PART IV

NATURAL FIBER—REINFORCED COMPOSITES

CHAPTER 11

Starch–Cellulose Fiber Composites

ANALÍA VÁZQUEZ

INTECIN, Facultad de Ingenería-Universidad Nacional de Buenos Aires, Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET)

VERA ALEJANDRA ALVAREZ

Research Institute on Science and Technology of Material Science (INTEMA), Universidad Nacional de Mar del Plata, J.B. Justo 4302, Mar del Plata, Argentina

---

Biodegradable Polymer Blends and Composites from Renewable Resources. Edited by Long Yu

11.1 INTRODUCTION

Starch and cellulose are some of the most abundant biopolymers. These materials are renewable, biodegradable, abundant, have low cost, and can be used in various applications (Vilpoux and Averous, 2004). The use of agricultural products is considered an important way to reduce surplus farm products and to develop nonfood applications.

The incorporation of starch into different types of biodegradable and nonbiodegradable polymers has been motivated by growing interest in enhancing the biodegradability of materials and in the reduction of the amount of waste. Since, 1970, starch has been used as a particulate filler or destructurized starch in commodity polymers (van Soest, 1997). Although such polymers were termed "biodegradable," only a part of them was starch and the rest of the polymer was not biodegradable. In order to prepare a strictly "biodegradable polymer" based on starch; the starch granules would be mixed with plasticizers or additives to make the starch thermoplastic.

The hydrophilic and moisture sensitivity characteristics of starch limit its application; for this reason starch is blended with other biodegradable polymer such as poly(hydroxyalkanoates), polycaprolactone, poly(vinyl alcohol), among others (Averous, 2004).

Starch reinforced with cellulose is one case of a natural fully biodegradable composite. The use of cellulose fiber to reinforce starch is improves the mechanical properties of starch. Cellulose fibers commonly used are sisal, wood, cotton, jute, and kenaf.

11.2 STARCH POLYMERS

11.2.1 Structure

Starch is made up of glucose repeat units. Native starch is based on two polysaccharides, the linear D-glucan amylose at 20–30 wt% and the highly branched amylopectin at 70–80 wt%. Figure 11-1 shows the structure of the polysaccharide component of starch (van Soest and Vliegenthart, 1997). Starch is a semicrystalline polymer: amylopectin is the major crystalline constituent; amylose and the amylopectin branches comprise the amorphous part. Figure 11-1 shows the double helices of the amylopectin outer chains arranged as thin laminar domains that represent the crystalline part. The co-crystallization of amylopectin and crystallization into single-helical structures can lead to additional crystallinity.

Starch is available from numerous resources such as potatoes and such grains as corn, wheat, etc. The proportion of amylopectin determines the character of the crystalline region and the strength (Placket and Vazquez, 2004).

11.2.2 Chemical Composition

Tables 11-1 and 11-2 show the chemical composition of different starches derived from maize, wheat, rice, potato, and tapioca. The values published in the literature

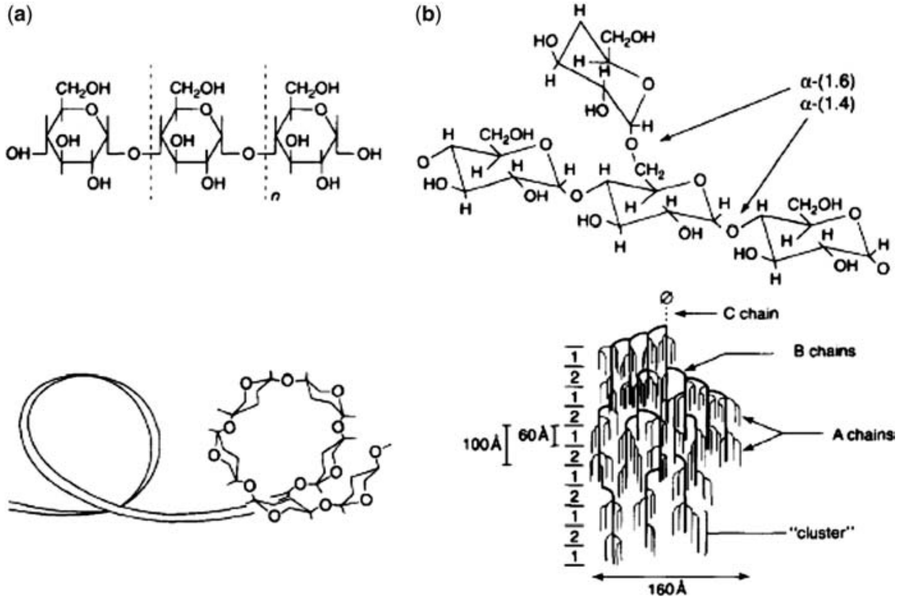


Fig. 11-1 (a) Structure of amylose and schematic representation of an amylose single helix; (b) Structure of amylopectin and schematic representation of the crystalline regions. (Reproduced with permission from *Trends in Biotechnology* **1997**, 15(6):208–213. Copyright 2008 Elsevier Editorial.)

present a range and the differences can be due to different growing conditions and the methods used in the chemical composition analysis.

The crystalline structure of starch granules can be disordered by heating in the presence of large quantities of water. During this process, the hydrogen bonds are broken

TABLE 11-1 Composition, Size, and Diameter of Different Starches[a]

Starch Source	Amylose Content (%)	Amylopectin Content (%)	Source	Diameter (μm)	Shape
Dent corn	25	75	Cereal	5–30	Polygonal, round
Waxy corn	<1	>99	Cereal	5–30	Polygonal, round
Tapioca	17	83	Root	4–35	Oval, truncated, "kettle drum"
Potato	20	80	Tuber	5–100	Oval, spherical
High-amylose corn	55–75 (or higher)	45–30 (or lower)	Cereal	5–30	Polygonal, round irregular
Wheat	25	75	Cereal	1–45	Round, lenticular
Rice	19	81	Cereal	1–3	Polygonal, spherical compound granules

[a] *Source*: Thomas DJ, William AA. 1999. Practical guides for the food industry. In: *Starches*. American Association of Cereal Chemists. Chapter 1, p. 6–9. ISBN 1–891127–01–2.

TABLE 11-2 Characteristics of Different Starches

Starch Source	Amylose (%)	Swelling Power (g/g) (ºC)	Solubility (%)(°C)	Gelatinization Temperature (°C)	Reference
Maize	29.3	–	–	70–81	
Chayote	12.9			64–75	Jiménez-Hernandez et al. (2007)
Cassava tapioca	18.6–23.6	51 (95)	26 (95)	57–84.1	Hoover (2001), Freitas et al. (2004), Chang et al. (2006)
Yam starch	30–36				Mali et al. (2004), Freitas et al. (2004)
Normal potato	21.1–31.0	1159 (95)	82 (95)	57.0–80.3	Hoover (2001)
Normal corn	23–27	22 (95)	22 (95)	62.3–84.3	Singh et al. (2003)
High-amylose corn	42.6–67.8	6.3 (95)	12.4 (95)	66.8–73.3	
Normal rice	5–28.4	23–30 (95)	11–18 (95)	57.7–97.5	
Waxy rice[a]	0–2.0	45–50 (95)	2.3–3.2 (95)	66.1–78.8	
High-amylose rice	25–33	–	–	–	
Normal wheat	18–30	18.3–26.6 (100)	1.55 (100)	46.0–76	
Normal wheat A-granules	28.4–27.8	–	–	–	
Normal wheat B-granules	27.5–24.5	–	–	–	
Waxy wheat	25.1–29.5	–	–	–	
Normal soybean	19.8			51.8–55.8	Stevenson et al. (2007)
Black bean	35–39			61.2–81.2	Zhou et al. (2004)

[a] Waxy starch: starch particularly rich in amylopectin.

and from exposed hydroxyl groups; new water–amylose and water–amylopectin hydrogen bonds are generated. The starch chain interactions in the amorphous and crystalline regions can be inferred from the swelling power and solubility. The higher content of phosphate groups on amylopectin, which produces repulsion between phosphate groups on adjacent chains in potato starch, increasing the hydration due to the weakness of bonding in the crystalline domains, gives higher swelling power and solubility (Hoover, 2001).

The mechanical properties—tensile strength, modulus, and elongation at break—of starch films can be directly correlated with the amylase content (Thunwall et al., 2006). The higher the amylase content, the stronger the film. The branches of amylopectin commonly produce films with reduced mechanical properties (Thranathna, 2003).

11.2.3 Gelatinization

Gelatinization, which is an order–disorder phase transition of starches when they are heated in the presence of water, is assumed to involve several steps: (i) diffusion of water into the granule; (ii) uptake of water by the amorphous regions and hydration; (iii) radial swelling of the starch granules; (iv) loss of optical birefringence; (v) absorption of heat; (vi) loss of crystalline order due to uncoiling and dissociation of double helices in the crystalline regions; and (vii) amylose leaching (Lelieve and Mitchell, 1975; Stevens, 1981; Hoover, 2001).

11.2.4 Thermoplastic Starch

By gelatinization of starch with a plasticizer, it is possible to obtain *thermoplastic starch* (TPS). This can be done by application of mechanical, thermal, or thermomechanical energy in the presence of water and plasticizer [glycerol, sorbitol, xylose, sucrose, poly(ethyleneglycol)] and leads, as described earlier, to starch destructurization and loss of the organization of the intermolecular hydrogen bonding combined with partial depolymerization.

The *degree of gelatinization* will depend on the plasticizer content and processing parameters (shear stress, melt viscosity, and temperature) (Röper and Koch, 1990; van Soest et al., 1996a).

Starches showed two relaxations, which appeared between −75°C and −40°C and between 70°C and 150°C. Some authors related this behavior to starch-rich and starch-poor regions caused by partially separation of phases. The high-temperature relaxation corresponds to the *glass transition temperature* and the other to a plasticizer-rich phase (Curvelo et al., 2001; Mathew and Dufresne, 2002; Forssell et al., 1997; Myllärinen et al., 2002). In the absence of glycerol, amylopectin showed only the upper glass transition.

The *type and content of plasticizer* influences the glass transition temperature, the mechanical properties (especially the modulus), and water absorption (Lourdin et al., 1997). An example of the effect of glycerol and water on the glass transition temperature is given in Fig. 11-2. Mali et al. (2006) have also determined the glass transition as a function of the glycerol content for corn, cassava, and yam starches, showing a decreasing trend with increasing glycerol content.

The *mechanical behavior* of TPS depends on the degree of destructurization reached and the plasticization effect (i.e., glass transition temperature and modulus) (Asa Rindlav-Westling et al., 1998; Rindlay et al., 1998; Chang et al., 2000; Myllarinen et al., 2002). The presence of intact or nondisrupted granular starch leads to inferior mechanical properties. In the case of high-amylose materials; the creation of a network leads to a stiffer and stronger product (van Soest and Borger, 2006). Thus, it is important to know how the mechanical properties are affected. Da Róz et al. (2006) showed that increasing the ethylene glycol content from 15 to

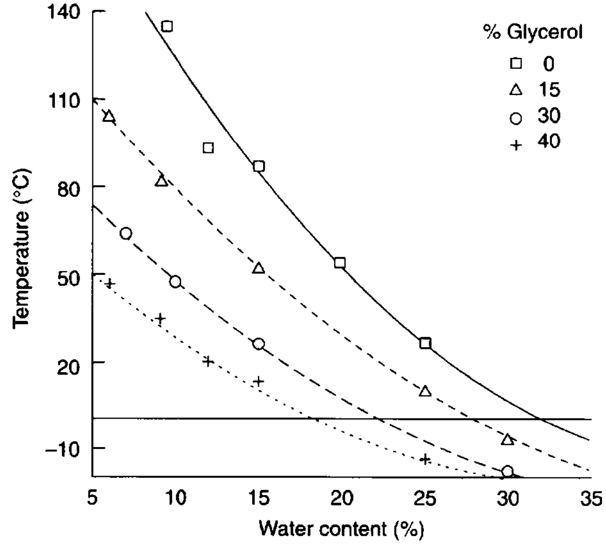


Fig. 11-2 Glass transition temperature vs. glycerol and water content. (Reproduced with permission from *Trends in Biotechnology* **1997**, 15(6):208–213. Copyright 2008 Elsevier Editorial.)

30 wt% in corn starch produces an increase on the tensile modulus from 63 MPa to 126 MPa due to the increase of crystallinity. However, when sorbitol or diethyleneoxide glycol was added to corn starch, the modulus decreased from 219 MPa to 59MPa with the increase of sorbitol from 15 to 30 wt%, due to the plasticization effect. Glycerol can produce strong hydrogen bonding with starch, increasing the strength and toughness of the finished material (van Soest, 1997). Some authors also studied the relation between water and glycerol and the phenomena of plasticization and antiplasticization (Chang et al., 2006). The flexibility and workability of the rigid neat polymer can be improved by the incorporation of low-molecular-mass compounds or diluents, which act as plasticizers. Conversely, when they are incorporated in low quantities they can stiffen the material and behave as mechanical antiplasticizers (Sears and Darby, 1982). Chang et al. (2006) found that water acts an antiplasticizer but glycerol behaved as antiplasticizer only when the tapioca starch films were dried. Water and glycerol have synergic effects as plasticizers. The tensile modulus of the film increased at low glycerol content (close to 2.5%) but only when the humidity was lower than $0.22a_w$ (water activity).

There have been several studies on the preparation of TPS; in the majority of these the films were obtained by *casting*, but *melt processing* seems to be a more realistic technique for industrial application. The temperature, time, and content and type of plasticizer, as well as shear stress (i.e., viscosity × rpm) produce different degrees of destructurization (Shogren et al., 1992; Da Róz et al., 2006). During processing an increase in the shear stress (higher extrusion screw speed or viscosity) causes an increase in the amount of single-helix-type crystallinity. High temperature or shear stress can also degrade the polymer (Warburton et al., 1993; Sagar and Merril, 1995), so that additives or plasticizer are also necessary to improve the flow behavior.

11.2.5 Retrogradation

Starches suffer aging by *retrogradation* during storage and this has a tendency to change their structure. During aging; starch molecules reassociate in more ordered structures by forming simple juncture points and entanglements, helices, and

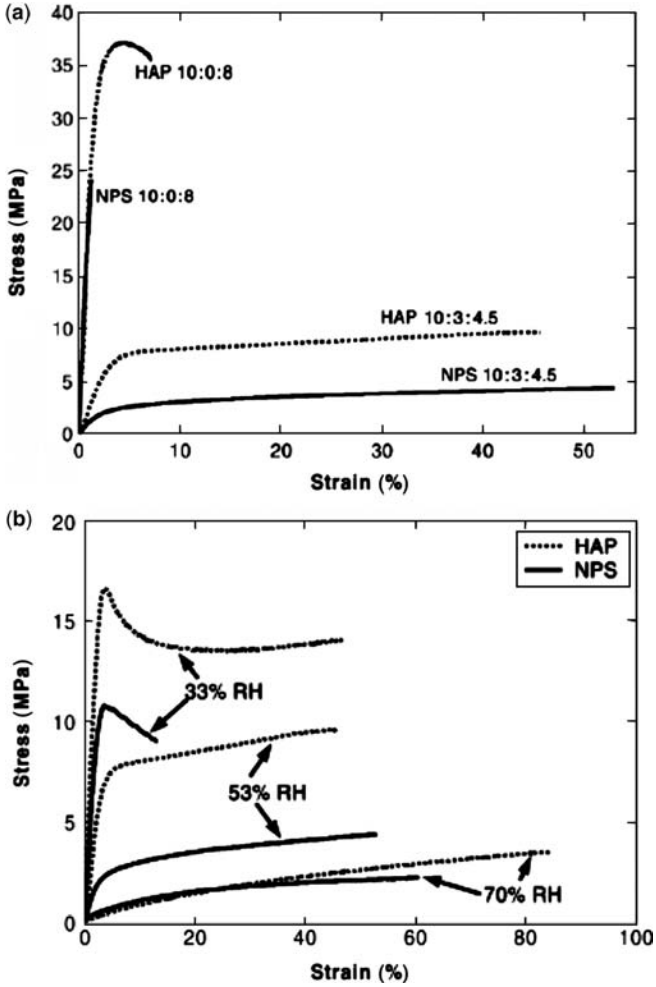


Fig. 11-3 Stress–strain behavior of HAP (higher amylose-content potato starch) and NPS (normal potato thermoplastic starch) (10 : 3 : 4.5 and 10 : 0 : 8): (a) conditioned at 21°C and 53% RH; (b) at 33% RH, 53% RH, and 70% RH. (Reproduced with permission from *Biomacromolecules* **2006**, 7:981–986. Copyright 2008 American Chemical Society.)

crystal structures. An X-ray diffraction pattern of the B-type develops slowly with time (Katz, 1930). The formation of B-type crystallinity in wheat starch gel polymers was explained using the crystalline growth theory by Marsh and Blanshard (1988). Miles et al. (1985) have proposed that, if the solution concentration is sufficiently high, an interconnected gel network can be formed in the polymer-rich region, with crystallization taking place subsequently. In another paper, Gidley (1989) suggested that the gelation behavior is based on the formation and subsequent aggregation of B-type double interchain helices of amylose. It was proposed that the gel contains rigid, crystalline, double-helical junction zones linked by single-chain segments which are amorphous and more mobile (Asa Rindlav-Westling et al., 1998). Amylose is responsible for the short-term changes and the amylopectin is responsible for all long-term rheological and structural changes (Gudmundsson, 1994). Starches from different botanical sources, despite similar amylase/amylopectin ratios, can retrogradate to different extents, indicating that the structure of amylopectin is of importance. Other compounds such as lipids and surfactants can retard the retrogradation. Because of retrogradation, the prepared samples should be kept under controlled atmosphere before measuring their final mechanical properties. Since starch is a hygroscopic polymer, the relative humidity determines the mechanical properties. As an example, Fig. 11-3 shows the different behavior in tensile test of different potato starch films (Thunwall et al., 2006).

The mechanical properties are clearly influenced by the moisture content; a lower value leads to an increased modulus and a reduced elongation at break. Mali et al. (2006) also demonstrated different mechanical properties at initial time and after storage of samples of cassava, corn, and yam starch.

11.3 STARCH–CELLULOSE FIBER BASED COMPOSITES

11.3.1 Natural Fibers

During the past decades there has been an increasing interest in the use of natural fibers as an alternative to synthetic fibers such as those of glass, carbon, and aramide. This interest is based on the potential advantages of such fibers, mainly weight reduction, lower raw material price, and the ecological advantages of using renewable resources.

Several cellulose-based products and wastes have been incorporated as reinforcement, mainly to achieve cost savings (Joseph et al., 1993) and, in the case of biodegradable polymers, to maintain their biodegradability. Natural fibers also have numerous advantages compared to man-made fibers (Rozman et al., 1998): they are inexpensive, abundant and renewable, lightweight, biodegradable, and nonabrasive to processing equipment. The use of these fibers in biodegradable matrices is primarily for ecological reasons. However, there is only limited literature regarding the mechanical properties of natural fibers with thermoplastic biodegradable polymers (Hanselka and Herrman, 1994; Bastioli, 1995; Dufresne and Vignon, 1998; Kuruvilla and Mattoso, 1998; Iannace et al., 1999). Nevertheless, natural fibers also have some disadvantages such as lower durability and lower strength, though their specific properties are comparable.

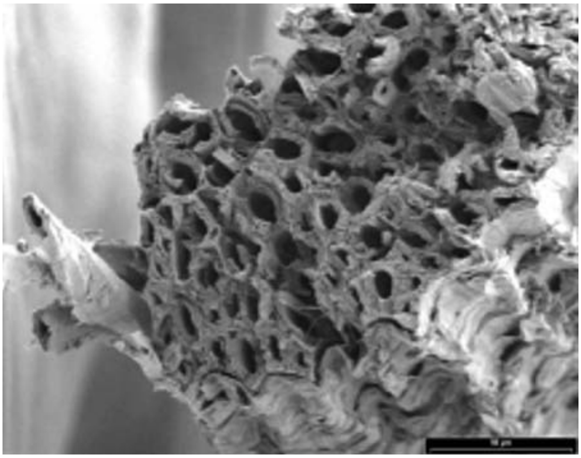


Fig. 11-4 SEM image of sisal fiber.

Each natural fiber (Fig. 11-4) is a composite material in which soft lignin and hemicellulose acts as matrix and rigid cellulose microfibrils act as reinforcement. Microfibrils form hollow cells and are helically wound along the fiber axis. Uncoiling of these spirally oriented fibrils consumes large amounts of energy and is one of the predominant failure modes.

In biocomposites, the biofibers (natural fibers) serve as reinforcement to improve the strength, stiffness, and toughness of the neat matrix. The origin, source, and nature of different fibers together with their properties (physical, chemical, and mechanical) have been studied by several authors (McGovern, 1987; Batra et al., 1998). Whereas the properties of conventional fibers are found in a defined range, in the case of natural fibers they depend on the factors previously described and also (Bledzki et al., 1996) on the extraction method, the quality of the soil in which they grew (Barkakaty et al., 1976), the age of the plant from which they came (Chand et al., 1993), and the preconditioning used (Ray et al., 1976; Chawa et al., 1979).

Cellulose is a natural polymer with high strength and stiffness per unit weight, and is the building material of long fibrous cells. These cells can be found in the stem, the leaves, or the seeds of plants. Natural fibers can be classified accordingly:

- *Bast fibers* (*flax, hemp, jute, kenaf, ramie*). These consist of a wood core surrounded by a stem. Within the stem there are a number of fiber bundles, each containing individual fiber cells or filaments. The filaments are made of cellulose and hemicellulose, bonded together by a matrix, which can be lignin or pectin. The pectin surrounds the bundles, thus holding them onto the stem. The pectin is removed during the retting process. This enables separation of the bundles from the rest of the stem (scutching).
- *Leaf fibers* (*sisal, abaca* (*banana*), *palm*). These are coarser than bast fibers. Applications include ropes, and coarse textiles. Within the total production of leaf fibers, sisal, obtained from the agave plant, is the most important. Its stiffness is relatively high and it is often used in binder twines.

- *Seed fibers* (*cotton, coir, kapok*). Cotton is the commonest seed fiber and is used for textiles all over the world. Coir is the fiber of the coconut husk, it is a thick and coarse but durable fiber.

The strength and stiffness of natural fibers can be correlated with the spiral angle (the lower the angle, the higher the mechanical property); also, the chemical composition and the complex structure of natural fibers strongly affect their properties. Although fibers with higher cellulose content exhibit higher strength and fibers with lower cellulose content have lower strength, because of their complex nature there is no strict correlation between the cellulose content and the strength of the fiber. The lignin content influences the structure, properties, and morphology of the fibers. Waxy components generally affect the wettability and the adhesion characteristics of the fibers.

Tables 11-3 and 11-4 summarize the composition and properties of several natural fibers.

