R., B. Harte., and S. Selke. 2004. An overview of polylactides as packaging materials. *Macromolecular Bioscience* 4,835-864.

Bax, B. and J. Müssig. 2008. Impact and tensile properties of PLA/cordenka and PLAIflax composites. *Comp. Sci. Tech.* 68,1601-1607.

Belgacem, M.N. and A. Gandini. (eds). 2008. *Monomers, Polymers and Composites from Biomass.* Elsevier Science and Technology, Oxford, UK.

Belgacem, M. N. and A. Gandini. 2011. Production, chemistry and properties of cellulose-based materials. Chapter 8 in Plackett D. (ed). *Biopolymers—New Materials for Sustainable Films and Coatings.* John Wiley and Sons, Ltd. Chichester, West Sussex, England.

Bengtsson, M.P., P. Gatenholm, and K. Oksman. 2005. The effect of crosslinking on the properties of polyethylene/wood flour composites. *Composites Science and Technology* 65(10), 1468-1479.

Billmeyer, F.W. Jr. 1984. *Textbook of Polymer Science.* John Wiley and Sons, New York.

Bledzki, A.K., A. Jaszkiewicz, and D. Scherzer. 2009. Mechanical properties of PLA composites with man-made cellulose and abaca fibres. *Composites: Part* A 40,404-412.

Carley, J.F. (ed.) 1993. *Whittington's Dictionary of Plastics.* 1993. Technomic Publishing Company, Inc. Lancaster, PA.

Carus, M., C. Gahle, and H. Korte. 2008. Market and future trends for wood-polymer composites in Europe: The example of Germany. In Oksman Niska, K. and Sain, M. Woodhead (eds). *Wood-Polymer Composites.* Publishing and CRC Press LLC, Boca Raton, FL.

Caulfield, D., R. Jacobson, K. Sears, and J. Underwood. 2001. Fiber reinforced engineering plastics. *In Proceedings: 2nd International Conference on Advanced Wood Composites,* Bethel, ME.

Cheung, H.-Y., K.-T. Lau, X.-M. Tao, and D. Hui. 2008. A potential material for tissue engineering: Silkworm silk/PLA biocomposite. *Composites Part B* 39,1026-1033.

Chodak, I. 2008. Polyhydroxyalkanoates: Origin, properties and applications. In Belgacem, M. and Gandini, A. (eds). *Monomers, Polymers and Composites from Renewable Resources.* Elsevier, Amsterdam.

Finkenstadt, V.L., L.S. Liu, and J.L. Willett. 2007. Evaluation of poly(lactic acid) and sugar beet pulp green composites. *J Polym Environ* 15,1-6.

García, M., I. Garmendia, and J. García. 2008. Influence of natural fiber type in eco-composites. *J. Appl. Polym. Sci.* 107,2994-3004.

Ganster, J., H.-P. Fink, and M. Pinnow. 2006. High-tenacity man-mad cellulose fibre reinforced thermoplastics—injection moulding compounds with polypropylene and alternative matrices. *Composites:* Part A 37,1796-1804.

Gordon, J.E. 1988. *The New Science of Strong Materials (or why you don't Fall Through the Floor).* Princeton University Press, Princeton, NJ.

Grijpma, D.W, A.J. Nijenhuis, P.G.T. van Wijk, and A.J. Pennings. 1992. High impact strength as-polymerized PLA. *Polym Bull* 29,571-578.

Grijpma D.W., G.J. Zondervan, and A.J. Pennings. 1991. High molecular weight polymers of L-lactide and as biodegradable elastomeric implants. *Polym Bull* 25,327-333.

Guo, G., G.M. Rizvi, and C.B. Park. 2008. Wood-polymer composite foams. In Oksman Niska, K. and Sain, M. (ed). *Wood-Polymer Composites.* Woodhead Publishing and CRC Press LLC, Boca Raton, FL.

Hiljanen-Vainio, M., P.A. Orava, and Seppala, J.V. 1997. Properties of ε-caprolactone/DL-lactide (ε-CL/DL-LA) copolymers with a minor ε-CL content. *J Biomed Mater Res* 34,39-46.

Huda, M.S., L.T. Drzal, M. Misra, and A.K. Mohanty. 2006. Wood-fiber-reinforced poly(lactic acid) composites: Evaluation of the physicomechanical and morphological properties. *J. Appl. Polym. Sci.* 102, 4856-4869.