Natural fibers also contribute to the enhancement of material toughness. Different energy dissipation mechanisms can be identified depending on the fiber length. In thermoplastics reinforced with short fibers, fibers of subcritical length are pulled out rather than broken, as they are too short to reach their strength. In this case, the relevant energy dissipation mechanisms are debonding, sliding, restricted pull-out, and brittle or ductile matrix fracture Other failure mechanisms (i.e., fiber splitting into ultimate cells, stretching and uncoiling of microfibrils in the cells of fibers, transverse microcracking, and multiple ultimate cell fracture) have also been described in polymers reinforced with natural fibers (Fig. 11-5).

11.3.2 Starch/Natural Fiber Composites

Various reinforcing materials are mixed with starch-based polymers to increase the modulus or impact toughness. For preparing starch/natural fiber composites, different processing techniques have been used including kneading, extrusion, and postcompression molding or injection molding. When a biodegradable thermoplastic polymer is blended with natural fibers, good dispersion and distribution of the fibers are necessary.

Kneading, intensive mixing, and twin-screw extrusion produce a high shear stress, which is the main factor in improving the quality of mixing. Figure 11-6 shows schematically the influence of shear and chemical treatment on natural fibers in terms of dispersion and distribution. Intensive or dispersive mixing is related to reduction of phase domains, breaking the solid agglomerations, and produces a good distribution. Such a mixing mechanism is associated with shear stress levels developed in the equipment. Agglomerates break into individual particles when internal stresses exceed a threshold value. This value will depend on the nature of the bonds holding the particles of the agglomerate together, as well as the sizes of the fibers.

Extensive or distributive mixing or blending is related to decrease of the concentration of the agglomerated phase. Such a situation can be improved by

TABLE 11-3 Composition of Different Natural Fibers

Natural Fiber	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Pectin (%)	Wax (%)	Spiral Angle (°)	Humidity (%)	Reference
Jute	61–71.5	12–13	13.6–20.4	0.2	0.5	8.0	12.6	Bledzky (1996), Hon (1992), Ugbolue (1990)
Flax	71	2.2	18.6–20.6	2.3	1.7	10.0	10.0	Bledzky (1996), Hon (1992), Ugbolue (1990)
Hemp	70.2–74.4	3.7–5.7	17.9–22.4	0.9	0.8	6.2	10.8	Bledzky (1996), Hon (1992), Ugbolue (1990)
Ramie	68.6–76.2	0.6–0.7	13.1–16.7	1.9	0.3	7.5	8.0	Bledzky (1996), Hon (1992), Ugbolue (1990)
Kenaf	31–39	15–19	21.5	–	–	–	–	Hon (1992), Rowell (1992),
Sisal	67–78	8.0–11.0	10.0–14.2	10.0	2.0	20.0	11.0	Bledzky (1996), Hon (1992), Ugbolue (1990)
Henequen	77.6	13.1	4–8	–	–	–	–	Hon (1992)
Cotton	82.7	–	5.7	–	0.6	–	–	Bledzky (1997)

TABLE 11-4 Properties of Various Fibers

Fiber	Density (g/cm^3)	Diameter (μm)	Strength (MPa)	Tensile Modulus (GPa)	Elongation at Break (%)	Price (U$/kg)	Reference
				Natural Fibers			
Cotton	1.5–1.6	–	287–800	5.5–12.6	7.0–8.0	0.40	Chand (1994), Bledzky (1999)
Jute	1.3–1.45	25–200	393–773	13–26.5	1.16–1.5	0.30	Bledzky (1996/99), Ugbolue (1990)
Flax	1.50	–	345–1100	27.6	2.7–3.2	0.26	Bledzky (1996/99), Ugbolue (1990)
Hemp	–	–	690	–	1.6	–	Bledzky (1996), Ugbolue (1990)
Ramie	1.50	–	400–938	61.4–128	1.2–3.8	0.29	Bledzky (1996/99), Chand (1994)
Sisal	1.45	50–200	468–640	9.4–22.0	3–7	0.36	Bledzky (1996/99), Chand (1994)
				Synthetic fibers			
Glass E	2.5	–	2000–3500	70	2.5	3.20	Bledzky (1996)
Glass S	2.5	–	4570	86	2.8	3.25	Saechttling (1987)
Aramide	1.4	–	3000–3150	63–67	3.3–3.7	–	
Carbon	1.7	–	4000	230–240	1.4–1.8	500	

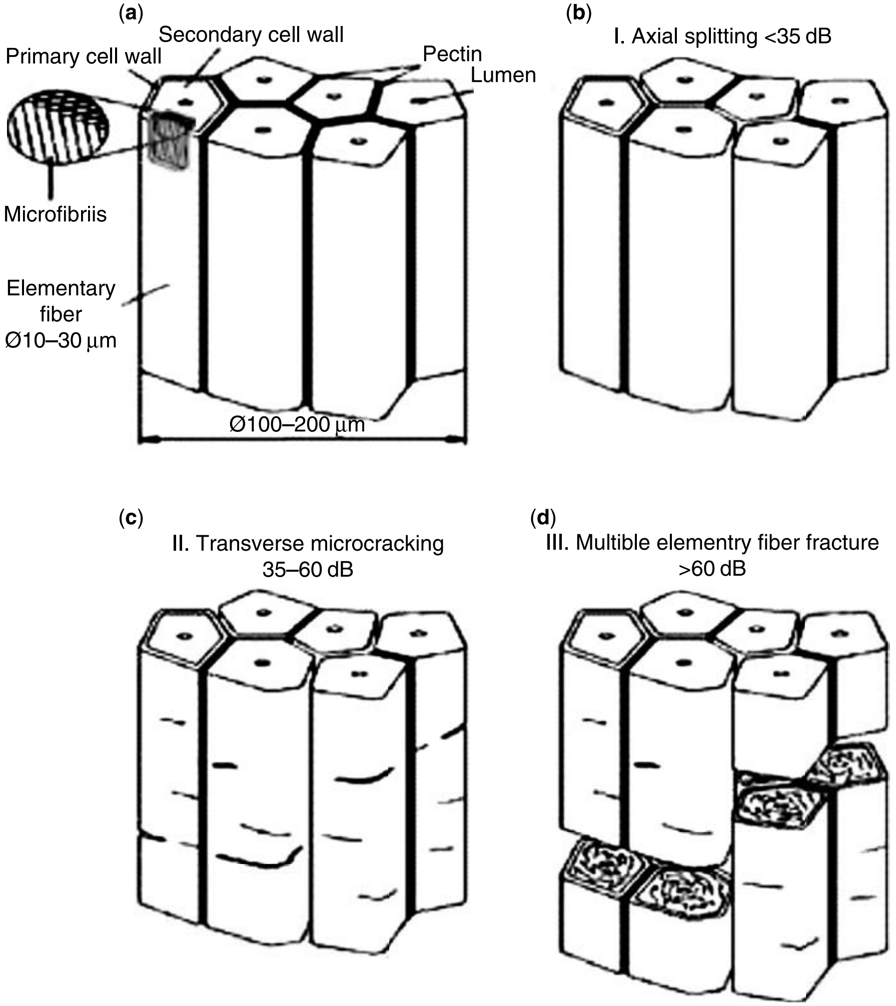


Fig. 11-5 Energy-dissipation mechanisms of natural fibers. (Reproduced with permission from *Macromolecular Materials and Eng*. **2003**, 288(9):699–707. Copyright 2008, Wiley Ed.)

good compatibility between matrix and fibers, because the agglomerate will be more easily separated and a greater interfacial area will be exposed to the polymer matrix.

Carvalho et al. (2003) studied the effect of processing conditions on the degradation of starch/cellulose composites, demonstrating that the degree of degradation could be evaluated by size-exclusion chromatography. Starch from waxy maize and bleached kraft pulp from *Eucalyptus urograndis* was used as raw material. The effect of chain scission is more important on the high-molecular-weight fraction of

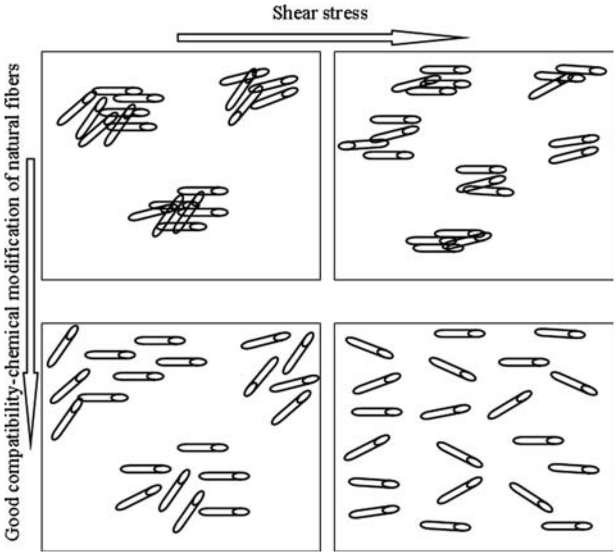


Fig. 11-6 Schematic of natural fiber mixing.

starch, mainly the amylopectin fraction. Increase of glycerol content reduced chain degradation, but increase of fiber content produced an increase of degradation, possibly due to the higher viscosity and as consequence higher shear stresses.

Curvelo et al. (2001) prepared pulp fibers with thermoplastic corn starch (with glycerol). Starch and 30 wt% of glycerol were premixed in a bags to obtain a powder. Then the composites were prepared in a Haake Rheomix 600 batch mixer at 170°C. Composites with low quantities of fiber (16 wt%) showed an significant increase in the tensile properties (tensile modulus and tensile strength). These composites exhibited good adhesion between the fibers and the matrix. Moisture sorption was reduced with the incorporation of fiber. These results are attributed to the fact that starch is more hydrophilic than cellulose and the fibers absorb some of the glycerol.

Gáspar et al. (2005) studied the effect of the addition of cellulose, hemicellulose, and zein (protein) to thermoplastic starch. The best mechanical properties were obtained with hemicellulose and zein; the addition of cellulose fibers produced a decrease in the mechanical properties of the starch. These authors also analyzed the water absorption behavior of these materials.

Averous et al. (2001) studied the effect of the addition of cellulose fibers to TPS matrix, and focused especially on the interaction between the fibers and the matrix. They observed an increase in the main transition temperature and correlate this behavior with the matrix–fiber interaction and a decrease in the mobility of the starch chains. Mechanical properties (an increment with fiber incorporation) and SEM observations clearly support the suggestion.

A series of papers were published by Gómez et al. (2006). They studied biocomposites of starch and natural fibers, processed by compression molding, using different starch sources: potato, sweet potato, and corn. Natural fibers, including jute, sisal, and cabuya, in the range of 2.5–12.5 wt%, were used as reinforcements and two different plasticizers (water and glycerol) were employed. The mechanical properties increased with fiber content. Whereas the tensile strength was particularly improved with 10 wt% of sisal, the higher values of impact strength were obtained with cabuya fibers.

A very interesting material was studied by Duanmu et al. (2007), who synthesized and prepared composites obtained from allylglycidyl-ether (AGE) modified potato starch as matrix, ethyleneglycol dimethacrylate (EGDA) as crosslinker, and wood fiber as reinforcement, showing that the tensile properties (modulus and strength) were higher (by approximately one order of magnitude) than cellulosic fiber-reinforced natural polymer composites previously reported. They also studied the effect of humidity on the mechanical properties of these materials, showing a clear detriment of mechanical behavior in wet environments.

Despite the mechanical properties of nanocellulose fibers (Young's modulus 140 GPa and tensile strength 1.76 GPa), the mechanical properties of nanocomposites based on nanofibers have not shown much better properties than natural fiber-based composites. This may be due to the fiber–matrix compatibility and processing techniques used in the fabrication of such nanocomposites. Lu et al. (2006) studied the effect of ramie nanocrystallites (0–40 wt%) on the behavior of plasticized starch. The nanocrystals were prepared by acid hydrolysis and had average length of 538.5 nm and diameter of 85.4 nm. Both the tensile strength and modulus were improved by the incorporation of nanocrystals. The authors observed the homogeneity of the biocomposites by SEM and also by studying the tensile stress–strain curves. Their results differ from those of Anglés and Dufresné (2001), who studied waxy maize starch reinforced with tunicin cellulose whiskers. The differences may be related to the plasticizer accumulation and to the strong interaction between the components and a plasticizer in the cellulose–amylopectin interface.

Takagi and Asano (2008) have obtained high reinforcing ratios ($E_{\mathrm{composite}}/E_{\mathrm{matrix}}$) using a stirrer and compression molding. They observed that when the molding pressure was increased, the density and the mechanical properties also increased. As consequence, low void content was obtained and the flexural strength increased from 10 to 65 MPa, and the flexural modulus increased from 1 to 6.5 GPa.

Table 11-5 shows the tensile properties of different starch/cellulose fiber composites; Fig. 11-7 shows the reinforcing ratio for the tensile strength of the composites with respect to each starch matrix.

It is clear that the incorporation of cellulose-based fibers into starch matrices produces an increase in the mechanical properties. The degree of reinforcement depends on the kind of starch (source), the plasticizer used (type and content), the fibers (type and aspect ratio), the processing technique, and the relative humidity of the environment. All of these parameters have to be taken into account in order to obtain a material with desired properties.

TABLE 11-5 Tensile Properties of Composites Based on Starch/Cellulose Fibers

Starch Type	Reinforcement	l/d	Glycerol (%)	E (GPa)	σ (MPa)	Reference
Corn	None	–	30	0.9	9.0	Gáspár et al. (2005)
	10 wt% cellulose	–		0.6	3.0	
Corn	None	–	30	0.125	5.0	Curvelo et al. (2001)
	16 wt% *Eucalyptus grandis* pulp-wood	–		0.320	11.0	
Corn	None	–	30(U/F)	0.042	4.1	Ma et al. (2005)
	5 wt% micro winceyette fiber	–		0.045	7.0	
	10 wt% micro winceyette fiber	–		0.051	8.2	
	15 wt% micro winceyette fiber	–		0.090	11.2	
	20 wt% micro winceyette fiber	–		0.140	15.2	
Wheat	None	–	18	0.087	3.6	Averous et al. (2001)
	10 wt% leaf-wood cellulose	3		0.348	7.2	
		15		0.435	10.8	
		45		0.510	14.4	
Wheat	None	0	3	0.056	2.8	Lu et al. (2006)
	5 wt% ramie cellulose nanocrystallites	6		0.07	4.0	
	10 wt% ramie cellulose nanocrystallites			0.15	5.15	
	20 wt% ramie cellulose nanocrystallites			0.23	5.35	
	30 wt% ramie cellulose nanocrystallites			0.41	6.15	
	40 wt% ramie cellulose nanocrystallites			0.475	6.9	

Wheat	None	–		0.052	3	Averous et al. (2001)
	15 wt% leaf-wood cellulose	3		0.296	7	
		15		0.350	10	
		45		0.430	13	
	20 wt% leaf-wood cellulose	3		0.757	13	
		15		0.630	15	
		45		0.670	22	
Waxy maize (amylomaize)	None		33		3	Funke et al. (1998)
	2 wt% Cellunier F				5.25	
	7 wt% Cellunier F				7	
	15 wt% Cellunier F				4.50	
	2 wt% Temming 500				4.75	
	7 wt% Temming 500				6.25	
	15 wt% Temming 500				7	
Potato (allyglycidylether modified)	None (LDS: low degree of substitution) dry			0.313	13	Duanmu et al. (2007)
	LDS 40 wt% wood dry	100		2.285	56	
	LDS 60 wt% wood dry			2.823	59	
	LDS 60 wt% wood wet			0.138	4	
	None (HDS: high degree of substitution) dry			0.359	15	
	HDS 40 wt% wood dry			2.875	77	
	HDS 60 wt% wood dry			3.130	90	
	HDS 60 wt% wood wet			0.428	26	
	HDS 70 wt% wood			3.777	146	

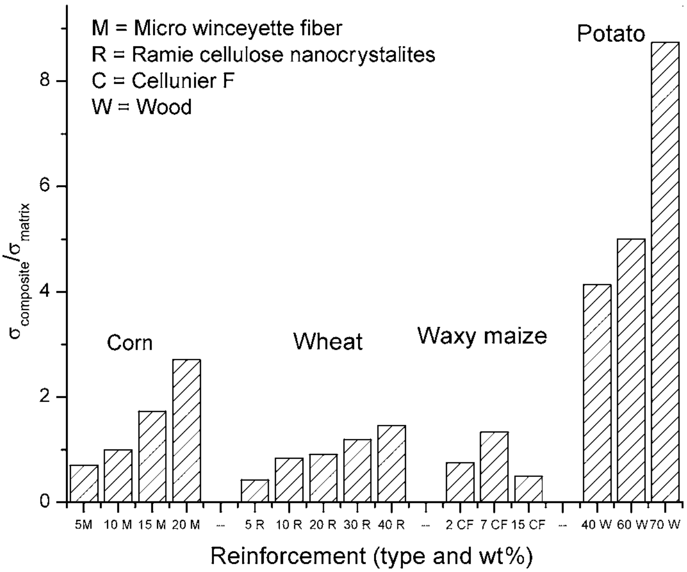


Fig. 11-7 Ratio of composite and matrix tensile strengths of different starches with degree of natural fiber incorporation.

11.4 STARCH-BASED POLYMER BLENDS AS POLYMER MATRIX

Another possibility for improving the behavior of starches is blending them with another polymer to produce starch-based blends. An number of important biodegradable polymers are derived from both synthetic and natural sources (Kaplan et al., 1993; Chiellini and Solaro, 1996; Amass et al., 1998), but most of these are quite costly. Starch is a potentially useful material for biodegradable plastics because of its natural abundance and low cost. However, starch-based materials, such as thermoplastic starch, have some drawbacks including poor long-term stability caused by water absorption, poor mechanical properties, and processability.

The development of low-cost biopolymers such as starch-based materials obtained from renewable resources has become crucial. For maintaining the biodegradability of the blend, known biopolymer components include aliphatic polyesters like polycaprolactone (PCL), poly(lactic acid) (PLA), poly(hydroxybutyrate-co-valerate) (PHBV), and poly(ester amide) (PEA) (Huang et al., 1993; Ramsay et al., 1993; Bastioli et al., 1995; Verhoogt et al., 1995; Chiellini and Solaro, 1996; Amass et al., 1998; Lorcks, 1998; Myllymäki et al., 1998; Averous et al., 2000; Bastioli, 2001). Some starch-based blends have been commercialized, such as MaterBi® (Novamont, Italy) and Bioplast® (Biotec, Germany).

Novamont, based in Italy, is a prominent European company in the business of manufacturing and supplying starch-based products. It markets its product under

TABLE 11-6 Biodegradable Starch-Based Polymers Commercially Used

Product	Company	Components
Amipol	Japan Cornstarch	Starch (100%)
Biofil	Samyang Genex Co.	Starch/polystyrene
Greenpol	Yukong Ltd.	Starch/polycaprolactone
MaterBi	Novamont	Starch/PVA–starch/PCL–starch/ cellulose derivatives
Novon	Chisso Warner Lambert	Starch (90–95%)/additives

the name MaterBi. Biotec GmbH in Germany has three product lines manufacturing Bioplast® granules for injection molding, Bioflex® film, and Biopur® foamed starch. Other manufacturers of starch-based polymer presently include Avebe, Earth-Shell, Groen Granulaat, Hayashibara Chemical Labs, Midwest Grain Products, National Starch, Rodensburg Biopolymers, Starch Tech, Supor, and Vegemat (Placket and Vazquez, 2004). Some commercial blends are summarized in Table 11-6.

Polycaprolactone (PCL)/starch blends and also cellulose derivative/starch blends are among the most widely used biodegradable polymers. Whereas the first of these is mainly used for films, the second is commonly processed by extrusion or injection. The properties of both matrices are summarized in Table 11-7.

PCL is commercially available and widely produced. The addition of PCL to starch produces an increase in the tensile strength as a function of PCL content (Koening and Huang, 1995; Pranamuda et al., 1996). Similar results were obtained with poly(hydroxyalkanoates) (PHA) and polylactides (PLA) (Ramsay et al., 1993; Koening and Huang, 1995; Kotnis et al., 1995; Ke and Sun, 2000).

Several workers have improved the mechanical behavior of starch-based blends by chemical treatment of one of the phases in the blend. The free hydroxyl groups in starch can be chemically modified to produce starch esters, starch ethers, and other derivatives. The C-2, C-3, and C-6 hydroxyl groups can be tailored, the C-6 primary hydroxyl being preferred due to its exposed position. Another possibility is to crosslink the starch, including starch modified by epoxidation and starch

TABLE 11-7 Physical and Mechanical Properties of Some Biodegradable Commercial Blends

Property	PCL/Starch Blend	Cellulose Derivative/Starch Blend
T_g (°C)	−60	105
T_m (°C)	66	–
MFI (g/10 ml)	2–4	6–30
Tensile strength (MPa)	20–50	15–35
Tensile modulus (MPa)	100–600	600–5000
Elongation at break (%)	200–600	20–150
Flexural modulus (MPa)	400–600	2000–2500

phosphates or diphosphates. For economic reasons, the last treatments are not often used in commercial products (Placket and Vazquez, 2004). Willett et al. (1998) reported improvements in tensile strength by grafting poly(glycidyl methacrylate) to starch granules. The size and shape of the granules as well as the chemical composition depend on the type of starch. For example, Willett and Felker (2005) obtained different results when potato or corn starch granules were used in the blend. The starch granules can be more easily debonded (i.e., at lower stress) from PEA matrix in potato/PEA blends than in corn/PEA blends.

However, the best properties were obtained by the addition of TPS (no granules) into other polymers because the matrix is more coherent. Averous et al. (2001) prepared a TPS/PEA blend in which PEA was the minor phase and reported that the blend had good interphase compatibility.

Chemical treatment such as grafting of one of the polymers in the blend does not improve only the interphase—the size of the separated phase decreases and the mechanical properties are also improved.

11.5 STARCH-BASED BLEND/NATURAL FIBER COMPOSITES

Starch-based blends have limited mechanical properties for several applications, but an increase of tensile strength can be achieved by compounding them with fibers. The fibers have a higher tensile strength and Young's modulus and a lower elongation at break than the matrix. As already mentioned, discontinuous fibers have been widely used as reinforcement (Mouzakis et al., 2000) of thermoplastic matrices in order to obtain better mechanical properties and processability. Several authors have studied the effect of incorporation of natural fibers on the behavior of starch-based blends, focusing on different aspects. In the following, we analyze each aspect separately.

11.5.1 Mechanical Properties

The mechanical properties of short-fiber-reinforced polymer composites depend on many factors: the mechanical properties of each component (the matrix and the reinforcement); the fiber content (volume fraction); fiber aspect ratio (length to diameter ratio) and fiber orientation; and the fiber-matrix interaction/adhesion, which is related to the compatibility between them. Fiber aspect ratio should be above a critical value for maximum stress in the fiber before composite failure. In addition, dissipation mechanisms, which determine the toughness, are also affected by the fiber aspect ratio: fibers with subcritical aspect ratio will be pulled out rather than broken. Similarly, fiber orientation has a significant influence on the mechanical properties of the composites, the stress value being maximum along the axis of orientation of the fiber. Processing conditions also have an important effect on the mechanical properties in terms not only of fiber orientation but also of fiber breakage, length reduction and defibrillation, and diameter reduction (Joseph et al., 1999).

***11.5.1.1 Tensile Properties* (Table 11-8; Fig. 11-8)** One of the most studied starch-based blends is starch–polycaprolactone. Wollerdorfer and Bader (1998) have studied the effect of incorporation of flax and ramie as reinforcements of MaterBi, type ZI01U which consists of corn starch and a biodegradable polyester and a starch blend produced by compounding thermoplastic wheat starch with 40% poly-ε-caprolactone (PCL). In the case of MaterBi, the tensile strength clearly increased when fibers were incorporated; nevertheless, there was no additional rise with fiber contents higher than 15 wt%. For noncommercial blends, while no reinforcement effect was observed with ramie, the TPS/PCL compounds displayed a similar effect to those based on MaterBi by the addition of flax.

Cyras et al. (2001) studied MaterBi ZF03 reinforced with short sisal fibers. They have demonstrated that the initial fiber bundles are separated during processing into smaller fibers that have a rough surface and that the reduction of fiber diameter contributes to the enhancement on the fiber–matrix contact due to higher available surface. Nevertheless, the aspect ratio (l/d) did not show not an important increase with the fiber content, because processing also produces a shortening of the fibers. Regarding mechanical properties, the authors shows that fibers operate as reinforcement: both the elastic modulus and the tensile strength were higher with incorporation of sisal fibers despite the damage occurred during processing.

Ali et al. (2003) reinforced MaterBi Z with short sisal fibers. They found an important increase in both the tensile strength and the tensile modulus of this matrix on the incorporation of 20 wt% of sisal fibers.

As can be seen from Table 11-8, the incorporation of around 20 wt% of sisal fibers into this kind of matrix produced an >600% increase in the tensile modulus. However, analysis of the tensile strength shows that the increment is related to the type of fiber (sisal > ramie > flax) and also to the fiber content (being higher for higher fiber content).

Another important starch-based blend is *starch/cellulose derivatives.* Within blends of this kind, Wollerdorfer and Bader (1998) studied Bioplast GS 902, which is a blend consisting of potato starch, modified cellulose, and synthetic polymers. The observation that resistance did not change with fiber incorporation or fiber content was probably related to incomplete disintegration of starch grains.

Ali et al. (2003) have also studied the effect of 20 wt% of short sisal fibers on the mechanical properties of MaterBi Y101, showing a clear increase in tensile modulus and a decrease in tensile strength.

Lanzillota et al. (2002) analyzed the effect of flax fiber addition on the tensile behavior of MaterBi Y101, showing that tensile strength as well as tensile modulus increased when fibers were incorporated into the neat matrix, but the fiber content did not show any important additional effect.

Alvarez et al. (2003) have analyzed the tensile properties of MaterBi Y/short sisal fiber composites. They determined that the elastic modulus and mechanical strength of the composites increase with fiber content, confirming the reinforcing

TABLE 11-8 Tensile Properties of Starch-Based Blends/Natural Fiber Composites

Matrix	Reinforcement[a]	σ (MPa)	E (MPa)	Reference
	Starch/Biodegradable Polyester			
MaterBI® ZI01U (corn starch and a biodegradable polyester)	None	15.26		Wollerdorfer and Bader (1998)
	15 wt% ramie	25.10		
	15 wt% flax	20.83		
	20 wt% flax	21.64		
	25 wt% flax	20.51		
MaterBi ZF03 (corn starch and a biodegradable polyester)	None	4.03 ± 0.68	28 ± 8	Ali et al. (2003)
	20 wt% sisal	10.4 ± 1.44	222 ± 24	
MaterBi-Z ZF03 (corn starch and a biodegradable polyester)	None	7.3 ± 1.3	37 ± 0.9	Cyras et al. (2001)
	10 wt% sisal	10.9 ± 0.9	138 ± 13	
	20 wt% sisal	12.7 ± 0.5	257 ± 17	
	30 wt% sisal	14.4 ± 1.6	687 ± 119	
TPS : PCL [thermoplastic wheat starch with 40% poly-ε-caprolactone (PCL)]	None	20.84		Wollerdorfer and Bader (1998)
	15 wt% ramie	19.95		
	15 wt% flax	27.61		
MaterBi® LF01U (potato, corn, and wheat starch)	None	24	95	Romhány et al. (2003b)
	20 wt% flax UD	48 ± 6	2600 ± 300	
	40 wt% flax UD	73 ± 3	5900 ± 600	
	60 wt% flax UD	78 ± 4	9300 ± 1400	
	20 wt% flax CP	30 ± 6	1800 ± 400	
	40 wt% flax CP	53 ± 5	4500 ± 500	
	60 wt% flax CP	55 ± 3	5900 ± 30	
Bioplast GS 902 (potato starch, modified cellulose, and synthetic polymers)	None	27.72		Wollerdorfer and Bader (1998)
	15 wt% ramie	24.77		
	15 wt% flax	24.23		
	25 wt% flax	29.37		
	35 wt% flax	27.15		
	Starch/Cellulose Derivatives			
MaterBi Y101(starch and cellulose derivatives)	None	17.6 ± 3.32	704.6 ± 16.9	Ali et al. (2003)
	20 wt% sisal	14.2 ± 0.92	1032.2 ± 39.7	
MaterBi Y101 (starch and cellulose derivatives)	None	12.6 ± 0.7	945 ± 90	Alvarez et al. (2003)
	5 wt% sisal	14.4 ± 0.7	1390 ± 150	
	10 wt% sisal	15.7 ± 0.9	1870 ± 169	
	15 wt% sisal	16.8 ± 0.9	2220 ± 178	
MaterBi Y101 (starch and cellulose derivatives)	None	28	1000	Lanzillota et al. (2002)
	20 wt% flax	48	3900	
	30 wt% flax	49	3900	
	40 wt% flax	51	4300	
SCA (starch and cellulose acetate)	None	31.5	1300	Cunha et al. (2004)
	20 wt% wood flour	19.0	3000	
	40 wt% wood flour	22.5	4200	
	50 wt% wood flour	33.0	5700	
	60 wt% wood flour	15.0	5700	

[a] UD, unidirectional; CP, cross-ply.

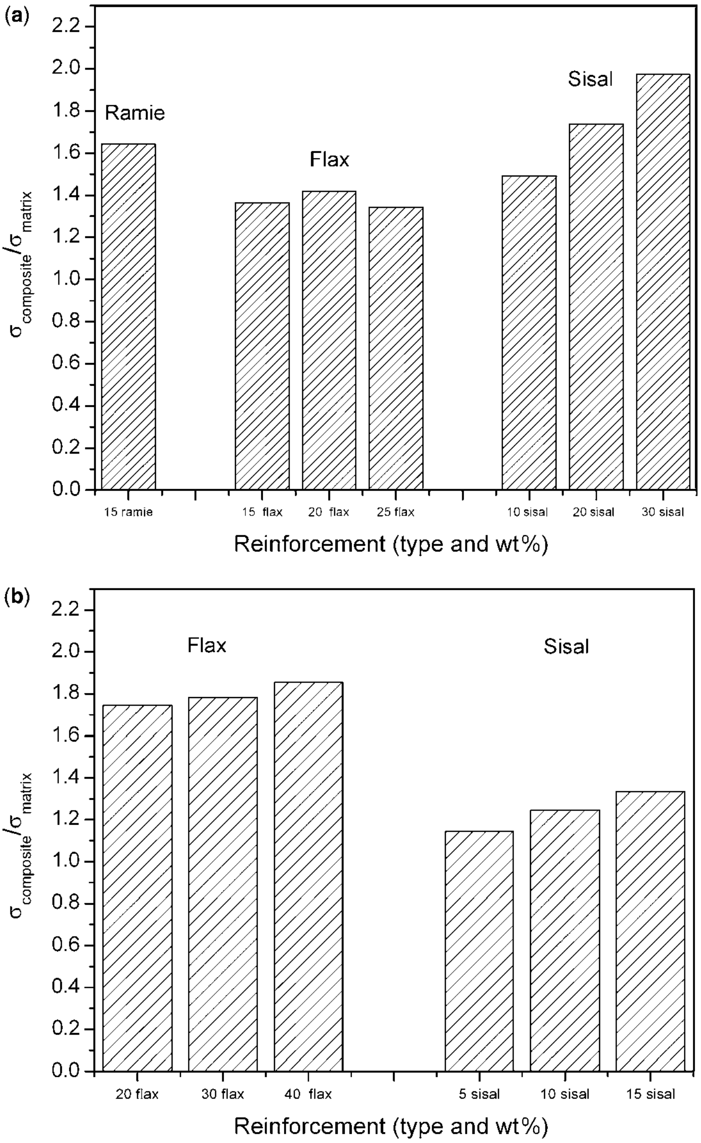


Fig. 11-8 Ratio of composite and matrix tensile strength as a function of fiber content for different fibers in (a) starch/polycaprolactone blends and (b) starch/cellulose derivative blends.

action of the fibers. They also established (Alvarez et al., 2006a) the effect of fiber orientation on the tensile properties, showing higher values for parallel-oriented fibers, intermediate values for random orientation, and lower values for perpendicular orientation. Also, the fiber orientation was correlated with the processing technique (injection, oriented at the skin and random at the core; and compression molding, random).

Cunha et al. (2004) analyzed the mechanical properties of starch–cellulose acetate blend/wood flour composites. They observed that the tensile strength and the modulus improve considerably up to 50 wt% of reinforcement. In contrast, the toughness decreases slowly. The material with 50 wt% wood flour displayed the highest tensile strength and tensile modulus but is difficult to process. However, Cunha and co-workers have demonstrated that the processability can be improved by using glycerol as plasticizer. They also analyzed the effect of orientation (radial and tangential) with respect to injection point.

Comparing the results of different authors (Table 11-8), it is clear that the tensile modulus increase with natural fiber incorporation (up to 330% for 40 wt% of flax fibers). On the other hand, dissimilar results have been found in relation to the tensile strength; whereas some authors (Wollerdorfer and Bader, 1998; Ali et al., 2003) have found no differences between the matrix and the biocomposites, others (Lanzillota et al., 2002; Alvarez et al., 2004a) have shown an increasing trend with fiber incorporation and fiber content. The differences, working with the same kind of matrices and fibers, could be related to the processing technique and the fiber aspect ratio (l/d), as will be explained later.

The starch based blends described exhibit important differences, first of all, in terms of the crystallinity: whereas starch/polycaprolactone blend is a semicrystalline polymer, starch/cellulose derivative blend is an amorphous polymer. The glass transition temperature of the first is below room temperature (around -60°C), whereas that of the second one is above room temperature (near to 100°C). These characteristics make the polymers very different (see Table 11-7) and the initial mechanical properties (without reinforcement) are also very different, especially the tensile modulus, which is 8 times higher for cellulose derivative/starch blends. Accordingly, the ratio of fiber modulus to matrix modulus (E_f/E_m) is also very different, being around 45 for polycaprolactone/starch blends and 6 for cellulose derivative/starch blends.

Romhany et al. (2003a) have analyzed the effect of flax fibers (unidirectional and crossed-ply arrangements) on the behavior of thermoplastic starch-based composites (MaterBi LF01U) obtained by hot pressing using the film stacking method. The mechanical performance and also the mode of failure of the composites depended strongly on the fiber content and the flax fiber lay-up. The tensile strength increased with higher flax fiber content up to 40 wt% and then remained almost constant. In particular, for MaterBi Y/40 wt% unidirectional fiber, the tensile strength was three times greater than that of the pure matrix. In addition, the fibers increased the tensile modulus of the neat matrix by several orders of magnitude. It should be noted that the strength depends on the interphase generated between fiber and matrix, and is related to compatibility but not the modulus.

***11.5.1.2 Flexural Properties* (Table 11-9)** Shibata et al. (2005) have studied composites prepared with a biodegradable resin, CP-300, which is blend of corn starch and PCL reinforced with kenaf and bagasse fibers. For kenaf, the flexural modulus increased as a function of fiber volume fraction up to 60% and then decreased. A similar trend was observed for flexural strength. They showed that on

TABLE 11-9 Flexural Properties of Starch-Based Blend/Natural Fiber Composites

Matrix	Reinforcement	σ (MPa)	*E* (GPa)	Reference
CP-300 (corn-starch and PCL)	None	18.75	0.49	Shibata et al. (2005)
	17 vol% kenaf	31.56	1.97	
	30 vol% kenaf	41.25	2.94	
	50 vol% kenaf	43.44	3.40	
	60 vol% kenaf	49.38	3.83	
	68 vol% kenaf	40.00	3.67	
	20 vol% bagasse	28.44	1.00	
	33 vol% bagasse	38.13	1.41	
	50 vol% bagasse	48.44	2.18	
	64 vol% bagasse	49.06	2.48	
	74 vol% bagasse	48.13	2.28	
MaterBi Y101 (starch and cellulose derivatives)	None		2.28 ± 0.25	Alvarez et al. (2004a)
	5 wt% sisal		2.32 ± 0.20	
	10 wt% sisal		2.86 ± 0.25	
	15 wt% sisal		3.42 ± 0.29	

the surface of the composites with fiber contents higher than 60%, many fibers were not sufficiently wetted by the resin; this was also observed for bagasse.

Alvarez et al. (2004a) studied the flexural modulus of MaterBi Y/short sisal fibers biocomposites. They demonstrated that incorporation of short sisal fibers notably improved the flexural stiffness of this matrix and that higher fiber content produced a higher enhancement.

***11.5.1.3 Impact Properties* (Table 11-10)** Johnson et al. (2003) studied the effect of incorporation of fiber from *Miscanthus* fiber on the impact performance of MaterBI Y101U. The miscanthus-filled MaterBi exhibited up to 30% higher impact load than the neat matrix.

Alvarez et al. (2005a) analyzed the out-of-plane impact fracture of MaterBi Y/short sisal fiber biocomposites. They established an increasing trend of the total fracture energy and related it to an increase on circumferential shear-cracking mechanism observed in impacted samples. The active mechanisms in these biocomposites were axial splitting, uncoiling of microfibrils, microcracking, and fiber pull-out. These authors have also demonstrated that under quasi-static loading the biocomposites exhibited higher resistance to crack initiation than did the neat matrix and attributed the differences to the new energy dissipation mechanisms derived from the fibers.

From the results (Table 11-10), a decrease in the disk strength in comparison to the neat matrix is evident for composites with low fiber content. A possible explanation for such behavior is that the fibers spread through the matrix can act as crack initiation points during impact (Mouzakis et al., 2000). However, an increasing tendency of

TABLE 11-10 Impact Properties of Starch-Based Blend/Natural Fiber Composites

Matrix	Reinforcement	σ (MPa)	E (kJ/m)	Reference
MaterBI® YI01U (starch, cellulose derivatives, additives)	None	106.4 ± 9.2		Johnson et al. (2003)
	10 vol% miscanthus	125.9 ± 10.1		
	20 vol% miscanthus	138.6 ± 1.9		
MaterBi-Y YI01U (starch, cellulose derivatives, additives)	None	111.0 ± 5.4	0.17 ± 0.03	Alvarez et al. (2005a)
	5 wt% sisal	80.1 ± 1.4	0.40 ± 0.13	
	10 wt% sisal	97.1 ± 1.4	0.43 ± 0.04	
	15 wt% sisal	106.4 ± 9.2	0.45 ± 0.03	
	20 wt% sisal	129.8 ± 7.6	0.61 ± 0.03	

strength with fiber content was observed. Indeed, there were enough fibers at some fiber content (20 wt% of sisal or 10 wt% of miscanthus) to enhance load transfer. For the same matrix, 20 wt% of sisal fibers gave an increase on the impact strength of around 17% whereas the same amount of miscanthus fiber produced increases up to nearly 30%. In addition, the energy values from Table 11-10 suggest that the incorporation of sisal fibers into the biodegradable matrix is an efficient way to improve impact fracture properties.

***11.5.1.4 Creep Properties* (Table 11-11)** Creep behavior is one of the most important mechanical properties that needs to be known for the structural design of thermoplastic composites where the dimensional stability of materials is important. Additionally, creep measurements are of primary interest in any application where the polymer must sustain loads for long periods. In spite of the importance of this subject, little information can be found in the scientific literature about creep of thermoplastic composites with natural fibers, and even less related to biodegradable polymers (Park and Balatinecz, 1998; Vázquez et al., 1999; Cyras et al., 2001; Alvarez et al., 2004a).

TABLE 11-11 Creep Properties of Starch-Based Blend/Natural Fiber Composites

Matrix	Reinforcement	Q (kJ/mol)	E_1 (MPa)	τ_2 (s)	Reference
MaterBi-Z ZF03 (corn starch and a biodegradable polyester)	None	318.7	320	250.0	Cyras et al. (2002)
	10 wt% sisal	343.3	590	269.0	
	20 wt% sisal	381.0	1020	236.4	
	30 wt% sisal	382.0	950	326.9	
	40 wt% sisal	350.3	805	232.6	
MaterBI-Y YI01U (starch, cellulose derivatives, additives)	None	102	2000	2.84	Alvarez et al. (2004a)
	5 wt% sisal	114	2700	1.83	
	10 wt% sisal	124	3400	1.05	
	15 wt% sisal	147	4000	0.81	

Cyras et al. (2002) analyzed the flexural creep behavior of MaterBi Z/short sisal fiber composites at different temperatures, demonstrating that creep performance was enhanced as a function of the fiber content but also that the fragmentation of the polymer chains and natural fibers clearly influenced the creep behavior.

Alvarez et al. (2004a) studied the creep performance of MaterBi Y/short-sisal fibers and analyzed the creep behavior at different temperatures and fiber content. They showed that the highest fiber content produces the highest creep resistance and flexural modulus.

Several models have been used to predict behavior and analyze properties. For MaterBi Y, the test temperature was below the T_g value. The elastic modulus E_1 increases with the fiber content. These results are in agreement with those obtained for flexural modulus. The viscosity η_1 increased with the fiber content, and lower flow occurred at the dashpot and the permanent deformation decreased. The relaxation time τ_2 decreased with the fiber content; this is an indication that the viscous creep decreases and adding fibers enhances the elastic part. For MaterBi Z, measurements were made above T_g value. The elastic modulus E_1 increases with fiber content up to 20 wt%. These results agree with those for flexural modulus. The viscosity η_1 increased with the fiber content, and lower flow occurred at the dashpot and the permanent deformation decreased. The relaxation time τ_2, increased with the fiber content; this is an indication that the viscous creep increases and adding fibers produces a smaller elastic part, perhaps due to some plasticization of the matrix related to with some kind of degradation of the natural fibers.

11.5.2 Effect of Processing Conditions (See Tables 11-12 and 11-13)

When composites are processed by extrusion, shear stresses are developed during mixing and extrusion and these stresses cause fiber damage. The shear stresses generated in extrusion process, used to disperse the fibers into the polymer, produce a great reduction in fiber length and diameter. The extent of fiber breakage depends on the residence time, the temperature, viscosity and speed of rotation, and the characteristics of the matrix (Joseph et al., 1993; Ali et al., 2003).

Several authors (e.g., Johnson, 2003) have stated that shear force in an extruder could cause fiber breakage. It was contended that as the rotational speed of the screw increases, the shear forces will increase and fiber breakage will increase, producing a greater degree of fiber damage.

Processing conditions can also influence the extraction of lignin from natural fibers and/or promote some chemical or physical modification of components during the mixing process. This effect can result from higher processing temperature, speed of rotation, or time of mixing employed (Ali et al., 2003). Thus, the appropriate selection of processing parameters is of crucial importance for the final behavior of the biocomposites.

Ali et al. (2003) studied the effect of processing conditions on the tensile and creep performance of MaterBi Y and MaterBi Z with short sisal fibers. They have shown a clear increase in the aspect ratio with increasing speed of rotation, whereas only a moderate change was seen by extending the time of mixing. The changes in aspect

TABLE 11-12 Effect of Processing Conditions on the Final Natural Fiber Dimensions

(a) MaterBi Y 20 wt% sisal, 180°C[a]

Conditions	l/d
20 rpm, 2 minutes	60.6
20 rpm, 4 minutes	66.4
20 rpm, 6 minutes	74.7
50 rpm, 2 minutes	73.4

(b) MaterBi Y 15 wt% sisal, double-screw extruder at 60 rpm[b]

T (°C)	l (mm)	d (mm)	l/d
180	2.23	0.17	14.48
185	1.57	0.13	14.64
190	1.19	0.09	16.40

(c) MaterBi Y 15 wt% sisal, double-screw extruder at 180°C[b]

SR (rpm)	l (mm)	Reduction (%)	d (mm)	Reduction (%)	l/d
25	2.16	58.2	0.173	49.0	13.41
60	1.53	70.4	0.130	57.0	14.66
80	1.47	71.0	0.098	67.3	21.07

[a] Ali et al. (2003).

[b] Alvarez et al. (2005b).

ratio were greater for MaterBi Z. These authors found an increase in the tensile properties when the speed of rotation was higher due to the higher final aspect ratio of the sisal fibers, related to higher shear forces. They have observed similar tendencies for creep performance.

Johnson et al. (2003) studied the effect of processing parameters on the impact performance of MaterBi Y101U/mischanthus fiber biocomposites, finding that the temperature of the barrel and the rotational speed of the screw affect the performance. They demonstrated that materials molded at higher temperature (190°C) have better impact properties than those molded at lower temperature (170°C). In addition, at higher speed of rotation (300 rpm) the composite molded at lower temperature resisted higher impact loads than that molded at higher temperature; they related this behavior to the degree of heating imparted by the screw to the polymer melt due to the shear forces, which can degraded the natural fibers and affect the impact performance of MaterBi Y/miscanthus biocomposites. On the other hand, at lower temperature, the speed of rotation can homogenize the material, improving the impact performance.

Alvarez et al. (2005b) evaluated the effect of the processing conditions on the final properties of MaterBi Y/short sisal fiber composites, using three different temperature profiles in a twin-screw extruder and varying the speed of rotation.