Inkinen, S., M. Hakkarainen, A-C. Albertsson, and A. Södergård. 2011. From lactic acid to poly(lactic acid) (PLA): Characterization and analysis of PLA and its precursors. *Biomacromolecules* 12, 523-532.

Ikada, Y., K. Jamshidi, H. Tsuji, and S.-H. Hyon. 1987. Stereocomplex formation between enantiomeric poly(lactides). *Macromolecules* 20,904-906.

Jacobson, R.E., R.M. Rowell, D.F. Caulfield, and A.R. Sanadi. 1996. Property improvement effects of agricultural fibers and wastes as reinforcing fillers in polypropylene-based composites. Woodfiber-Plastic Composite: Virgin and recycled wood fiber and polymers for composites, D.F. Caulfield, R.M. Rowell and J.A. Youngquist, eds. pp 211-219, Forest Products Society, Madison, WI.

Jacobson, R.E., R. Rowell, D. Caulfield, and A.R. Sanadi. 1995a. United States based agricultural "waste products" as fillers in a polypropylene homopolymer. *Proceedings, Second Biomass Conference of the Americas: Energy, Environment, Agriculture, and Industry.* August, 1995, Portland, OR, NREL/CP-200-8098, DE95009230, 1219-1227.

Jacobson, R.E., R.M. Rowell, D.F. Caulfield, and A.R. Sanadi. 1995b. Mechanical properties of natural fiber-polyolefins composites: Dependence on fiber type. In *Proceedings, Inside Automotives 95',* Dearborn, MI.

Jacobson, R., D. Caulfield, K. Sears, and J. Underwood. 2002. Low Temperature Processing (LTP) of Ultra-Pure Cellulose Fibers into Nylon 6 and other Thermoplastics, In *Proceedings: Sixth International Conference on Woodfiber/Plastic Composites.* Madison, WI, April.

Jonoobi, M., J. Harun, A.P. Mathew, and K. Oksman. 2010. Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. *Comp. Sci. Tech.* 70,1742-1747.

Kadla, J.F., S. Kubo, R.A. Venditti, R.D. Gilbert, A.L. Compere, and W. Griffith. 2002. Lignin-based carbon fibers for composite fiber applications. *Carbon* 40(15), 2913-2920.

Kimura, S. and Itoh, T. 2004 Cellulose synthesizing terminal complexes in the Ascidians. *Cellulose* 11, 377-383.

Kricheldorf, H.R. 2001. Synthesis and applications of polylactides. *Chemosphere* 43,49-54.

Lemoigne, R. 1923. Production of ß-hydroxybutyric acid by certain bacteria of the B. subtilis group. *Compt Rend* 176,1761-1763.

Lemoigne, R. 1924a. Mechanism of the production of ß-hydroxybutyric acid by the biochemical method. *Compt Rend* 178,1093-1095.

Lemoigne, R. 1924b. Production of ß-hydroxybutyric acid by a bacterial process. *Compt Rend* 179,253-256.

Letchford, K., A. Sodegraad, D. Plackett, S. Gilchrist, and H. Burt. 2011. Lactide and glycolide polymers. Chapter 9 in (A. Domb, N. Kumar, A. Azra eds.) *Biodegradable Polymers in Clinical Use and Clinical Development.* John Wiley and Sons, Chichester, West Sussex, England.

Li, S.M., H. Garreau, and M. Vert. 1990. Structure-property relationships in the case of the degradation of massive aliphatic poly(Ŭ-hydroxy acids) in aqueous media. Part 1. Poly(D,L-lactic acid). *J Mater Sci, Mater Med.* 1,123-130.

Lu, J.Z., Q. Wu, and H.S. McNabb Jr. 2000. Chemical coupling in wood fiber and polymer composites: A review of coupling agents and treatments. *Wood and Fiber Science,* 32(1): 88-104.

McDonough, W. and M. Braungart. 2002. *Cradle to Cradle-Rethinking the Way We Make Things.* North Point Press, New York.

Macrae, R.M. and J.F. Wilkinson. 1958. Poly-ß-hydroxybutyrate metabolism in washed suspensions of Bacillus cereus and Bacillus megaterium. *J Gen Microbiol* 19,210-222.