TABLE 11-13 Effect of Processing Conditions on the Mechanical Properties of Starch-Based Blends/Natural Fiber Composites

Matrix	Reinforcement	σ (MPa)	*E* (MPa)	Reference
(a) Tensile Properties				
MaterBi ZF03 (corn starch and a biodegradable polyester)	20 wt% sisal; 120°C; 110 rpm			Ali et al. (2003)
	2 minutes	9.03 ± 0.49	198.6 ± 27	
	6 minutes	10.39 ± 1.44	222.0 ± 24.2	
	20 wt% sisal; 120°C; 6 minutes			
	60 rpm	6.67 ± 1.65	116.7 ± 9.1	
	110 rpm	10.39 ± 1.44	222.0 ± 24.2	
	20 wt% sisal; 110 rpm; 6 minutes			
	120°C	10.39 ± 1.44	222.0 ± 24.2	
	140°C	10.09 ± 2.32	275.8 ± 58.1	
MaterBi Y101 (starch and cellulose derivatives)	20 wt% sisal; 180°C; 20 rpm			Ali et al. (2003)
	2 minutes	14.15 ± 0.92	1032.2 ± 39.7	
	4 minutes	12.00 ± 5.80	1081.6 ± 93.2	
	6 minutes	18.60 ± 1.98	1183.3 ± 25.8	
	20 wt% sisal; 20 rpm; 2 minutes			
	140°C	12.30 ± 0.57	958.0 ± 5.9	
	160°C	12.60 ± 2.83	995.9 ± 59.5	
	180°C	14.15 ± 0.92	1032.2 ± 39.7	
	20 wt% sisal; 180°C; 2 minutes			
	20 rpm	14.15 ± 0.92	1032.2 ± 39.7	
	50 rpm	22.35 ± 0.21	1249.5 ± 13.6	
MaterBI-Y YI01U (starch, cellulose derivatives, additives)	15 wt% sisal; 60 rpm			Alvarez et al. (2005b)
	180°C	15.2 ± 1.6	880 ± 79	
	185°C	16.8 ± 0.9	1552 ± 160	
	190°C	16.4 ± 1.8	1601 ± 91	
	15 wt% sisal; 185°C			
	25 rpm	14.8 ± 1.1	1172 ± 158	
	60 rpm	16.8 ± 0.9	1552 ± 160	
	80 rpm	16.1 ± 1.5	1443 ± 99	

(*Continued*)

TABLE 11-13 *Continued*

Matrix	Reinforcement	σ (MPa)		E (MPa)		Reference
(b) Impact Properties						
		170°C		190°C		
		150 rpm	300 rpm	150 rpm	300 rpm	
MaterBI® YI01U (starch, cellulose derivatives, additives)	10 vol% miscanthus	117.0 ± 13	122.3 ± 10	135.5 ± 21	125.9 ± 10	Johnson et al. (2003)
	20 vol% miscanthus	107.5 ± 33	113.4 ± 22	135.5 ± 11	138.6 ± 2	
		σ (MPa)		E (kJ/m)		
MaterBI-Y YI01U (starch, cellulose derivatives, additives)	15 wt% sisal; 60 rpm					Alvarez et al. (2005b)
	180°C	101.0 ± 1.6		0.74 ± 0.01		
	185°C	134.0 ± 0.9		0.84 ± 0.10		
	190°C	116.7 ± 1.8		0.82 ± 0.05		
	15 wt% sisal; 185°C					
	25 rpm	130.2 ± 0.6		0.68 ± 0.01		
	60 rpm	134.0 ± 0.9		0.84 ± 0.10		
	80 rpm	128.8 ± 1.2		0.74 ± 0.04		

The mechanical properties increased when rotation speed changed from 25 to 60 rpm; they then decreased because fiber breakage increased with rotational speed. Aspect ratio also increases (Table 11-12), but at high speed degradation of the matrix occurs. Impact properties increased with temperature but decreased at temperatures higher than 185°C, again related to the thermal degradation of the matrix. The changes in the aspect ratio were evidently greater as a function of the speed of rotation than as a function of the temperature.

As a general result, we can say that higher temperature produces a decrease in the viscosity of the matrix and better mixing, but it is also possible that the viscous dissipation increases and the matrix may experience some thermal degradation; the viscosity of the matrix increases as a result of this effect, especially in the case of cellulose derivative/starch blends whose processing temperatures are higher (around 180°C) than those of polycaprolactone/starch blends (around 100–120°C). Shear stresses increase due to the increase in viscosity, and the fiber aspect ratio increases. The tensile stress transfer to the fibers increases when the aspect ratio of the fibers increases. In addition, lignin extraction could lead to different surface properties of the fibers, which are responsible for the fiber–matrix adhesion. Carvalho et al. (2003) found a similar tendency for matrix degradation studied by changes in the molecular weight and molecular weight distribution during the mixing of thermoplastic starch (TPS) compounds of conventional corn starch and glycerol reinforced with cellulosic fibers.

Fiber breakage increases with rotational speed, but aspect ratio also increases; this effect was observed independently of the other blend component (polycaprolactone or cellulose derivatives) but the changes are more important in the case of polycaprolactone/starch blends for which the viscosity is clearly lower and the processing temperature is far from the degradation temperature, avoiding other possible consequences.

11.5.3 Rheological Behavior

The design of the most suitable processing conditions is guided mainly by the rheological behavior of the composites (Jayamol et al., 1996). A number of investigations on the rheological behavior of short natural fiber-reinforced thermoplastic and elastomers have reported (Wang and Lee, 1987; Fujiyama and Kawasaki, 1991) that incorporation of fillers in thermoplastics and elastomers will increase the melt viscosity, which may result in unusual rheological effects.

Alvarez et al. (2004b) studied the rheological behavior of MaterBi Y/short sisal fiber composites, demonstrating that the viscosity of all materials decreased with frequency (pseudoplastic behavior) but increased with fiber content. In addition, the enlargement of viscosity and storage modulus with fiber content was not linear, showing a saturation effect at higher fiber concentrations. They also analyzed the effect of processing technique, showing that compression-molded composites displayed higher viscosities than injected ones and were more difficult to process.

Cunha et al. (2004) analyzed the rheological properties of starch-cellulose acetate blend/wood fiber composites. They determined that the effect of the wood flour content on the shear viscosity was complex and a linear relationship was not established. The shear viscosity decreases with shear rate, but for composites with wood flour contents higher than 40 wt% there was evidence of quasi-newtonian behavior independently of the temperature.

11.5.4 Effect of Fiber Dimensions (See Table 11-14)

Transference of stress from the matrix to the fibers takes place when the experimental aspect ratio is higher than the critical value. For fibers with an aspect ratio lower than the critical value, pull-out occurred more than fiber breakdown. A weak interface between fiber and matrix leads to a lower reinforcement effect. The critical aspect ratio can be estimated from the interfacial strength (obtained from pull-out or micro-droplet test) and fiber strength (obtained form the single-fiber test) by use of the Kelly–Tyson equation:

$$\frac{l}{d} = \frac{\sigma_f}{2\tau} \tag{11.1}$$

where σ_f is the fiber strength and τ is the fiber–matrix interfacial strength.

Shibata et al. (2005) have also studied the effect of natural fiber length on the flexural properties of CP-300, determining that the flexural modulus rapidly decreased for fiber lengths less than 2.8 mm for kenaf and 3.2 mm for bagasse, and founding a similar trend for the flexural strength. They related this result to the critical aspect ratio (l/d) because, according to results of Hsueh (2002), the elastic modulus decreases sharply below a fiber aspect ratio of 15. The authors calculated the critical length of kenaf (3.4 mm) and bagasse (3.6 mm): fibers below these values are possibly pulled out, not broken, in the flexural test.

It is clear that the reinforcement effect depends on the experimental aspect ratio (in relation to the critical value), which is directly correlated with the fiber and matrix properties and the interfacial adhesion, which depends on the fiber–matrix compatibility (wettability of the fibers by the matrix, etc). Whereas the critical aspect ratio for sisal–starch/cellulose derivatives was around 20, in the case of sisal–starch/polycaprolactone it was near to 79; this is related to the higher fiber–matrix compatibility in the former case, which is also linked to the matrix polarity (8.7 vs. 6.7). Given that natural fibers have polar character, the higher the polarity, the higher the fiber–matrix compatibility and also the higher the interfacial adhesion. It is also necessary to take into account that in some cases the additives in the blends can occupy the interphase and make it less compatible.

11.5.5 Influence of Fiber Treatments (See Tables 11-11, 11-15–11-17)

One of the most important factors for achieving good fiber reinforcement in composites is the fiber–matrix adhesion, which depends on the structure and polarity of both

TABLE 11-14 Effect of Fiber Dimensions on the Mechanical Properties of Starch-Based Blend/Natural Fiber Composites

(a) Flexural Properties

Matrix	Reinforcement	l (mm)	σ (MPa)	l (mm)	E (GPa)	Reference
CP-300 (corn-starch and PCL)	60 vol% kenaf	2	38.0	2	2.80	Shibata et al. (2005)
		3	40.0	3	2.95	
		6	41.5	6	3.90	
		11	49.5	9	4.00	
		17	47.0	15	3.90	
	66 vol% bagasse	1	23.0	2	1.50	
		4	40.0	3	2.30	
		9	50.0	9	2.50	
		16	48.0	15	2.50	

(b) Impact Properties

		σ (MPa)		
Matrix	Reinforcement	<1 mm	>3 mm	Reference
MaterBI$^{®}$ YI01U (starch, cellulose derivatives, additives)	10 vol. % Mischantus	125.9 ± 10.1	140.2 ± 5.6	Johnson et al. (2003)
	20 vol. % Mischantus	138.6 ± 1.9	130.8 ± 7.7	

TABLE 11-15 Effect of Chemical Treatments on the Diameter and Mechanical Properties of Sisal Fibers

Sisal Fibers	E (MPa)	σ (MPa)	ε (%)	d (mm)
Untreated	7.5	190	3.2	0.30
Alkali-treated	8.7	399	4.9	0.15
Acetylated	3.7	53	2.1	0.24

TABLE 11-16 Interfacial Shear Strength and Estimated Critical Aspect Ratio for Untreated and Treated Sisal–Starch/PCL Blend and Sisal–Starch/Cellulose Derivative Blend Composites

	Starch/Polycaprolactone		Starch/Cellulose Derivatives	
Sisal Fibers	τ (MPa)	$(l/d)_c$	τ (MPa)	$(l/d)_c$
Untreated	1.2 ± 0.6	79.2	3.3 ± 1.4	20.2
Alkali-treated	1.5 ± 0.6	95.0	4.4 ± 2.5	26.6
Acetylated	1.6 ± 0.4	13.3	3.7 ± 1.8	5.9

components. In order to improve this parameter, a number of fiber treatments can be carried out on the natural fibers to modify, not only the interphase but also the morphology of the fibers (Vázquez et al., 1999; Cyras et al., 2001; Rong et al., 2001; Plackett and Vázquez, 2004; Alvarez and vázquez, 2006b). Of these processes, the most used is the alkaline treatment (Ray and Sarkar, 2001) in which impurities such as waxes, pectins, hemicelluloses, and mineral salts are removed; the change from cellulose I to cellulose II takes place and the texture of the fibers, principally their accessibility in aqueous media, is modified, which also changes the morphology of natural fibers. The other commonly used method is termed acetylation, which makes the fiber surface more hydrophobic.

The equations for both treatments are summarized here:

Alkali treatment:

$$\text{Fiber—OH} + \text{NaOH} \longrightarrow \text{Fiber—O}^{-}\text{Na}^{+} + \text{H}_2\text{O} \tag{11.2}$$

Acetylation:

$$\text{Fiber—OH} + \text{CH}_3\text{COOH} \xrightarrow[\text{H}^+]{(\text{CH}_3\text{CO})_2\text{O}} \text{Fiber—O—C=O(CH}_3) + \text{H}_2\text{O} \tag{11.3}$$

Previous treatments influence the dimensions of the natural fibers and also their mechanical properties. Table 11-15 shows the changes in the fiber dimensions, the mechanical properties, and interfacial adhesion due to chemical treatments.

The interfacial strength increases with alkali treatment, but in the case of acetylated fibers it decreases with treatment, showing the lower adhesion between fibers and matrix.

TABLE 11-17 Effect of Fiber Treatments on the Tensile Properties of Starch Based Blend/Natural Fiber Composites

Matrix	Reinforcement	Properties				Reference
		σ (MPa)		*E* (MPa)		
MaterBi ZF03 (corn starch and a biodegradable polyester)	20 wt% sisal; 120°C; 110 rpm; 6 minutes					Ali et al. (2003)
	Untreated	10.39 ± 1.44		222.0 ± 24.2		
	Treated	13.03 ± 1.68		292.2 ± 31.8		
		σ (MPa)		*E* (MPa)		
		Untreated	Treated	Untreated	Treated	
MaterBi ZF03 (corn starch and a biodegradable polyester)	10 wt% sisal	10.9 ± 0.9	6.4 ± 0.8	138 ± 13	112 ± 16	Cyras et al. (2006)
	20 wt% sisal	12.7 ± 0.5	8.8 ± 0.9	257 ± 17	221 ± 24	
	30 wt% sisal	14.4 ± 1.6	10.9 ± 2.1	410 ± 36	687 ± 119	
MaterBi YI01U (starch, cellulose derivatives, additives)	20 wt% sisal; 180°C; 20 rpm; 6 minutes					Ali et al. (2003)
	Untreated	18.60 ± 1.98		1183.3 ± 25.8		
	Treated	22.35 ± 0.21		1249.5 ± 13.6		
		σ (MPa)		*E* (GPa)		
		Untreated	Treated	Untreated	Treated	
MaterBi YI01U(starch, cellulose derivatives, additives)	5 wt% sisal	14.4 ± 0.7	15.2 ± 1.0	1.39 ± 0.2	1.41 ± 0.2	Alvarez et al. (2003)
	10 wt% sisal	15.7 ± 0.9	16.8 ± 1.2	1.87 ± 0.2	1.91 ± 0.2	
	15 wt% sisal	16.8 ± 0.9	18.1 ± 0.8	2.20 ± 0.2	2.16 ± 0.2	

For alkaline-treated fibers, the critical aspect ratio becomes higher. On the other hand, acetylated fibers show the lowest value of the critical aspect ratio, but this may be due to the low strength of that fiber that appears in equation (11.1).

Ali et al. (2003) have studied the effect of fiber treatment on the tensile properties of MaterBi Y and MaterBi Z with 20 wt% of short sisal fibers. They showed that alkaline treatment favored an increased fiber aspect ratio and improved mechanical properties of the MaterBi Z and MaterBi Y/short sisal fiber composites.

Vázquez et al. (1999) and Cyras et al. (2001) observed that the alkaline treatment used on the sisal fibers produced fibrillation and collapse of the cellular structure due to the removal of the cementing material, which leads to a better packing of cellulose chains. The higher fiber density allowed them to increase the fiber content in the extruder, limited by the fiber volume.

For MaterBi Y/short sisal fiber composites Alvarez et al. (2003) found that the water-uptake rate decreased on alkaline treatment of the fibers due to the network formed by the high content of fibers, which impairs the diffusion of the water through the matrix. However, alkaline treatment makes the sisal fibers more hydrophilic and the composites absorb more water at equilibrium in comparison with untreated fiber composites. These authors also showed that the critical strain energy release rate G_{Ic} of the treated sisal fiber composite was higher than that of the untreated ones, probably due to the fibrillar morphology, which increases the toughening and the fiber energy dissipation mechanisms of the composite.

Other results are quite dissimilar; in the case of starch/PCL matrix the modulus clearly increased (up to 70% for 30 wt% of fibers) when fibers were alkali-treated, whereas the tensile strength can either increase or decrease with respect to the composites with untreated fibers. In the case of starch/cellulose derivatives, the change in the modulus of the composite induced by fiber treatment is almost negligible.

In addition, it must be taken into account that the fiber treatment combined with the processing technique can lead to damaged fibers with properties different from those of the treated fibers alone (measured by the single-fiber test).

Alvarez et al. (2004b) have also analyzed the effect of fiber treatment on the rheological behavior of MaterBi Y/short sisal fiber composites, showing that treated fiber composites exhibited higher viscosities than untreated ones. The fiber aspect ratio increased from 17.9 for untreated fibers to 19.5 for the treated ones, so the effects can be attributed to fiber fragmentation (Cyras et al., 2004). The results argue for more severe processing conditions in the case of treated fibers.

11.5.6 Aqueous and Soil-Burial Degradation (See Table 11-18)

Information on the environmental biodegradability composites with starch-based blends is still limited. Bastioli (1998) have reported that the presence of starch influences the biodegradation rate of the intrinsically biodegradable synthetic component during composting of MaterBi Y. On the other hand, the same material exposed to a respirometric test simulating soil burial conditions was only partially degraded up to about 18% (Solaro et al., 1998). The effect of natural fibers on the biodegradation of starch-based polymers and blends is still under study.

TABLE 11-18 Components of Starch Based Blend/Natural Fiber Composites Before and After Soil-Burial Degradation

Matrix	Reinforcement	Starch (%)	Other (%)	Additives (%)	Cellulose (%)	Reference
MaterBi-Z ZF03 (corn starch and a biodegradable polyester)	*Initial*					di Franco et al. (2004)
	None	16	75 (PCL)	9	–	
	15 wt% sisal	25 (starch + hemicellulose)	45	8	21	
	Final					
	None	7	93 (PCL)	0	–	
	15 wt% sisal			0		
MaterBi-Y Y101 (starch and cellulose derivatives)	*Initial*					Alvarez et al. (2006c)
	None	38	38 (cellulose derivatives)	22	–	
	15 wt% sisal	41 (starch + hemicellulose)	47 (cellulose + cellulose derivatives)	12	47 (cellulose + cellulose derivatives)	
	Final					
	None	2	98	0	–	
	15 wt% sisal	0	100 cellulose + cellulose derivatives)	0	100 cellulose + cellulose derivatives)	

di Franco et al. (2004) have also evaluated the susceptibility of the MaterBi Z/sisal fiber composites to different degrading environments. In hydrolytic tests, both the matrix and the composites displayed stability at pH 7.2 at 25°C and 40°C. In addition, sisal fibers support water access, which swells the material and produces hydrolysis of the starch (the most bioavailable component). When fiber content increased, the material became more hydrolytically stable, which was related to the presence of a fiber–fiber physical network. Microbial attack was evidence by the presence of a biofilm, particularly on the fiber surface. In soil burial, the matrix was degraded to about 50%, the weight loss pattern of the composite being associated with the presence of strong fiber–fiber and fiber–matrix interactions.

When Alvarez et al. (2006c) studied the degradation in soil of MaterBi Y/short sisal fiber composites, they observed that water sorption was predominant during the first month, followed by weight loss; the composites absorbed less water than the pure MaterBi-Y due to the fiber–fiber and fiber–matrix interactions. Also, the amorphous nature of the matrix favored the preferential abstraction of starch, as was determined by thermogravimetry. Only an insignificant difference in weight loss between the matrix and the composites were observed. The authors also analyzed the decrease in mechanical properties as a function of the exposure time.

The same authors have also studied the effect of water on the mechanical behavior of such materials (Alvarez et al., 2004c, d, 2007), determining that the rate of water absorption (measured by the diffusion coefficient) increased with temperature; the water acts as plasticizer and increases flexibility, and the flexural modulus was related to the water content. The decrease of modulus was slightly greater with higher fiber content, but the effect of temperature was more pronounced.

The results obtained for MaterBi Y (cellulose derivative/starch blend) composites differ from those for composites based on MaterBi Z (polycaprolactone/starch blend) where fibers were found to promote the biodegradation and then the preferential removal of starch. MaterBi Z is a semicrystalline blend ($T_m = 60°C$), whereas MaterBi Y is amorphous. Crystalline regions are more difficult to degrade and may act as preference points for microorganism intake. Fibers may act as channels and facilitate microbial ingress in natural-fiber semicrystalline matrix composites. In the case of MaterBi Y, the amorphous structure favors microbial access to the matrix (mainly to the destructurized starch) and fibers have a minor role, as can be concluded from the slight difference in weight loss suffered by the matrix and the composites.

11.6 CONCLUSIONS

Starch is one of the most abundant natural polymers and can be obtained from various botanical sources. However, its drawbacks are water absorption and mechanical instability with humidity, and fragility when dry. One of the most common uses is in packaging films and the possibility blending with other biodegradable polymers with better and more stable mechanical properties has been studied and is currently studied. Another possibility for improving the final properties is to mix starch with natural fibers or nanocellulose fibers. The potential improvement in mechanical properties is greater with nanocellulose, due to the high mechanical properties of the nanocellulose fiber, the higher aspect ratio, and better compatibility between starch and cellulose. However, the cost of the nanofibers will limit the application of these nanofillers. Natural fibers have the problem that they have lower mechanical properties, but they could be used for common applications. A future direction of study to reveal about the final material is the use of nanocellulose fibers as reinforcement and their distribution in the composite. Another important area of study needed on natural fibers is the modification of starch and the fibers themselves in order to produce a more water-resistant material. Time-dependent properties (creep, fatigue) also need to be studied, and nondestructive methods to evaluate the behavior of the composites need to be developed. There is some work in the literature on starch foams and reinforced foam, and this is an interesting application of the material; this subject was not included here for reasons of space restrictions. The use of starch and cellulose in multilayers is another interesting area, which is treated in other chapter.

ACKNOWLEDGMENTS

The authors gratefully acknowledge CONICET (Consejo Nacional de Investigaciones Científicas y Ténicas) and Ministerio de Ciencia y Technología for their financial support and SECYT.

REFERENCES

Ali R, Iannace S, Nicolais L. 2003. Effect of processing conditions on mechanical and viscoelastic properties of biocomposites. *Journal of Applied Polymer Science* 88:1637–1642.

Alvarez VA, Ruseckaite RA, Vázquez A. 2003. Mechanical properties and water absorption of MaterBi-Y sisal fibres composites: Effect of alkaline treatment. *Journal of Composite Materials* 37(17):1575–1588.

Alvarez VA, Kenny JM, Vázquez A. 2004a. Creep behaviour of biocomposites based on sisal fibre reinforced MaterBi-Y. *Polymer Composites* 25(3):280–288.

Alvarez VA, Terenzi A, Kenny JM, Vázquez A. 2004b. Melt rheological behaviour of starch based matrix composites reinforced with short sisal fibres. *Polymer Engineering and Science* 44(10):1907–1914.

Alvarez VA, Fraga A, Vázquez A. 2004c. Effect of the moisture and fibre content on the mechanical properties of biodegradable polymer and sisal fibre biocomposites. *Journal of Applied Polymer Science* 91(6):4007–4016.

Alvarez VA, Vázquez A. 2004d. Effect of water sorption on the flexural properties of a fully biodegradable composite. *Journal of Composite Materials* 38(3):1165–1182.

Alvarez VA, Vázquez A. 2004e. Thermal degradation of cellulose derivatives/starch blends and sisal short fibres composites. *Polymer Degradation and Stability* 84:13–21.

Alvarez VA, Vázquez A, Bernal CR. 2005a. Fracture behaviour of sisal fibre reinforced starch based composites. *Polymer Composites* 26(3):316–323.

Alvarez VA, Ianonni A, Kenny JM, Vázquez A. 2005b. Influence of the twin-screw processing conditions on the mechanical properties of biocomposites. *Journal of Composite Materials* 39:2023–2038.

Alvarez VA, Vázquez A, Bernal CR. 2006a. Effect of microstructure on the tensile and fracture properties of sisal fibre/starch based composites. *Journal of Composites Materials* 40(1):21–35.

Alvarez VA, Vázquez A. 2006b. Influence of fibre chemical modification procedure on the mechanical properties of MaterBi-Y/sisal fibre composites. *Composite Part A* 37:1672–1680.

Alvarez VA, Ruscekaite RA, Vázquez A. 2006c. Degradation of sisal fibre/Mater Bi-Y biocomposites buried in soil. *Polymer Degradation and Stability* 91(12):3156–3162.

Alvarez VA, Ruseckaite RA, Vázquez A. 2007. Aqueous degradation of Mater Bi Y–sisal fibre biocomposites. *Journal of Thermoplastic Composite Materials* 20(5):291–303.

Amass W, Amass A, Tighe B. 1998. A review of biodegradable polymers: uses, current developments in the synthesis and characterization of biodegradable polyester, blends of biodegradable polymers and recent advances in biodegradation studies. *Polymer International* 47:89–144.

Anglès MN, Dufresne A. 2001. Plasticized starch/tunicin whiskers nanocomposite materials. 2: Mechanical behaviour. *Macromolecules* 34(9):2921–2931.

Avérous L, Fringant C. 2001. Association between plasticized starch and polyesters: processing and performances of injected biodegradable systems. *Polymer Engineering and Science* 41(5):727–734.

Averous L, Fauconnier N, Moro L, Fringant C. 2000. Blends of thermoplastic starch and polyesteramide: Processing and properties. *Journal of Applied Polymer Science* 76(7):1117–1128.

Averous L, Fringant C, Moro L. 2001. Plasticized starch-cellulose interactions in polysaccharide composites. *Polymer* 42:6565–6572.

Averous L. 2004. Biodegradable multiphase systems based on plasticized starch: A review. *Journal of Macromolecular Science Part C – Polymer Reviews* C44(3):231–274.

Bastioli C. 1998. Properties and applications of MaterBi starch-based materials. *Polymer Degradation and Stability* 59:263–272.

Biastioli C. 1995. Starch-polymer composites. In: Scott G, Gilead D, editors. *Degradable Polymers: Principles and Applications*. 2nd edn. London: Chapman & Hall.

Bastioli C. 2001. Global status of the production of biobased packaging materials. *Starch/Staerke* 53(8):351–355.

Batra SK, 1981. Other long vegetable fibres. In: Lewin M, Pearce EM. editors. *Handbook of Fibre Science and Technology.* New York: Marcel Dekker. p. 727–808.

Bastioli C, Cerrutti A, Guanella I, Romano GC, Tosin M. 1995. Physical state and biodegradation behaviour of starch-polycaprolactone systems. *Journal of Environmental Polymer Degradation* 3(2):81–95.

Bledzki AK, Gassan J. 1997. Natural fiber reinforced plastics. In: Cheremisinoff NP, editor. *Handbook of Engineering Polymeric Materials.* New York: Marcel Dekker.

Bledzki AK, Gassan J. 1999. Composites reinforced with cellulose based fibres. *Progress in Polymer Science (Oxford)* 24(2):221–274.

Bledzki AK, Reihmane S, Gassan J. 1996. Properties and modification methods for vegetable fibres for natural fibre composites. *Journal of Applied Polymer Science* 29:1329–1336.

Carvalho AJF, Zambon MD, Curvelo AAS, Gandini A. 2003. Size exclusion chromatography characterization of thermoplastic starch composites. 1. Influence of plasticizer and fibre content. *Polymer Degradation and Stability* 79:133–138.

Chand N, Hashmi SAR. 1993. *Metals Materials and Processes* 5:51.

Chand N, Rohatgi, PK. 1994. Natural fibres and their composites. Periodical Experts Publishers: Delhi. p. 55.

Chang YP, Abd Karim A, Scow CC. 2006. Interactive plasticizing-antiplasticizing effects of water and glycerol on the tensile properties of tapioca starch films. *Food Hydrocolloids* 20:1–8.

Chang YP, Cheah PB, Seow CC. 2000. Plasticizing and antiplasticising effects of water on physical properties of tapioca starch films in the glassy state. *Journal of Food Science* 65(3):445–451.

Chawa KK, Bastos AC. 1979. Mechanical properties of jute fibres and polyester-jute composites. *International Conference on the Mechanical Behavior of Materials* 3:191.

Chiellini E, Solaro R. 1996. Biodegradable polymeric materials. *Advanced Materials* 8(4):305–313.

Chiellini E, Corti A, D'Antone S, Solaro R. 2003. Biodegradation of poly(vinyl alcohol) based materials. *Progress in Polymer Science* 28(6):963–1014.

Cunha AM, Liu ZQ, Feng Y, Yi X-S, Bernardo CA. 2004. Preparation, processing and characterization of biodegradable wood flour/starch-cellulose acetate compounds. *Journal of Materials Science* 36(20):4903–4909.

Curvelo AAS, de Carvalho AJF, Agnelli JAM. 2001. Thermoplastic starch/cellulosic fibres composites: preliminary results. *Carbohydrate Polymers* 45:183–188.

Cyras VP, Iannace S, Kenny JM, Vázquez A. 2001. Relationship between processing and properties of biodegradable composites based on PCL/starch matrix and sisal fibres. *Polymer Composites* 22(1):104–110.

Cyras VP, Martucci JF, Iannace S, Vázquez A. 2002. Influence of the fibre content and the processing conditions on the flexural creep behaviour of sisal–PCL–starch composites. *Journal of Thermoplastic Composite Materials* 15:253–265.

Cyras VP, Vallo C, Kenny JM, Vázquez A. 2004. Effect of chemical treatment on the mechanical properties of starch-based blends reinforced with sisal fibre. *Journal of Composite Materials* 38(16):1387–1399.

Cyras VP, Zenklusen MCT, Vazquez A. 2006. Relationship between structure and properties of modified potato starch biodegradable films. *Journal of Applied Polymer Science* 101(6):4313–4319.

Da Róz AL, Carvalho AFJ, Gandini A, Curvelo AAS. 2006. The effect of plasticizers on thermoplastic starch compositions obtained by melt processing. *Carbohydrate Polymers* 63:417–424.

di Franco CR, Cyras VP, Busalmen JP, Ruseckaite RA, Vázquez A. 2004. Degradation of polycaprolactone/starch blendsand composites with sisal fibre. *Polymer Degradation and Stability* 86:95–103.

Duanmu J, Gamstedt EK, Rosling A. 2007. Hygromechanical properties of composites of crosslinked allylglycidyl-ether modified starch reinforced by wood fibres. *Composites Science and Technology* 67(15–16):3090–3097.

Dufresne A, Vignon MR. 1998. Improvement of Starch film performances using cellulose microfibrils. *Macromolecules* 31(8):2693–2696.

Forssell P, Mikkilä J, Moates G, Parker R. 1997. Phase and glass transition behaviour of concentrated barley starch-glycerol-water mixtures, a model for thermoplastic starch. *Carbohydrate Polymers* 34:275–282.

Freitas RA, Paula RC, Fitosa JPA, Rocha S, Sierakowski MR. 2004. Amylose contents, rheological properties and gelatinization kinetics of yam (*Dioscorea alata*) and cassava (*Manihot utilissima*) starches. *Carbohydrate Polymers* 55:3–8.

Fujiyama M, Kawasaki Y. 1991. Rheological properties of polypropylene/high-density polyethylene blend melts. II. Dynamic viscoelastic properties. *Journal of Applied Polymer Science* 42(2):481–488.

Funke U, Bergthaller W, Lindhauer MG. 1998. Processing and characterization of biodegradable product based on starch. *Polymer Degradation and Stability* 59:293–296.

Gáspár M, Benkó Zs, Dogossy G, Réczey K, Cigány T. 2005. Reducing water absorption in compostable starch-based plastics. *Polymer Degradation and Stability* 90:563–569.

Gómez C, Torres FG, Nakamatsu J, Arroyo OH. 2006. Thermal and structural analysis of natural fibre reinforced starch-based biocomposites. *International Journal of Polymeric Materials* 55(11):893–907.

Gidley MJ. 1989. Molecular mechanism underlying amylase aggregation and gelation. *Macromolecules* 22:351–358.

Gudmundsson R. 1994. Retrogradation of starch and the role of its components. *Thermochimica Acta* 246:329–41.

Hanselka H, Herrman AS. 1994. Fibre properties and characterization. In: Internationales Techtexil Symposium. Frankfurt: Germany. p. 20–22.

Hon DN-S. 1994. Degradative effects of ultraviolet light and acid rain on wood surface quality. *Wood and Fiber Science* 26(2):185–191.

Hoover R. 2001. Composition, molecular structure, and physicochemical properties of tuber and root starches: a review. *Carbohydrate Polymers* 45(3):253–267.

Hsueh H. 2000. Young's modulus of unidirectional discontinuous-fibre composites. *Composites Science and Technology* 60:2671–2680.

Huang SJ, Koening MF, Huang M. 1993. Design, synthesis, and properties of biodegradable composites. In: Ching C, Kaplan DL, Thomas EL, editors. *Biodegradable Polymers and Packaging*. Basel: Technomic. p. 97–110.

Iannace S, Nocilla L, Nicolais L. 1999. Biocomposites based on sea algae fibres and biodegradable thermoplastic matrices. *Journal of Applied Polymer Science* 73:583–592.

Jayamol G, Janardhan R, Anand JS, Bhagawan SS, Sabu T. 1996. Melt rheological behaviour of short pineapple fibre reinforced low density polyethylene composites. *Polymer* 37(24):5421–5431.

Jiménez-Hernández J, Salazar-Montoya JA, Ramos-Ramírez EG. 2007. Physical, chemical and microscopic characterization of a new starch from chayote tuber (*Sechium edule*) and its comparison with potato and maize starches. *Carbohydrate Polymers* 68:679–686.

Johnson RM, Tucker N, Barnes S. 2003. Impact properties of Miscanthus/Novamont MaterBI biocomposites. *Polymer Testing* 22:209–215.

Joseph K, Thomas S, Pavithran C, Brahmakumar M. 1993. Tensile properties of short sisal fibre-reinforced polyethylene composites. *Journal of Applied Polymer Science* 47:1731–1739.

Joseph PV, Joseph K, Thomas S. 1999. Effect of processing variables on the mechanical properties of sisal-fibre-reinforced polypropylene composites. *Composites Science and Technology* 59:1625–1640.

Kaplan DJ, Mayer JM, Ball D, McMassie J, Allen AL, Stenhouse P. 1993. Fundamentals of biodegradable polymers chap 1.In: Ching C, Kaplan DL, editors. *Biodegradable Polymers and Packaging*. Basel: Technomic. 1–42.

Katz JR. 1930. Adhandlungen zur physikalschen Chemie der Starke und der Brotbereitung. *Zeitschrift für Physikalische Chemie* 150:37–59.

Ke T, Sun X. 2000. Physical properties of poly(lactic-acid) and starch. Composites with various blending ratios. *Cereal Chemistry* 77(6):761–768.

Koening MF, Huang SI. 1995. Biodegradable blends and composites of polycaprolactone and starch derivatives. *Polymer* 36(9):1877–1882.

Kotnis MA, O'Brien GS, Willett JL. 1995. Processing and mechanical properties of biodegradable Poly(hydroxybutyrate-co-valerate)-starch compositions. *Journal of Environmental Polymer Degradation* 3(2):97–105.

Kuruvilla J, Mattoso LHC. 1998. Sisal fibre reinforced polymer composites: status and future. In *Natural Polymers and Composites*.p. 333.

Lörcks J. 1998. Properties and applications of compostable starch-based plastic material. *Polymer Degradation and Stability* 59:245–249.

Lanzillota C, Pipino A, Lips D. 2002. New functional biopolymer natural fiber composites from agricultural resources. In: *Proceedings of the Annual Technical Conference – Society of Plastics Engineers*, San Francisco, California,Vol. 2. p. 2185–2189.

Lelieve J, Mitchell J. 1975. A pulsed NMR study of some aspects of starch gelatinization. *Stärke* 27:113–115.

Lourdin D, Coignard L, Bizot H, Colonna P. 1997. Influence of equilibrium relative humidity and plasticizer concentration on the water content and glass transition of starch materials. *Polymer* 38:5401–5406.

Lu Y, Weng L, Cao, X. 2006. Morphological, thermal and mechanical properties of ramie crystallites—reinforced plasticized starch biocomposites. *Carbohydrate Polymers* 63(2):198–204.

Mali S, Karam LB, Pereira Ramos L, Grossman MVE. 2004. Relationships among the composition and physicochemical properties of starches with the characteristics of their films. *Journal of Agricultural and Food Chemistry* 52:7720–7725.

Mali S, Grossman MVE, García MA, Martino MN, Zaritzky NE. 2006. Effect of controlled storage on thermal, mechanical and barrier properties of plasticized films form different starch sources. *Journal of Food Engineering* 75:453–460.

Marsh RDL, Blanshard JMV. 1988. The application of polymer crystal growth theory to kinetics of formation of the β-amylose polymorph in a 50% wheat-starch gel. *Carbohydrate Polymers* 27:261–270.

Mathew AP, Dufresne A. 2002. Morphological investigation of nanocomposites from sorbitol plasticized starch and tunicin whiskers. *Biomacromolecules* 3(3):609–617.

Mc. Govern JN. 1987. "Other Fibers" Chapter 9 of Pulp and Paper Manufacture. In: Hamilton F, Leopold B, Kocurek MI, editors. *Secondary Fibers and Non-Wood Pulping*, 3rd ed. TAPPI, Atlanta: GA. Vol. 3. p. 110–121.

Miles MJ, Morris VJ, Ring SG. 1985. Gelation of amylase. *Carbohydrate Research* 135:257–269.

Mouzakis DE, Harmia T, Karger-Kocsis J. 2000. Fracture behaviour of discontinuous long glass fibre reinforced injection molded polypropylene. *Polymers and Polymer Composites* 8:167–175.

Myllärinen P, Partanen R, Seppala J, Forsell P. 2002. Effect of glycerol on behaviour of amylose and amylopectin films. *Carbohydrate Polymers* 50:355–361.

Myllymäki O, Myllärinen P, Forssell P, et al. 1998. Mechanical and permeability properties of biodegradable extruded starch/polycaprolactone films. *Packaging Technology and Science* 11:265–274.

Park B-D, Balatinecz JJ. 1999. Short term flexural creep behaviour of wood-fibre/polypropylene composites. *Polymer Composites* 19:377–382.

Plackett D, Vázquez A. 2004. Biopolymers and biocomposites. In: Baille C, editor. *Green Composites: Polymer Composites and the Environment*. Cambridge: Woodhead Publishers. Chapter 5. ISBN 1 85573 739 6.

Pranamuda H, Tokiwa J, Tanaka H. 1996. Physical properties and biodegradability of blends containing poly(ε-caprolactone) and tropical starches. *Journal of Environmental Polymer Degradation* 4:1–7.

Röper H, Koch H. 1990. The role of starch in biodegradable thermoplastic materials. *Starch* 42:123–130.

Ramsay BA, Langlade V, Carreau PJ, Ramsay JA. 1993. Biodegradability and mechanical properties of poly(hydroxyubutyrate-co-hydroxyvalerate)-starch blends. *Applied Environmental Microbiology* 59:1242–1246.

Ray D, Sarkar BK. 2001. Characterization of alkali-treated jute fibres for physical and mechanical properties. *Journal of Applied Polymer Science* 80:1013–1020.

Ray PK, Chakravarty AC, Bandyopadhay SB. 1976. Fine structure and mechanical properties of jute differently dried after retting. *Journal of Applied Polymer Science* 20:1765–1766.

Rindlav-Westling A, Stading M, Hormansson A-M, Gatenholm P. 1998. Structure and mechanical properties of amylase and amylopectin films. *Carbohydrate Polymers* 36(2–3):217–224.

Rindlay A, Stading M, Hermansson A, Gatenholm P. 1998. Structure, mechanical and barrier properties of amylase and amylopectin films. *Carbohydrate Polymers* 36:217–224.

Romhány G, Karger-Kocsis J, Czigány T. 2003. Tensile fracture and failure behavior of thermoplastic starch with unidirectional and cross-ply flax fiber reinforcements. *Macromolecular Materials and Engineering* 288(9):699–707.

Romhány G, Karger-Kocsis J, Czigány T. 2003a. Tensile fracture and failure behaviour of technical flax. *Journal of Applied Polymer Science* 90(3):3638–3645.

Romhány G, Karger-Kocsis J, Czigány T. 2003b. Tensile fracture and failure behaviour of thermoplastic starch with unidirectional and cross-ply flax fibre reinforcements. *Macromolecular Engineering* 288(9):699–707.

Rong MZ, Zhang MQ, Lui Y, Yang GC, Zeng HM. 2001. The effect of fibre treatment on the mechanical properties of unidirectional sisal reinforced epoxy composites. *Composites Science and Technology* 61:1437–1447.

Rowell RM. 1992. Opportunities for lignocellulosic materials and composites. In: *Materials and Chemicals from Biomass*. American Chemical Society, Chapter 2. p. 12–27.

Rozman HD, Peng GB, Mohd Ishak ZA. 1998. The effect of compounding techniques on the mechanical properties of oil palm empty fruit bunch-polypropylene composites *Journal of Applied Polymer Science* 70:2647–2655.

Saechtling H. 1987. Starch-polymer composites (Chapter 6). In: Munich, editor. *International Plastics Handbook for the Technologist, Engineer and User*. 2nd ed. Hansen. p. 12.

Sagar AD, Merril EW. 1995. Starch fragmentation during extrusion processing. *Polymer* 36(9):1883–1995.

Sears JK, Darby JR. 1982. *The Technology of Plasticizers*. New York: Wiley.

Shibata S, Cao Y, Fukumoto I. 2005. Press forming of short natural fibre-reinforced biodegradable resin: Effects of fibre volume and length on flexural properties. *Polymer Testing* 24:1005–1011.

Shogren RL, Swason CL, Thompson AR. 1992. Extrudates of cornstarch with urea and glycols: Structure/mechanical properties relations. *Starch* 44:335–338.

Singh N, Singh J, Lovedeep Kaur L, Singh Sodhi N, Singh Gill B. 2003. Morphological, thermal and rheological properties of starches from different botanical sources. *Food Chemistry* 81(2):219–231.

Solaro R, Corti A, Chiellini E. 1998. A new respirometric test simulating soil burial conditions for the evaluation of polymer biodegradation. *Journal of Environmental Polymer Degradation* 4:203–208.

Stevens DJ, Elton GA. 1981. Thermal properties of the starch/water system. I Measurement of heat of gelatinization by differential scanning calorimetry. *Starke* 23:8–11.

Stevenson DG, Jane JL, Inglett GE. 2007. Structure and physicochemical properties of starch from immature seeds of soybean varieties (glycine max) exhibiting normal, low-linoleic or low-saturated fatty acid oil profiles at maturity. *Carbohydrate Polymers* 70:149–159.

Takagi H, Asano A. 2008. Effect of processing conditions on flexural properties of cellulose nanofiber reinforced "green" composites. *Composite Part A* 39(4):685–689.

Thranathna RN. 2003. Biodegradable films and composite coatings: past, present and future. *Trends in Food Science and Technology* 14:71–78.

Thunwall M, Boldizar A, Rigdah M. 2006. Compression molding and tensile properties of thermoplastic potato starch materials. *Biomacromolecules* 7:981–986.

Torres FG, Arroyo OH, Grande C, Esparza E. 2006. Bio-Photo-degradation of natural fibre reinforced starch-based biocomposites. *International Journal of Polymeric Materials* 55(12):1115–1132.

Ugbolue SCO. 1990. Structure-property relationships in textile fibres. *Text Inst* 20(4):1–12.

Vázquez A, Domínguez V, Kenny JM. 1999. Bagasse-fibre-polypropylene based composites. *Journal of Thermal Composite Materials* 12:477–497.

van Soest JJG, Borger DB. 2006. Structure and properties of compression-molded thermoplastic starch materials from normal and high-amylose maize starches. *Journal of Applied Polymer Science* 64(4):631–644.

van Soest JJG, De Wit D, Vliegenthart JFG. 1996a. Mechanical properties of thermoplastic waxy maize starch. *Journal of Applied Polymer Science* 61(11):1927–1937.

van Soest JJG, Hulleman SHD, Vliegenthart JFG. 1996b. Crystallinity in starch bioplastics. *Industrial Crops and Products* 5:11–22.

van Soest JJG, Vliegenthart JFG. 1997. Crystallinity in starch plastics: consequence for material properties. *TIBTECH* 15:208–213.

van Soest JJG. 1995. In: van Soest JJG, editor. *Starch Plastics: Structure–Properties Relationship*. p. 1–168.

Verhoogt H, St-Pierre N, Truchon FS, Ramsay BA, Favis BD, Ramsay JA. 1995. Blends containing poly(hydroxybutyrate-co-12%-hydroxyvalerate) and thermoplastic starch. *Canadian Journal of Microbiology* 41(1):323–328.

Vilpoux O, Averous L. 2004. Starch-based plastics. In: Cereda MP, editor. *Technology, Use and Potentialities of Latin American Starchy Tubers*. Chapter 18. p. 551–553.

Wang K, Lee LJJ. 1987. Rheological and extrusion behaviour of dispersed multiphase polymeric systems. *Journal of Applied Polymer Science* 33:431–453.

Warburton SD, Donald AM, Smith AC. 1993. The deformation of thin films made from extruded starch. *Carbohydrate Polymers* 21(1):17–21.

Willett JL, Felker FC. 2005. Tensile yield properties of starch filled poly(ester amide) materials. *Polymer* 46:3035–3042.

Willett JL, Kotnis MA, O'Brien GS, Fanta GF, Gordon SH. 1998. Properties of starch-graft-poly(glycidyl methacrylate)-PHBV composites. *Journal of Applied Polymer Science* 70:1121–1127.

Wollerdorfer M, Bader H. 1998. Influence of natural fibres on the mechanical properties of biodegradable polymers. *Industrial Crops and Products* 8:105–112.

Yongshang Lu, Lihui Weng, Xiaodong Cao. 2006. Morphological, thermal and mechanical properties of ramie crystallites-reinforced plasticized starch biocomposites. *Carbohydrate Polymers* 198–204.

Zhou Y, Hoover R, Liu Q. 2004. Relationship between amylase degradation and the structure and physicochemical properties of legume starches. *Carbohydrate Polymers* 57:200–317.