Mapleston, P. 2001a. Processing technology: A wealth of options exist. *Modern Plastics* June, 56-60.

Mapleston, P. 200 lb. Wood composite suppliers are poised for growth in Europe. *Modern Plastics* October, 41

Mathew, A.J., K. Oksman, and M. Sain. 2005. Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC). *J. Appl. Polym. Sci.* 97,2014-2025.

Osswald, T.A. and G. Menges. 1996. *Materials Science of Polymers for Engineers.* Carl Hanser Verlag, New York.

Pan, P., B. Zhu, W. Kai, S. Serizawa, M. Iji, and Y. Inoue. 2007. Crystallization behavior and mechanical properties of bio-based green composites based on poly(L-lactide) and kenaf fiber. *J. Appl. Polym. Sci.* 105, 1511-1520.

Penning, J.P., H. Dijkstra, and A.J. Pennings. 1993. Preparation and properties of adsorbable fibres from L-lactide copolymers. *Polymer* 34,942-951.

Pilla, S., S. Gong, E. ÓNeill, L. Yang, and R.M. Rowell. 2009. Polylactide-recycled wood fiber composites. *J. Appl. Polum. Sci.* 111,37-47.

Pollet, E. and L. Averous. 2011. Production, chemistry and properties of polyhydroxyalkanoates. In: Plackett (ed) *Biopolymers-New Materials for Sustainable Films and Coatings.* John Wiley & Sons Ltd.,Chichester, UK

Rowell, R.M. 1992. Opportunities for lignocellulosic materials and composites, In R.M. Rowell, T.P. Schultz. and R. Narayan, eds. *Emerging Technologies for Materials and Chemicals from Biomass,* American Chemical Society, Washington, DC.

Rowell, R.M., E. O'Neill, A. Krzysik, A.D. Bossman., D.F. Galloway, and M. Hemenover. 2008. Industrial applications of animal manure filled thermoplastics. *Mol. Cryst. Liq. Cryst.* 484:616-622.

Rowell, R.M., A. Sanadi, R. Jacobson, and D. Caulfield. 1999. Properties of kenaf/polypropylene composites. *Kenaf Properties, Processing and Products,* T. Sellers, Jr. and N.A. Reichert, Eds, Mississippi State University Press, Mississippi State, MS, Chapter 32,381-392.

Rowell, R.M., A.R. Sanadi, D.F. Caulfield, and R.E. Jacobson. 1997. Utilization of natural fibers in plastic composites: Problems and opportunities. *Lignocellulosic-Plastics Composites,* A.L. Leao, F.X. Carvalho, and E. Frollini, Eds., pp. 23-52, Universidade de Sao Paulo Press, Sao Paulo, Brazil.

Sanadi, A.R., D.F. Caulfield, K. Walz, L. Wieloch, R.E. Jacobson, and R.M. Rowell. 1994a. Kenaf fibers-Potentially outstanding reinforcing fillers in thermoplastics, In *Proceedings, Sixth Annual International Kenaf Conference,* New Orleans, LA, pp. 155-160.

Sanadi, A.R., D.F. Caulfield, and Rowell, R.M. 1994b. Reinforcing polypropylene with natural fibers. *Plastic Engineering* L(4), 27-28.

Sanadi, A.R., R.E. Jacobson, D.F. Caulfield, and R.M. Rowell. 1995a. Mechanical properties of natural fiber-polyolefins composites: An overview. *In Proceedings, Seventh Annual International Kenaf Conference,* Irving, TX, March, 1995, pp. 47-59.

Sanadi, A.R., D.F. Caulfield, R.E. Jacobson, and R.M. Rowell. 1995b. Renewable agricultural fibers as polyolefins composites: An overview. In *Proceedings, Seventh Annual International Kenaf Conference*, Irving, TX, March, 1995, pp. 47-59.

Sanadi, A.R., D.F. Caulfield, R.E. Jacobson, and R.M. Rowell. 1995b. Renewable agricultural fibers as reinforcing fillers in plastics: Mechanical properties of kenaf fiber-polypropylene composites *Ind. Eng Chem, Research* 34, 1889-1896.

Sanadi, A.R., R.M. Rowell, and D.F. Caulfield. 1996a Agro-based fiber/polymer composites, blends and alloys, *Polymer News* 21(1), 7-17.