CHAPTER 12

Poly(Lactic Acid)/Cellulosic Fiber Composites

MITSUHIRO SHIBATA

Department of Life and Environmental Sciences, Faculty of Engineering, Chiba Institute of Technology, Narashino, Chiba 275-0016, Japan

12.1 INTRODUCTION

Biocomposites composed of polymers from renewable resources (PFRR) and cellulosic fibers from plants have been gathering much attention from the standpoint of protection of the natural environment and saving of petroleum resources (Bledzki and Gassan, 1999; Saheb and Jog, 1999; Mohanty et al., 2000, 2002; Wool and Sun, 2005; Yu et al., 2006). Poly(lactic acid) (PLA) is one of the most promising PFRR, because it is derived from abundant agricultural products such as corn, sugar cane, and sugar beat via fermentation and chemical processes, and can be used as a structural material with sufficient lifetime to maintain mechanical properties without rapid hydrolysis even under humid conditions, as well as showing good compostability (Garlotta, 2001; Warmington, 2001; Inoue, 2003; Ohara, 2003; Sawyer, 2003; Scott and Sissell, 2003; Vink et al., 2003). Lignocellulosic natural fibers are grouped into leaf, bast, leafstalk, stalk, seed, and fruit origins. Well-known examples include (i) *Leaf:* sisal, pineapple leaf fiber, and henequene; (ii) *Bast:* flax, ramie, jute,

Biodegradable Polymer Blends and Composites from Renewable Resources. Edited by Long Yu

hemp, and kenaf; (iii) *Leafstalk:* abaca (manila hemp) and banana; (iv) *Stalk:* bamboo and wood fiber; (iv) *Seed:* cotton and kapok; and (v) *Fruit:* coconut (coir) (Bledzki and Gassan, 1999; Mohanty et al., 2000). Most of them have until now been investigated as reinforcing materials for PLA. As examples, PLA composites using flax (Oksman et al., 2003; Wong et al., 2003, 2004; Shanks, 2006a, b), jute (Plackett et al., 2003), kenaf (Nishino et al., 2003; Serizawa et al., 2006), abaca (Shibata et al., 2003; Teramoto et al., 2004), bamboo (Lee and Ohkita, 2004; Lee and Wang, 2006), and wood flour (Plackett, 2004; Mathew et al., 2005, 2006; Gamstedt et al., 2006; Yu et al., 2007) as cellulosic natural fibers have been reported by several groups for improvement of mechanical properties. As a whole, it is relatively easy to improve the rigidity of PLA by natural fiber reinforcement. However, the improvement of mechanical properties related to toughness, such as tensile and flexural strength and impact strength, is very difficult. Recently, it has been reported that the impact strength of PLA composites is improved by use of kenaf fibers form which fine particles have been eliminated. The PLA/kenaf composite can be used as casing materials for electronic products such as mobile phones (Serizawa et al., 2006). Recently, wood pulp, microcrystalline cellulose, and cellulose whisker, which are derived from plant-based lignocellulose fibers (Mathew et al., 2005, 2006; Hou et al., 2006; Oksman et al., 2006; Petersson and Oksman, 2006), and rayon (Fink and Ganster, 2006) and lyocell (Shibata et al., 2004), which are known as cellulosic man-made fibers, have also been investigated as reinforcing materials for PLA. This section describes the improvement of rigidity by reinforcement of PLA with short abaca fiber and wood flour, and the improvement of toughness by the reinforcement of PLA with lyocell fabric.

12.2 PLA/ABACA COMPOSITES

Abaca fiber is produced from leafstalk of a banana-shaped plant, *Musa textiles* Née (Manila hemp), which is mainly supplied from Philippines. Abaca fiber has relatively high tensile strength (810 MPa) and modulus (34 MPa) among various natural fibers (Table 12-1) (Shibata et al., 2002, 2003). The abaca fiber was used as natural fiber reinforcing PLA (Shibata et al., 2003). Because strongly polarized lignocellulosic fibers are inherently incompatible with hydrophobic polymers (Luo and Netravali, 1999a, b), the esterification of abaca fiber with acetic anhydride (AA-abaca) or butyric anhydride (BA-abaca), alkali treatment (Alk-abaca), and cyanoethylation (AN-abaca) with acrylonitrile were carried out as shown in Fig. 12-1 (Shibata et al., 2002).

The reactions were confirmed by FT-IR spectral analysis of the modified fibers. The AA-, BA-, and Alk-abaca fibers exhibited slightly lower tensile strength and slightly higher tensile modulus than untreated abaca fiber (Shibata et al., 2003). The tensile strength and modulus of AN-abaca were considerably lower than those of the untreated abaca fiber. The untreated and modified abaca fibers chopped into ~5 mm length (fiber content: 0, 5, 10, 15, 20 wt%) and PLA were mixed at 190°C and subsequently injection-molded to give PLA/abaca composites.

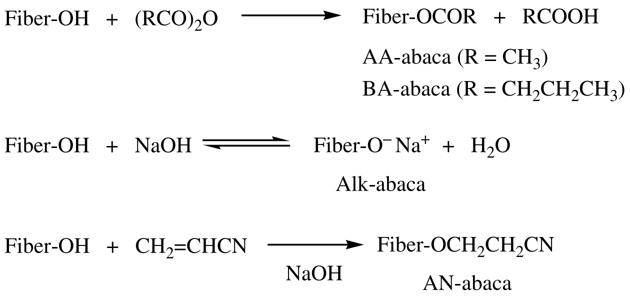
TABLE 12-1 Mechanical Properties of Natural Fibers[a]

Fiber	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation at Break (%)	Density (g/cm^3)
Flax	345–1100	27.6	2.7–3.2	1.50
Jute	393–773	13–26.5	1.2–1.5	1.3–1.45
Ramie	400–938	61.4–128	1.2–3.8	1.45
Sisal	468–640	9.4–22.0	3–7	1.5
Abaca	756–813	31.1–33.6	2.9	1.5
Cotton	287–800	5.5–12.6	7.0–8.0	1.5–1.6
Coir	131–175	4–6	15–40	1.2
Lyocell	450–630	16–18	4–10	1.5
E-glass	2000–3500	70	2.5	2.5

[a] Data for fibers except for abaca and lyocell are cited from Mohanty et al. (2000). Data for abaca are cited from Shibata et al. (2002, 2003). Data for lyocell are cited from Mieck et al. (2002).

Flexural properties of the PLA/abaca composites as a function of fiber content are shown in Fig. 12-2. Flexural moduli of the PLA composites increased with fiber content. Although the PLA composites with BA-abaca or AA-abaca showed slightly higher modulus, the influence of fiber treatment was not so large. On the other hand, flexural strength did not increase regardless of the fiber treatment in the fiber content range below 20 wt%.

It is generally considered that the biodegradation of PLA in soil at room temperature takes longer time than that of other biodegradable aliphatic polyesters such as poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), poly(ε-caprolactone) (PCL), and poly(butylene succinate) (PBS). Control PLA and PLA/AA-abaca composite with fiber content of 10 wt% showed no weight loss after burial for 6 months in 1 : 1 mixture of black soil and leaf mold for gardening (Teramoto et al., 2004). It is thought that the penetration of water or microorganism through the fiber–matrix interface is restricted for PLA/AA-abaca composite because the interfacial adhesion is improved due to the surface modification of the fiber. On the other hand, ~10% of the original weight of PLA/untreated abaca composite with fiber content of 10 wt%



$$\text{Fiber-OH} + (\text{RCO})_2\text{O} \longrightarrow \text{Fiber-OCOR} + \text{RCOOH}$$

AA-abaca (R = CH_3)
BA-abaca (R = $CH_2CH_2CH_3$)

$$\text{Fiber-OH} + \text{NaOH} \rightleftharpoons \text{Fiber-O}^-\text{Na}^+ + \text{H}_2\text{O}$$

Alk-abaca

$$\text{Fiber-OH} + \text{CH}_2\text{=CHCN} \xrightarrow[\text{NaOH}]{} \text{Fiber-OCH}_2\text{CH}_2\text{CN}$$

AN-abaca

Fig. 12-1 Surface modifications of abaca fiber.

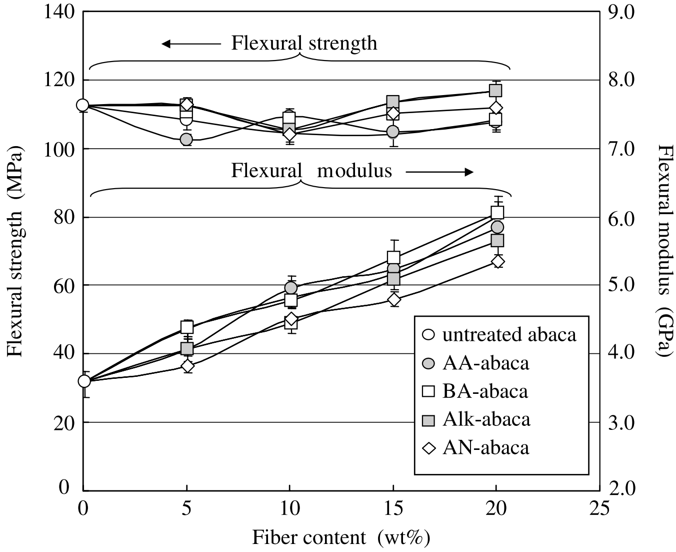


Fig. 12-2 Flexural properties of PLA composites as a function of fiber content.

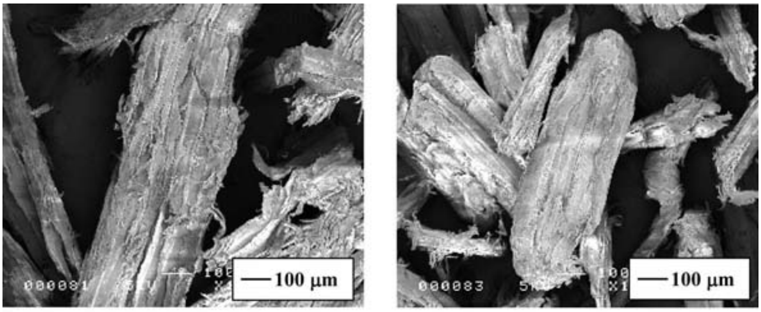
was lost at 60 days; the weight loss did not increase thereafter. The slowdown of the weight loss around 10% is presumably related to the preferential decomposition of the fiber in the early stage and a much slower biodegradability of the matrix PLA in the next stage. The buried specimen of PLA/untreated abaca was very fragile and some parts were broken in the washing process. The PLA near the fiber–matrix interface of PLA/untreated abaca composite may be somewhat degraded by the action of water absorbed by the fiber. However, the surface of the matrix PLA of PLA/untreated abaca and PLA/AA-abaca composites appeared unchanged after the burial test. For PLA/untreated abaca composite, some cracks around the interface were observed. The cracks are thought to be formed by interfacial delamination and the shrinkage of matrix PLA due to the crystallization of PLA. The degradation of abaca fiber in the composite may occur through the cracks. Such cracks were not observed in PLA/AA-abaca composite. This result is thought to be related to the improvement of interfacial adhesion due to the surface modification of abaca fiber.

12.3 PLA/WOOD FLOUR COMPOSITES

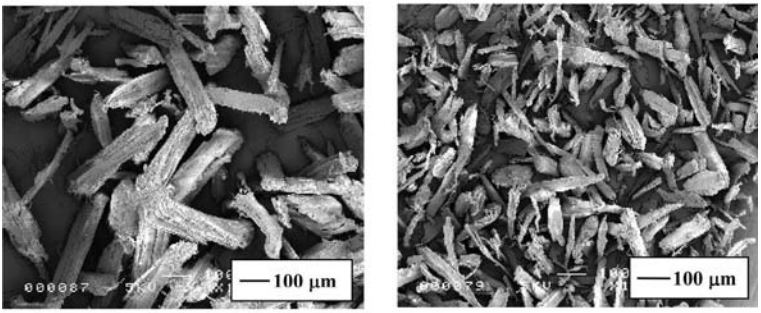
Wood is an abundant and cheap natural resource, composed of cellulose, lignin, and hemicellulose. For composites of PLA and chopped abaca fibers of ~5 mm, the preparation of PLA/abaca composites with fiber content more than 25 wt% by injection molding was difficult because the injection molding gate becomes stopped up. In order to prepare PLA composites with higher fiber content by injection molding, wood flour (WF) which is much finer than the chopped abaca fiber, was used.

Wood pulverized using a grinder was passed through successive sieves of different mesh sizes. SEM images of the separated WFs are shown in Fig. 12-3. The aspect ratio of all the WF particles was ~5. Because the WF of 635 mesh contains all the particles passing through a 635 mesh, some fine particles appeared. Figs. 12-4 and 12-5 show the tensile and flexural properties of PLA/WF composites.

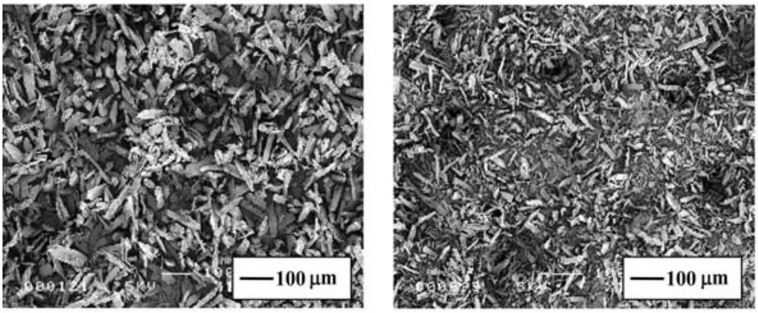
The tensile and flexural moduli increased with increasing WF content. The composites with the WF of 635 mesh showed slightly lower modulus because of the



26 mesh (600~300 µm) **50 mesh** (300~150 µm)



100 mesh (150~75 µm) **200 mesh** (75~38 µm)



390 mesh (38~20 µm) **635 mesh** (<20 µm)

Fig. 12-3 SEM images of wood flour particles separated with sieves of different mesh sizes.

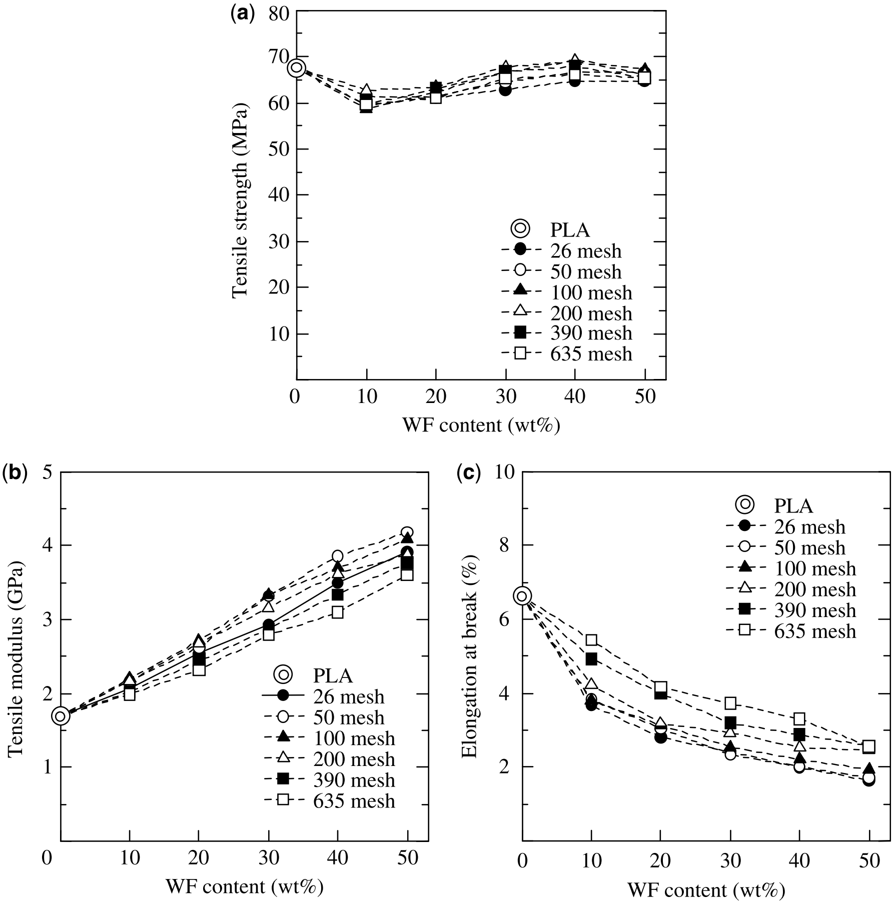


Fig. 12-4 Tensile properties of PLA/WF composites.

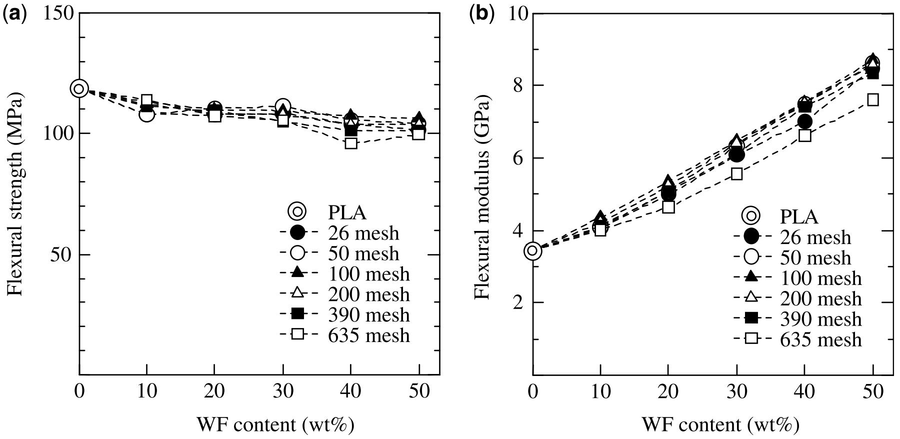


Fig. 12-5 Flexural properties of PLA/WF composites.

presence of the fine particles. The tensile strength of all the composites was somewhat lower than that of control PLA. The tensile strength was lowest for the composite with WF content of 10 wt% and then increased gradually with increasing WF content. When composites with the same WF content are compared, the composites with mesh size between 50 and 200 mesh showed higher strength and moduli in both the tensile and flexural tests. Elongation at break decreased with increasing WF content. The strength decrease is due to the lowering of flexibility. The PLA/abaca composites had slightly higher modulus than PLA/WF composites with the same fiber content (Fig. 12-5 vs. Fig. 12-2). This is attributed to the fact that the abaca fiber has higher aspect ratio than WF.

Figure 12-6 shows dynamic viscoelastic curves of PLA/WF composites with WF content of 20 wt%. For control PLA, the storage modulus (*E*′) dropped around 50°C due to the glass transition, and rose again around 120°C due to crystallization of PLA. For PLA/WF composites, although the temperature at which *E*′ starts to decrease is almost the same, that at which it starts to increase due to PLA crystallization is shifted to ~75°C, which is considerably lower than that for PLA. This suggests that cold crystallization of PLA is promoted by the presence of WF. The tan δ peak temperature corresponding to the glass transition temperature was almost unchanged, indicating that WF does not affect the mobility of PLA chains.

Figure 12-7 shows dynamic viscoelastic curves of PLA composites with the WF of 100 mesh as a function of WF content. There was little difference in the temperature

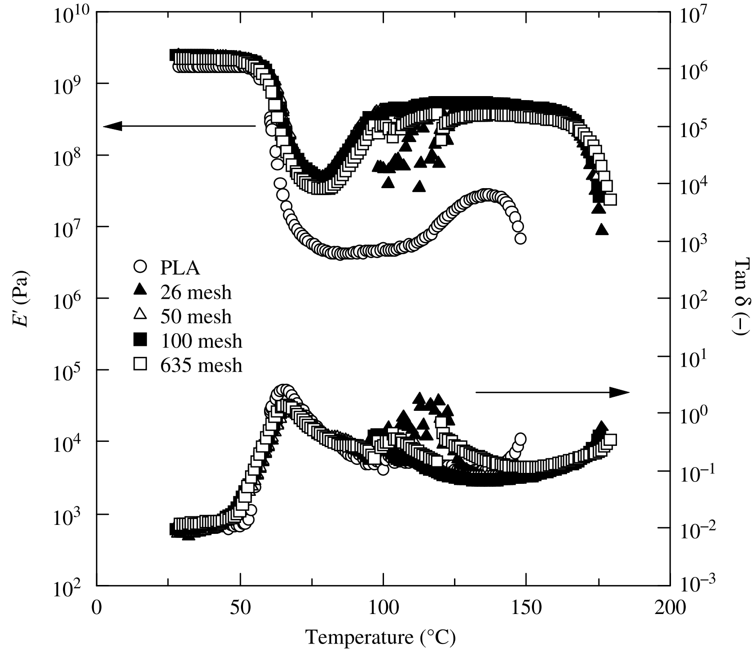


Fig. 12-6 Dynamic viscoelastic curves of PLA and PLA/WF composites with WF content of 20 wt%.

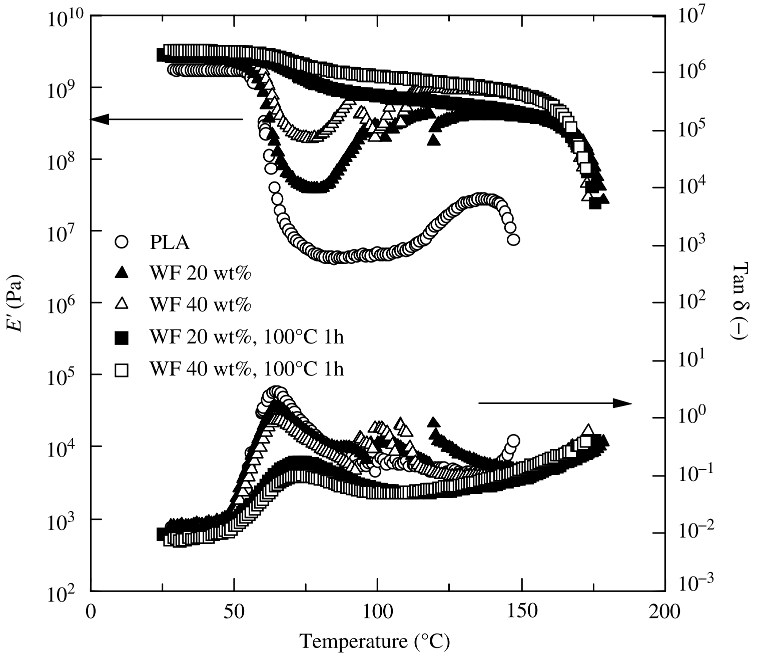


Fig. 12-7 Dynamic viscoelastic curves of PLA and PLA/WF (100 mesh) composites.

at which E' starts to increase due to PLA crystallization between the composites with WF contents of 20 and 40 wt%. When the PLA/WF composites were annealed at 100°C for 1 h, the decrease of E' due to the glass transition of the PLA component became much smaller because of the increase in crystallinity. The annealed PLA composite with WF content of 40 wt% showed a higher storage modulus at 100–150°C than the annealed composite with WF content of 20 wt%.

When the esterification of the WF surface with acetic anhydride/pyridine was investigated in an attempt to improve the interfacial adhesiveness, there was slight improvement of tensile strength and modulus. The use of acetic anhydride-treated WF (AA-WF) was rather effective in diminishing the water absorption of the PLA composites. Thus, PLA/AA-WF with WF content of 40 wt% showed lower water absorption (2.4%) after dipping in water for 24 h than the PLA/WF with the same WF content (3.1%). Composites with a higher WF content showed higher water absorption, and the use of finer WF resulted in a slight decrease in water absorption.

12.4 PLA/LYOCELL COMPOSITES

The man-made fiber lyocell is environmentally benign because it is manufactured from wood pulp by dissolution of cellulose in *N*-methylmorpholine *N*-oxide, which is used repeatedly by recycling (Firgo, 1995). Compared with flax and abaca, lyocell fiber has a considerably greater elongation at break (see Table 12-1). In addition, variations in the mechanical properties as well as in the shape between different batches of lyocell fiber are less than for natural fibers. Very tough and flexible fabrics are manufactured from lyocell fibers. Although lyocell fiber/biodegradable polymer composites are very interesting eco-friendly composites ("green composites"), little is reported in the literature (Mieck et al., 2002). PLA/lyocell composites were prepared by sandwiching lyocell fabric (300 dtex, 600 dtex, 2/2 twill, thickness ~0.35 mm) between two layers of PLA sheet at 160–190°C and 3–10 MPa pressure (Shibata et al., 2004). The PLA/lyocell composites obtained were also annealed at 100°C for 3 h in order to enhance the crystallinity. For PLA-based composites, multilayered laminate composites for Izod impact tests were also prepared by sandwiching 6–8-ply lyocell fabrics between alternating 7–9-ply PLA sheets.

Figure 12-8 shows the tensile properties of PLA/lyocell composites with various fiber contents. PLA sheets prepared by pressure molding were used for measurements at fiber content of 0%, Tensile strength and moduli of the composites increased with increasing fiber content. PLA composites showed higher elongation at break (6.4–10.4%) than pure PLA sheet (2.1%). This are attributed to the fact that lyocell fiber has a higher elongation than PLA.

The crystallization of PLA at room temperature is very slow because of a high T_g value (60°C). The original degree of crystallinity (χ_c) of the composite can be evaluated from the value of ($\Delta H_m - \Delta H_{g,c}$), where ΔH_m and $\Delta H_{g,c}$ are respectively the heats of melting and of crystallization from the glassy state of the composite in the first heating DSC scan, respectively. Taking the heat of melting of 100% crystalline PLA as 93 J/g (Fisher et al., 1973), χ_c values of the PLA component of the original and annealed PLA/lyocell composites (fiber content ~40 wt%) were evaluated as 15% and 35%. Figure 12-8 also shows the comparison of tensile properties between the original and annealed PLA/lyocell composites. Despite the increase of χ_c by annealing, the annealed composites showed significantly lower tensile strength and moduli than the original composites.

Figure 12-9 shows SEM images of the surface of the original and annealed PLA/lyocell composites. The annealed composite had much more cracking than the original sample, which should be why the annealed PLA composite showed a lower tensile strength than the original composite.

Figure 12-10 shows SEM images of the fractured surface of the original PLA/lyocell composite at different magnifications. It is obvious that PLA permeates among the lyocell fibers in the cloth, indicating that interfacial delamination between lyocell cloth and PLA is difficult. It is therefore thought that the shrinkage of PLA adhering to lyocell cloth caused the cracks after annealing. The occurrence of microcracks is assumed to be the reason for the lowering of tensile properties.

Izod impact testing of multilayered PLA/lyocell laminate composites with fiber content ~50 wt% compared with PLA sheet prepared by pressure molding was done to evaluate the improvement of toughness in the PLA/lyocell composites. The PLA composites with 6-ply (28.2 kJ/m^2) and 8-ply (40.8 kJ/m^2) lyocell fabrics showed approximately two and three times respectively higher impact strength

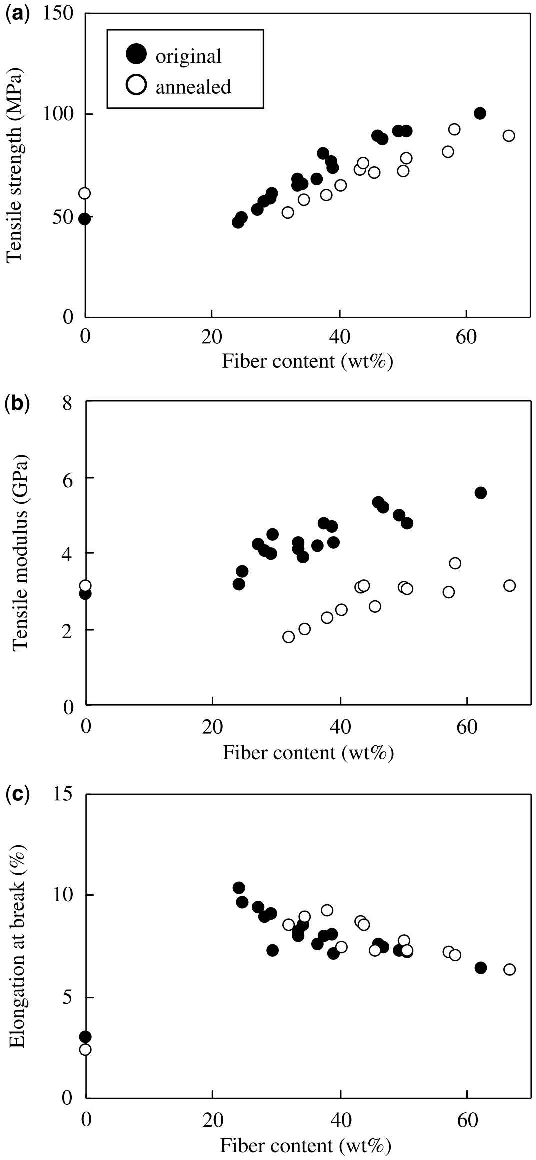


Fig. 12-8 Tensile properties of native and annealed PLA/lyocell composites as a function of fiber content.

than pure PLA (14.1 kJ/m^2) (Fig. 12-11). Although a simple comparison between a laminate composite and an injection-molded short-fiber composite may be inappropriate, the short abaca fiber-reinforced PLA composite (fiber length 5 mm; fiber content 10 wt%) prepared by injection molding (Shibata et al., 2003) showed a

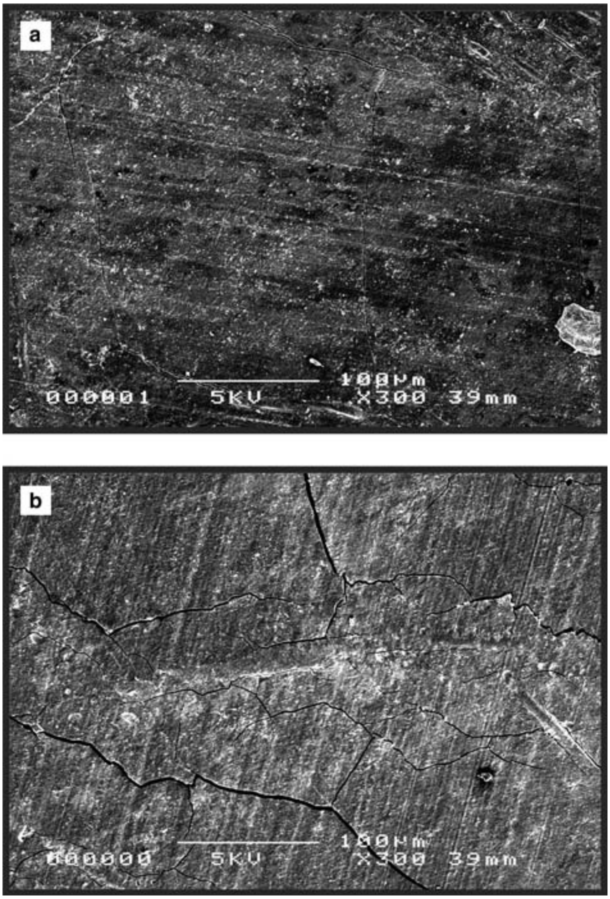


Fig. 12-9 SEM images of the surface of the original and annealed PLA/lyocell composites: (a) original sample, and (b) annealed sample.

considerably lower Izod impact strength (10–12 kJ/m^2). Mieck and co-workers found that the impact strength of lyocell fiber composites was much higher than that of natural fiber composites when the composites were prepared with the same fiber length and by the same method (Benevolenski et al., 2000). The improvement of impact strength for the PLA/lyocell composite may be attributed to the use of lyocell fabric and the fact that lyocell fiber has greater elongation than plant-based fibers such as abaca and flax.

The lyocell fabric itself biodegraded after 30 days, as shown in Fig. 12-12. The lyocell fabric in PLA/lyocell composite also clearly degraded after 60 days (Fig. 12-12). Because pure PLA film was almost unchanged after 120 days, degradation of the PLA in the composite is not thought to occur. Microcracking or delamination in the PLA/lyocell composite may be responsible for the direct biodegradation of the lyocell fabric in the composite.

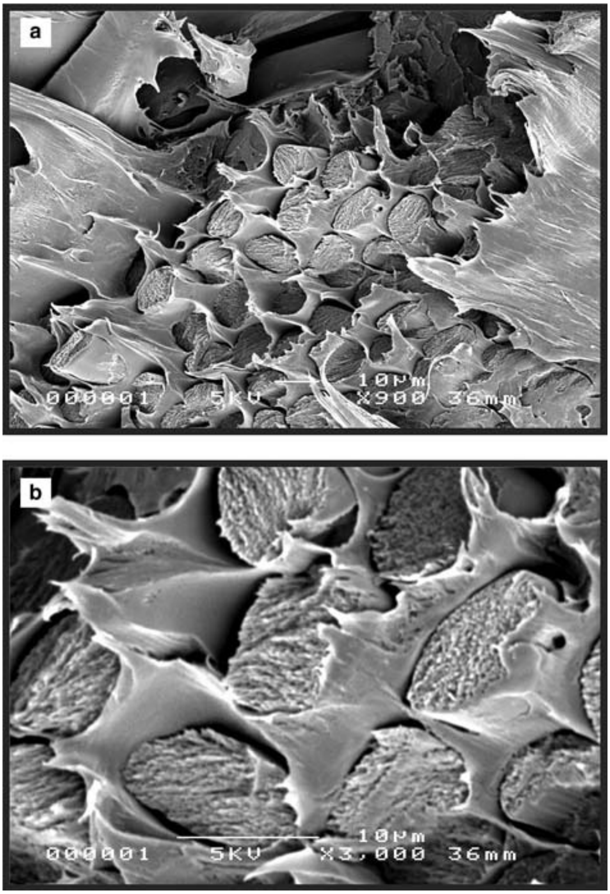


Fig. 12-10 SEM images of the fractured surface of the original PLA/lyocell composites at different magnifications: (a) ×900, (b) ×3000.

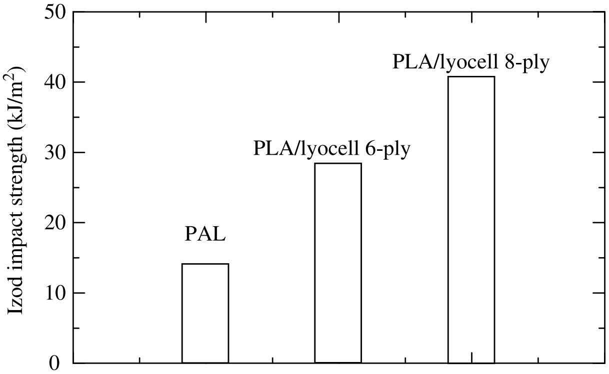


Fig. 12-11 Izod impact strength of PLA and multi-layered PLA/lyocell composites.

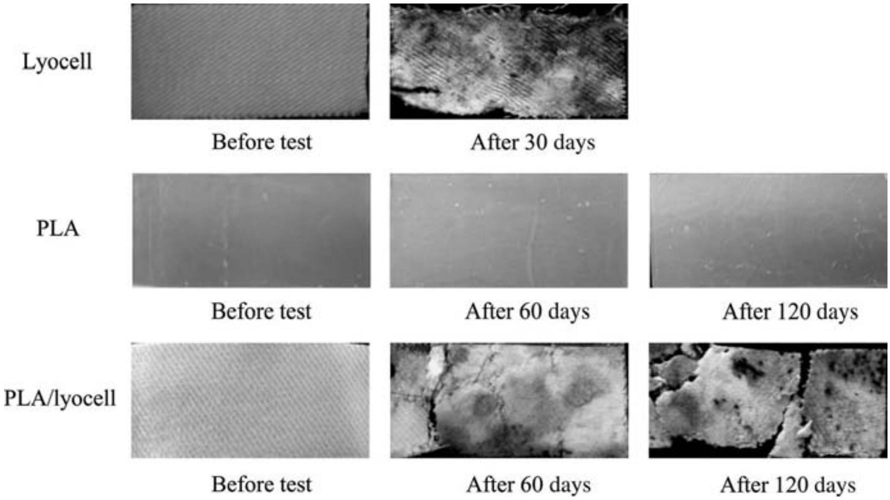


Fig. 12-12 Photographs of lyocell fabric, PLA, and PLA/lyocell composite before and after the soil-burial test.

12.5 CONCLUSION

PLA/abaca and PLA/WF composites were prepared by melt mixing and subsequent injection molding. For both composites, tensile and flexural moduli increased with increasing fiber content, but the strength of the composites was somewhat lower than that of control PLA. The influence of fiber surface treatment on the mechanical properties of the PLA composites was less marked. PLA/lyocell fabric composites with fiber content 40–67 wt% prepared by pressure molding showed considerably higher tensile strength and elongation at break than PLA. Multilayered PLA/lyocell laminate composites showed considerably higher Izod impact strength than PLA. These results are attributed to the fact that lyocell fiber itself has higher strength and elongation than PLA, and that interfacial adhesion is good. Consequently, reinforcement with natural plant fibers is effective in improving the rigidity of the composites, while improvement of toughness this way is very difficult. Reinforcement with lyocell fabric was very effective in improving the toughness of PLA. In soil burial tests on the PLA composites, fiber degradation occurred with interfacial delamination and/or microcracking of matrix PLA.

REFERENCES

Benevolenski OI, Karger-Kocsis J, Mieck KP, Reussmann T. 2000. Instrumented perforation impact response of polypropylene composites with hybrid reinforcement flax/glass and flax/cellulose fibers. *J Thermoplast Compos Mater* 13:481–496.

Bledzki AK, Gassan J. 1999. Composites reinforced with cellulose based fibres. *Prog Polym Sci* 24:221–274.

Fink HP, Ganster J. 2006. Novel thermoplastic composites from commodity polymers and man-made cellulose fibers. *Macromol Symp* 244:107–118.

Firgo H. 1995. Lyocell process. *Lenzinger Berichte* 75:47–50.

Fisher EW, Sterzel HJ, Wegner G. 1973. Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions. *Kolloid Z Z Polym* 251:980–990.

Gamstedt EK, Bogren KM, Neagu RC, Akerho LMM, Lindstrom M. 2006. Dynamic-mechanical properties of wood-fiber reinforced polylactide: Experimental characterization and micromechanical modeling. *J Thermoplast Compos Mater* 19:613–637.

Garlotta D. 2001. A literature review of poly(lactic acid). *J Polym Environ* 9:63–84.

Hou QX, Chai XS, Yang R, Ragauskas AJ, Elder T. 2006. Characterization of lignocellulosic-poly(lactic acid) reinforced composites. *J Appl Polym Sci* 99:1346–1349.

Inoue Y. 2003. Environmentally safe biodegradable plastics from oil-alternative renewable plant resources. *Foods & Food Ingred J Jpn* 208:648–654.

Lee SH, Ohkita T. 2004. Eco-composite from poly(lactic acid) and bamboo fiber. *Holzforschung* 58:529–536.

Lee SH, Wang S. 2006. Biodegradable polymers/bamboo fiber biocomposite with bio-based coupling agent. *Composites Part A* 37:80–91.

Luo S, Netravali AN. 1999a. Interfacial and mechanical properties of environment-friendly "green" composites made from pineapple fibers and poly(hydroxybutyrate-co-valerate) resin. *J Mater Sci* 34:3709–3719.

Luo S, Netravali AN. 1999b. Mechanical and thermal properties of environment-friendly "green" composites made from pineapple leaf fibers and poly(hydroxybutyrate-co-valerate) resin. *Polym Compos* 20:367–378.

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

Mathew AP, Oksman K, Sain M. 2006. The effect of morphology and chemical characteristics of cellulose reinforcements on the crystallinity of polylactic acid. *J Appl Polym Sci* 101:300–310.

Mieck KP, Luetzkendorf R, Reussmann T, Nechwatal A, Eilers M, Biehl D. 2002. Lyocell fiber reinforced plastics composites—state-of-the-art and prospects. *Technical Textiles* 45, E58–60.

Mohanty AK, Misra M, Hinrichsen G. 2000. Biofibres, biodegradable polymers and biocomposites: An overview. *Macromol Mater Eng* 276/277:1–24.

Mohanty AK, Misra M, Drzal LT. 2002. Sustainable bio-composites from renewable resources: Opportunities and challenges in the green materials world. *J Polym Environ* 10:19–26.

Nishino T, Hirao K, Kotera M, Nakamae K, Inagaki H. 2003. Kenaf reinforced biodegradable composites. *Compos Sci Technol* 63:1281–1286.

Ohara H. 2003. Polylactate produced from biomass. *J Appl Glycosci* 50:405–410.

Oksman K, Skrifvars M, S Eli JF. 2003. Natural fibres as reinforcement in polylactic acid (PLA) composites. *Compos Sci Technol* 63:1317–1324.

Oksman K, Mathew AP, Bondeson D, Kivien I. 2006. Manufacturing process of cellulose whiskers polylactic acid nanocomposites. *Compos Sci Technol* 66:2776–2784.

Petersson L, Oksman K. 2006. Biopolymer based nanocomposites: Comparing layered silicates and microcrystalline cellulose as nanoreinforcement. *Compos Sci Technol* 66:2187–2196.

Plackett D. 2004. Maleated polylactide as an interfacial compatibilizer in biocomposites. *J Polym Environ* 12:131–138.

Plackett D, Andersen TL, Pedersen WB, Nielsen L. 2003. Biodegradable composites based on L-polylactide and jute fibres. *Compos Sci Technol* 63:1287–1296.

Saheb DN, Jog JP. 1999. Natural fiber polymer composites: A review. *Adv Polym Technol* 18:351–363.

Sawyer DJ. 2003. Bioprocessing—no longer a field of dreams. *Macromol Symp* 201:271–282.

Scott A, Sissell K. 2003. Green chemistry starts to take root. *Chem Week* 165:18.

Seriwzawa S, Inoue K, Iji M. 2006. Kenaf-fiber-reinforced poly(lactic acid) used for electronic products. *J Appl Polym Sci* 100:618–624.

Shanks RA, Hodzic A, Ridderhof D. 2006a. Composites of poly(lactic acid) with flax fibers modified by interstitial polymerization. *J Appl Polym Sci* 99:2305–2313.

Shanks RA, Hodzic A, Ridderhof D. 2006b. Composites of poly(lactic acid) with flax fibers modified by interstitial polymerization. *J Appl Polym Sci* 101:3620–3629.

Shibata M, Takachiyo K, Ozawa K, Yosomiya R, Takeishi H. 2002. Biodegradable polyester composites reinforced with short abaca fiber. *J Appl Polym Sci* 85:129–138.

Shibata M, Ozawa K, Teramoto N, Yosomiya R, Takeishi H. 2003. Biocomposites made from short abaca fiber and biodegradable polyesters. *Macromol Mater Eng* 288:35–43.

Shibata M, Oyamada S, Kobayashi S, Yaginuma D. 2004. Mechanical properties and biodegradability of green composites based on biodegradable polyesters and lyocell fabric. *J Appl Polym Sci* 92:3857–3863.

Teramoto N, Urata K, Ozawa K, Shibata M. 2004. Biodegradation of aliphatic polyester composites reinforced by abaca fiber. *Polym Degrad Stab* 86:401–409.

Vink ETH, Rabago KR, Glassner DA, Gruber PR. 2003. Applications of life cycle assessment to NatureWorks polylactide (PLA) production. *Polym Degrad Stab* 80:403–419.

Warmington A. 2001. Green progress. *Eur Plast News* 28:49–50.

Wong S, Shanks RA, Hodzic A. 2003. Poly(L-lactic acid) composites with flax fibers modified by plasticizer absorption. *Polym Eng Sci* 43:1566–1575.

Wong S, Shanks RA, Hodzic A. 2004. Mechanical behavior and fracture toughness of poly(L-lactic acid)-natural fiber composites modified with hyperbranched polymers. *Macromol Mater Eng* 289:447–456.

Wool RP, Sun XS. 2005. *Bio-based Polymers and Composites*. Burlington: Elsevier Academic Press.

Yu L, Dean K, Li L. 2006. Polymer blends and composites from renewable resources. *Prog Polym Sci* 31:576–602.

Yu L, Petinakis S, Dean K, Bilyk A, Wu D. 2007. Green polymeric blends and composites from renewable resources. *Macromol Symp* 249/250:535–539.

CHAPTER 13

Biocomposites of Natural Fibers and Poly(3-Hydroxybutyrate) and Copolymers: Improved Mechanical Properties Through Compatibilization at the Interface

SUSAN WONG and ROBERT SHANKS

Co-operative Research Centre for Polymers, School of Applied Sciences, Science, Engineering and Technology, RMIT University, Melbourne, Victoria, Australia

---

Biodegradable Polymer Blends and Composites from Renewable Resources. Edited by Long Yu

13.1 TRADITIONAL COMPOSITES AND NOVEL BIODEGRADABLE COMPOSITES

Composites are comprised of two discrete phases: one is the dispersed reinforcing phase such as fibers and organic and mineral fillers; the other is the continuous binding phase (referred to as the matrix) such as thermoplastics, thermosetting resins, and concrete. These have been widely used in many diverse fields over the past few decades. Their uses range from automotive interior parts, sporting goods, electronic components, artificial joints, insulation materials, and building structures, to furniture. The idea of introducing fillers such as fibers into a matrix is for them to act as a reinforcing component to yield improved properties compared with the individual components. The most common fibers used in conventional composites are glass, carbon, or aramid fibers with polypropylene, epoxy resins, unsaturated polyester resins, and polyurethanes. Although conventional composites give high strength and modulus, one major disadvantage is the difficulty of disposal after use. Synthetic composites are well interconnected and relatively stable and therefore separation for recycling is difficult.

With increasing environmental interest, the idea of a "green" environment is of great concern; thus many manufacturers are forced to seek alternative materials to produce many products to address environmental and recycling problems. An innovative idea that began in the late 1980s was to use natural fibers as an alternative to conventional fibers in consumer products. To keep to the idea of green materials, the use of biodegradable polymers as a matrix to replace synthetic matrices was introduced. These materials combined together yielded new materials known as biocomposites.

At present, composites comprised of natural fibers are not commonly used and have been restricted to uses in automotive interior parts where high load-bearing properties are not of great importance. Natural fibers such as flax, sisal, or kenaf have being introduced for automotive interior trim parts such as door panels, parcel shelves, and roofing (Pou et al., 2001). Vehicle manufactures such as Opel, Daimler Chrysler, BMW, Audi, and Ford have already introduced this type of technology into their vehicles (Karus, 1999). The use of natural fibers offers the advantages of weight reduction of 10–30%, good mechanical and manufacturing properties, good performance in accidents (high stability, no splintering), no emission of toxic substances, and overall reduction in costs.

However in the light of these advantages, the use of biocomposites is limited in further applications due to their properties being less than those in conventional composites such as epoxy resin/polypropylene-glass/carbon fiber composites. If possible, the production of these composites should employ existing equipment and technologies that are used to fabricate conventional composites.