Sanadi, A.R., K. Walz, L. Wieloch, R.E. Jacobson, D.F. Caulfield., and R.M. Rowell. 1996b Effect of Matrix Modification on Lignocellulosic Composite Properties, D.F. Caulfield, R.M. Rowell and J.A. Youngquist eds. pp 166-172, Forest Products Society, Madison, WI.

Sarasua, J-R., R.E. Prud'homme, M. Wisniewski, A. Le Borgne, and N. Spassky. 1998 Crystallization and melting behavior of polylactides. *Macromolecules* 31, 3895-3905.

Sawpan, M.A., K.L. Pickering, and A. Fernyhough. 2007. Hemp fibre reinforced poly(lactic acid) composites. *Adv. Mater. Res*. 29-30, 337-340.

Sir· , I. and D. Plackett. 2010. Microfibrillated cellulose and new nanocomposite materials: a review, Cellulose 17(3): 459-494

Sødergård, A. and M. Stolt. 2002. Properties of lactic acid based polymers and their correlation with composition. *Progress in Polymer Science* 27,1123-1163.

Stark, N.M. and R.E. Rowlands. 2003. Effects of wood fiber characteristics on mechanical properties of wood/polypropylene composites. *Wood and Fiber Science.* 35(2), 167-174.

Stark, N.M. and L.M. Matuana. 2009. Co-Extrusion of WPCs with a Clear Cap Layer to Improve Color Stability. In *The Proceedings of 4thWood Fibre Polymer Composites International Symposium.* Bordeaux, France, 1-13.

Sykacek, E., M. Hrabalova, H. French, and N. Mundigler. 2009. Extrusion of five biopolymers reinforced with increasing wood flour concentration on a production machine, injection moulding and mechanical performance. *Composites:* Part A 40,1272-1282.

Toloken, S. 2010. China's WPC firms see growth from Europe and China. *PlasticsNews.com/China* Crain Communications Inc.

Uihlein, A., S. Ehrenberger, and L. Schebeck. 2008. Utilisation options of renewable resources: A life cycle assessment of selected products. *J Cleaner Prod* 16,1306-1320.

US Patent 2008207840, Assignees: Tate & Lyle PLC. Inventors: Sodergard, N.D.A., Stolt, E.M., Siistonen, H.K. et al., 2008.

Vazquez, A., M.L. Foresti, and V. Cyras. 2011. Production, chemistry and degradation of starch-based polymers. In: Plackett D. (ed). *Biopolymers—New Materials for Sustainable Films and Coatings.* John Wiley and Sons, Ltd. Chichester, West Sussex, England.

Vink, E.T.H., K.R. Rabago, D.A. Glassner, and P.R. Gruber, P.R. 2003. Applications of life cycle assessment to NatureWorksTM polylactide (PLA) production. *Polym Degrad Stab* 80,403-419.

Vink, E.T.H., K.R. Rabago, D.A. Glassner, R. Springs, R.P. O'Connor, J.J. Kolstad, and P.R. Gruber. 2004. The sustainability of NatureWorksTM polylactide polymers and IngeoTM polylactide fibers: Aan update of the future. *Macromol Biosci* 4,551-564.

Vink, E.T.H., D.A. Glassner, J.J. Kolstad, R.J. Wooley, and R.P. O'Connor. 2007. The eco-profiles for current and near-future Nature Works® polylactide (PLA) production. *Ind Biotech* 3, 58-81.

Vink, E.T.H., S. Davies., and J.J. Kolstad. 2010. The eco-profile for current Ingeo® polylactide production. *Ind Biotech* 6,212-224.

Wolcott, M.P., P.M. Smith, and D.A. Bender. 2009. Natural fiber thermoplastic composites for Naval facilities. In *The Proceedings of the International SAMPE Symposium and Exhibition.* Baltimore Convention Center, Baltimore, Maryland, p. 54.

Youngquist, J.A. 1999. Wood-based composites and panel products. *Wood Handbook: Wood as an Engineering Material.* USDA Forest Serv. Forest Prod. Lab. Forest Prod. Soc., Madison, WI. 27-28.

Zhang, J.F. and Sun, X. 2005. Poly(lactic acid) based bioplastics. Chapter 10 in Smith R (ed) *Biodegradable Polymers for Industrial Applications.* CRC, Woodhead Publishing Ltd, Cambridge, England, pp. 251-288.

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