The properties of the biocomposites need to be improved to increase the range of applications so that, ideally, the composites exhibit high modulus and strength and have good thermal and dimensional stability and resistance to impact (high toughness). The main controlling factor of these properties identified in literature is the degree of bonding or adhesion between the fiber and the matrix at the interface.

The interface is extremely important as the modulus, strength, and toughness of a composite relies heavily on the chemical interactions or mechanical interlocking between the fiber and the matrix. The strength and toughness are largely dependent on the ability of the matrix to transfer the applied stress to the reinforcing fibers. The inferior fiber–matrix adhesion arises from the hydrophilic nature of natural fibers, which have limited compatibility with the hydrophobic nature of thermoplastics. In brief, methods such as surface modification of the fibers and the use of additives have been investigated to combat such problems, with some success. However, in order to produce a composite with superior properties for specific applications, knowledge of the properties of the individual constituents is important so that conflicting characteristics can be identified and altered accordingly.

13.2 NATURAL FIBERS

Natural fibers with good mechanical performance are found in many natural sources such as varieties of plants. There are many different types of natural fibers as they can be extracted from many types and parts of plants. Generally, they are sourced primarily from the structural components such as the stems, leaves, and seeds. There are various classifications of these fibers, but the widely accepted one is based on their location in the plant. Accordingly, they have been subgrouped into three categories such as seed, bast, and leaf fibers. Some examples are cotton and coir (seed), flax and hemp (bast) and sisal and abaca (leaf). The bast and leaf fiber families are the most commonly used for polymer composites as they generally exhibit higher strength than seed fibers.

13.2.1 Types of Natural Fibers

In brief, leaf fibers found in the leaves of the plant have a coarser texture than bast fibers. Sisal and abaca fibers are among the most common leaf fibers. Sisal fibers can be obtained from three different zones of a leaf, and two kinds of fibers—"mechanical" and "ribbon"—can be extracted. The characteristics of the fibers depend largely on the maturity of the leaves. The fibers from mature leaves are generally coarser, longer and stronger than those from immature leaves. The extraction processes are by retting (controlled decay), hand-scraping, or decortication (mechanical separation). These fibers exhibit moderately high stiffness, high tensile strength (Table 13-1) and durability and have been used as wall coverings, floor mats, floor coverings and upholstery padding.

Coir fibers are categorized as seed fibers that are extracted from the husk of coconuts, and two types of fibers are classed as white or brown. The white variety is finer and lighter in color and is obtained from immature coconuts. They are flexible and therefore can be spun into yarn or twine, tufted to make floor mats and woven in carpets. The brown variety, obtained from mature coconuts, is coarse and stiff and is used in mattresses, brooms, nets, and air filters. These applications are those where high strength is not required as their tensile strength is generally weaker (see

TABLE 13-1 Typical Properties of Natural Fibers[a]

Properties	Flax	Coir	Sisal	E-glass
Density (g/cm^3)	1.4	1.25	1.33	2.55
Tensile strength (MPa)	800–1500	220	600–700	2400
Tensile modulus (GPa)	60–80	6	38	73
Specific modulus	26–46	5	29	29
Elongation at break (%)	1.2–1.6	15–25	2–3	3
Spiral angle (°)	10.0	41–45	20.0	–

[a] Adapted from Brouwer (2000).

Table 13-1). The extraction processes are wet milling or defibering on special machines.

The most common bast fibers are flax; these are extracted from the flax plant and have many uses depending on their quality. Finer flax is used mainly for linen, sheeting, lace, and apparel, while coarser fibers are used in twines, canvases, bags, fishnets, sewing threads, fire hoses, and sail cloth. The oil extracted from the flax seeds are used as linseed oil. Flax fibers will be discussed in some detail as they have been chosen as the fibers for the following studies.

13.2.2 Plant and Bast Fiber Structure (Flax)

The cross-section of the flax plant stem has five distinct regions, identified as the outer surface (epidermis layer), the intermediate layer (cortical parenchyma), the bast layer containing the fibers, the cambium layer, and woody tissue. Their regions are illustrated in Fig. 13-1.

In the outer surface layer (epidermis layer), there is a thin layer of wax to prevent excessive evaporation of moisture and to protect the plant from environmental conditions. The next, cortex, layer consists of circular cortical cells that contain pectin substances and coloring matter. In the third, bast, layer, the fiber bundles are found and they are surrounded by parenchyma. The fourth layer, the cambium layer, contains the tender growth tissue composed of thin-walled cells that separate the fiber layer from the fifth layer. The fifth layer is composed of woody tissue consisting of thick-walled cells and thin-walled cells surrounding the pith cavity, which is an air chamber throughout the length of the stalk. The fiber bundle located in the third layer of the stem can be further divided into subgroups according to the type of fibers.

As the schematic of the structure of the flax shows in Fig. 13-2, the fiber bundles are comprised of technical fibers with diameters of 50–100 μm and finer fibers within the technical fibers called elementary fibers (or ultimates) with diameters of 10–20 μm (Singleton et al., 2003). The technical fibers are bonded together with weak pectin and lignin interphase, and within the technical fiber 40 or more elementary fibers are found. The elementary fibers are bonded together by a stronger pectin interphase. Generally the elementary fibers have a higher tensile modulus of

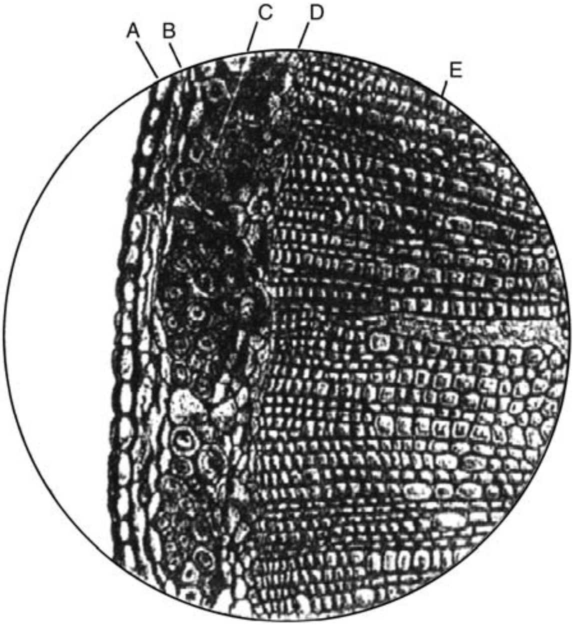


Fig. 13-1 Cross-section of flax plant stem: (A) outer layer (epidermis), (B) intermediate layer, (C) bast layer, (D) cambium layer, (E) woody tissue. (Reprinted from Rouette, 2001, *Encyclopedia of Textile Finishing*, Woodhead Publishing Limited, Cambridge, UK.)

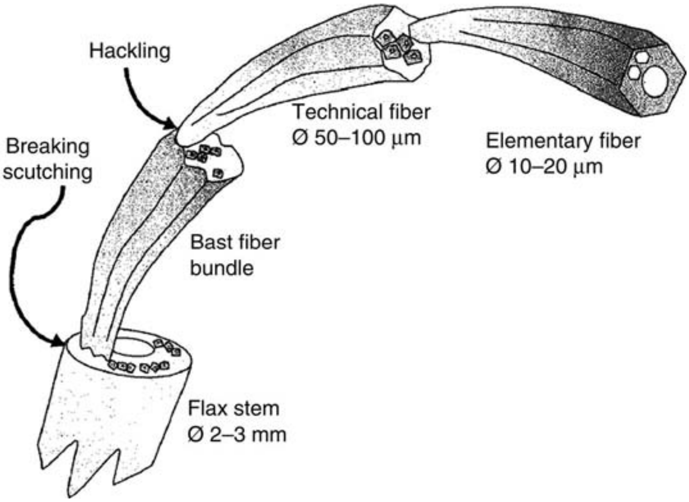


Fig. 13-2 Schematic of flax fiber showing the sub-grouping of fibers. (Reprinted from Van Den Oever et al., 2000, Influence of the physical structure of flax fibers on the mechanical properties of flax fiber reinforced polypropylene composites, *Applied Composite Materials* 7:387–402. With kind permission of Springer Science and Business Media.)

up to 80 GPa and tensile strength of approximately 1.5 GPa compared with the technical fibers with a typical tensile modulus of 50–60 GPa and a tensile strength of 0.6–0.7 GPa (Singleton et al., 2003). Further discussion of fiber properties will be presented in a later section. In practice, most fibers used in many studies are technical fibers or fiber bundles.

The separation techniques or processes that separate the fibers into their individual filaments can be retting and scutching, and the steam explosion technique. The fiber extraction is thought to have some influence on the fiber properties as it alters the chemical composition of the fibers.

The retting process is performed after harvesting and it can be done through biological action (use of enzymes) or chemical action. In brief it is basically a method of controlled rotting/decay and the harvested stalks are left in the fields under conditions of moderate humidity and warmth. Biological retting can remove some chemical components that are detrimental to the fiber strength such as pectic substances, proteins, sugars, starch, fats, and waxes. Lignin is usually resistant to biological degradation, and chemical methods of extraction can be employed.

After retting, the process called scutching is used to extract the fibers from the stalks. The stalks are first mechanically broken from the woody matter into small pieces of shrives that are then scraped to loosen the fibers from the shrives. Fluted rollers are used to break the core into pieces of shrive and the stalks are fed into a machine with rotating bladed-wheels that scutch the fibers clean. During this process, some fibers are broken and the longer fibers are sorted from the short. The long fibers are termed “scutched flax” or “line” and they can be spun after a special combing technique known as “hackling” which further separates the fibers according to length.

In the steam explosion method, the fibers are subjected to steam and additives (if necessary) at high pressures and elevated temperatures so that the steam can penetrate the space between the fibers of the fiber bundles. The middle lamella and the substances adhering on the fibers are dissolved, become water soluble, and can subsequently be removed by washing.

13.2.3 Chemical Components of Bast Fibers

Natural fibers are considered as lignocellulosic since they are composed of cellulose, hemicellulose, and lignin. The compositions of natural fibers depend on the type of fiber as well as the age, origin, and mode of extraction. These are shown in Table 13-2, which shows that most natural fibers consist of major components of cellulose, hemicellulose, and lignin. Other minor components are wax and pectin that function as protective barriers in plants.

Cellulose is the major component of natural fibers and is a polymer of hydrophilic glucan with linear chains of β-1,4-bonded anhydroglucose units containing hydroxyl groups (Mohanty et al., 2000b, 2001). The degree of polymerization of native cellulose is as high as 14,000, but purification usually reduces this to the order of 2500 (Bledzki and Gassan, 1999). Cellulose is chemically defined as poly(1,4-β-D-anhydroglucopyranose). The structure of cellulose is illustrated in Fig. 13-3.

TABLE 13-2 Chemical Components of Some Natural Fibers[a]

Type	Cellulose (wt%)	Lignin (wt%)	Hemicellulose (wt%)	Pectin (wt%)	Wax (wt%)	Moisture (wt%)
Bast						
Jute	61–71.5	12–13	13.6–20.4	0.2	0.5	12.6
Flax	71	2.2	18.6–20.6	2.3	1.7	10.0
Hemp	60.2–74.4	3.7–5.7	17.9–22.4	0.9	0.8	10.8
Ramie	68.6–76.2	0.6–0.7	13.1–16.7	1.9	0.3	8.0
Kenaf	31–39	15–19	21.5	–	–	–
Leaf						
Sisal	67–78	8.0–11.0	10.0–14.2	10.0	2.0	11.0
PALF[b]	70–82	5–12	–	–	–	–
Henequen	77.6	13.1	4–8	–	–	–
Seed						
Cotton	82.7	–	5.7	–	0.6	–

[a] Adapted from Mohanty et al. (2000b).
[b] Pineapple leaf fiber.

The function of cellulose in nature is to impart strength and rigidity to plants. The organization of cellulose chains within the fiber cell is depicted in Fig. 13-4. The structure of natural fibers is quite complex and each fiber could be considered as essentially a composite in itself. Crystalline cellulose is located in many cell walls including the primary and secondary walls and can be oriented or disordered. Disordered crystalline cellulose can be found in the primary wall, while the oriented crystalline cellulose (crystallites) is mainly found in the secondary walls. Elementary fibers (or ultimates) are made of oriented crystalline cellulose in a helical formation wound along the fiber axis at some angle (called the spiral angle), which differs depending on the type of natural fiber. The helical cellulose fibrils exist in a series of layers in the secondary walls and the direction of the spiral changes from Z-spiral to S-spiral successively. The cellulose microfibrils are generally embedded in a soft lignin and hemicellulose matrix in the amorphous regions of the fiber walls. When the helical cellulose chains are fully extended, they form a flat ribbon

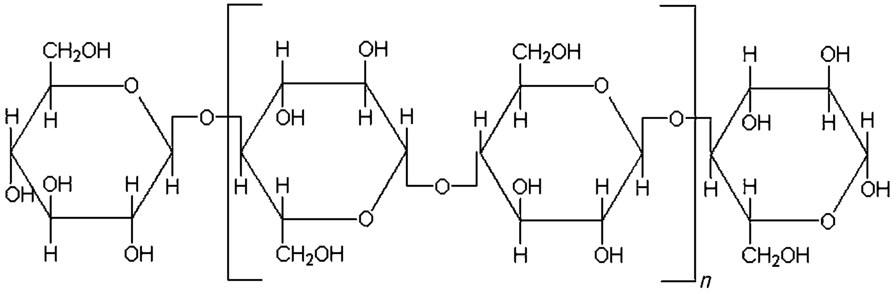


Fig. 13-3 Structure of cellulose.

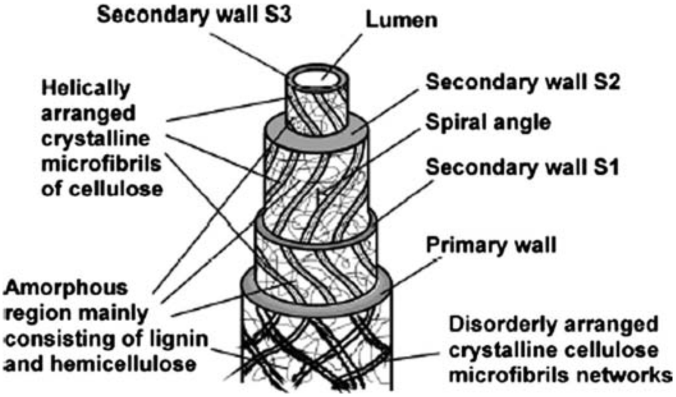


Fig. 13-4 Organization of cellulose chains in fiber cells. (Reprinted from Rong et al., 2001, The effect of fibre treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites, *Composites Science and Technology* 61:1437–1447. With permission from Elsevier.)

with the hydroxyl groups protruding laterally. These hydroxyl groups form intramolecular and intermolecular hydrogen bonds that give the fibers their hydrophilic nature. Moisture content ranges from 8% to 13%.

Hemicellulose is amorphous and consists of short-chained isotropic polysaccharides. It is chemically linked or partly intermingled and oriented with cellulose molecules as depicted in Fig. 13-5. Hemicellulose is not a form of cellulose as the name would suggest. There are three major differences between hemicellulose and cellulose. Hemicellulose contains several different sugar units, whereas cellulose contains only β-1,4-D-glucopyranose units. It also exhibits a considerable degree of chain branching, whereas cellulose is strictly linear. In addition, the degree of polymerization of native cellulose is about 10–100 times greater than that of hemicellulose. Although the chemical bonds between cellulose and hemicellulose are not covalent, they are still very strong and difficult to separate even through stringent extraction processes.

Lignin is a component that acts as a structural support material in plants by binding the other components together. Lignin is found between cellulose and hemicellulose

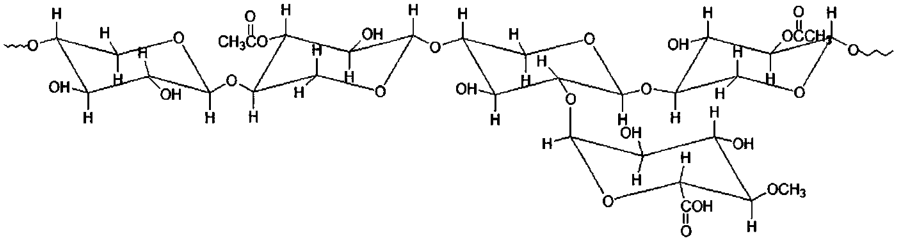


Fig. 13-5 Structure of hemicellulose.

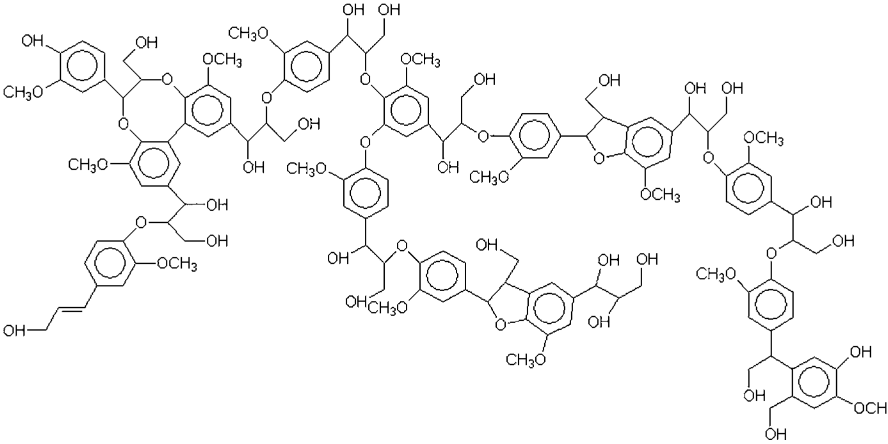


Fig. 13-6 Structure of lignin.

and on walls of cells. The exact chemical structure of lignin has not been established, but through identification of its functional groups it is said to be a phenolic polymeric material (Mohanty et al., 2001). It is found that lignin contains high carbon and low hydrogen content, which suggests that it is highly unsaturated or aromatic in nature. A probable structure of lignin is given in Fig. 13-6.

Although the chemistry of lignin in natural fibers is not well known, it is believed that two types of linkages form between the carbohydrate groups and lignin. One is an ester-type, which is formed between the hydroxyl of lignin and the carboxyl of hemicellulose uronic acid. The second is of an ether-type that occurs between hydroxyls of lignin and hydroxyls of cellulose. The ester-type linkage is sensitive to alkali and the ether-type is insensitive to alkali. Because lignin exists in combination with more than one neighboring cellulose/hemicellulose chain, a crosslinked structure is formed.

Pectins are polygalacturonosyl-containing polysaccharides that have other polysaccharides covalently associated with them. The branched, hydrated pectin molecules are capable of forming semirigid gels in the presence of calcium ions. The calcium ions bind neighboring galacturonan chains, which provide crosslinks that enhance the rigidity of the plant walls. During biological retting, acetic and butyric acids are formed. Pectin can be readily removed by boiling with alkali.

13.3 MECHANICAL PROPERTIES OF NATURAL FIBERS

Extensive studies on the mechanical properties of natural fibers are presented in numerous literature reports as the final composite properties are largely dependent on the reinforcing component. It has been established that natural fibers can compete with glass fibers in terms of mechanical properties. However, the mechanical properties of the fibers can vary depending on the quality of the fibers, which in turn is strongly affected by factors such as the different growing conditions, methods of fiber extraction, and maturity of the plant at harvest. With these sources of variability in mind, a general comparison of the natural fibers can still be made with careful control to minimize the variability in the determination of these properties. The mechanical properties of different types of natural fibers in reported studies are summarized and comparisons between the properties of glass fibers and natural fibers are presented.

It has been established that properties such as density, ultimate tensile strength, and modulus are related to the internal structure as well as the chemical composition of the fibers. More specifically, the strength and stiffness (modulus) of the natural fibers have been found to be dependent on the cellulose content and the spiral angle of the cellulose microfibrils in the inner secondary cell walls along the fiber axis (Li et al., 2000). Some typical properties of selected natural fibers are presented in Table 13-1.

E-glass fibers exhibited higher tensile modulus compared with all the natural fibers as expected, and consequently exhibited higher tensile strength and elongation at break. If the fibers are viewed in relation to the density of the fibers, that is, the specific modulus which takes account of the density, the specific modulus of flax and sisal are comparable with those of E-glass fibers. This is one advantage of natural fibers over conventional fibers when weight is important, since composites comprised of natural fibers are of much lower density. The elongation at break of natural fibers is similar to that of glass fibers, with the exception of coir fibers. As coir fibers have a much lower modulus than the other fibers shown, the elongation at break is expected to be higher than that of materials with higher modulus.

Of the natural fibers shown, higher tensile strength and modulus are exhibited by those with high cellulose content and lower content of amorphous chemical components such as hemicellulose, lignin, and wax (see Table 13-1). The strengths of the individual components of natural fibers are thought to be greatest for cellulose and the strength decreases in the following order for the other components: noncrystalline cellulose, hemicellulose, and lignin (Mohanty et al., 2000b).

The higher tensile strength and modulus of the natural fibers has been explained in terms of the fiber failure mechanism. In relation to the organization of cellulose chains within the fiber presented earlier, the cellulose chains are arranged in a helical formation in the secondary walls and are bound together by amorphous hemicellulose and lignin within the secondary walls and in the primary wall. When under tension, the primary wall consisting of amorphous materials fractures in a brittle manner, while the secondary walls are bridged by relatively thick cellulose fibrils. It has been reported that the higher the cellulose content, the greater the number of cellulose chains that can bridge a crack, resulting in greater strength for fracture to occur (Joffe et al., 2003). Another approach to the cause of breakage of native cellulose under tension was discussed on a molecular level. It has been stated that tensile breakage could be due to rupture of covalent bonds in the cellulose molecules or between secondary valence bonds (primarily hydrogen bonds) between the cellulose molecules (Gassan and Bledzki, 2001).

It is well recognized that the spiral angle of the cellulose chains has some influence on the tensile strength and modulus. It was established that the fibers with smaller spiral angles (such as flax and sisal) have higher strength and modulus compared with fibers with larger angles (coir). It was postulated that the chains with smaller spiral angles consume more energy to uncoil the helically oriented fibrils to their flat state (when subjected to tension) compared with chains with larger angles.

As mentioned earlier, flax fibers are the chosen fibers in the following studies of composites because they are natural fibers with exceptionally good mechanical properties. Comparison of the properties of flax with other natural fibers and E-glass is illustrated in Fig. 13-7.

Breaking length is a term for tenacity (breaking stress), a specific measure used in the textile industry, and is given in kilometers. It is the length at which the fiber breaks due to its own weight (Mohanty et al., 2000b). From the graph, flax fibers exhibit the highest stiffness along with hemp and ramie. It is worth noting that the stiffness of hemp even exceeds that of E-glass. The breaking length of flax is one of the highest compared with sisal, spruce, and cotton, and is comparable with that of E-glass. When subjected to tension, flax fibers have been known to undergo some amount of strain hardening, which is due to the progressive reorientation of the microfibrils with off-axis orientation in the unstrained fiber (Joffe et al., 2003). The elongation values are similar, with breakage occurring at about 3% strain. Based

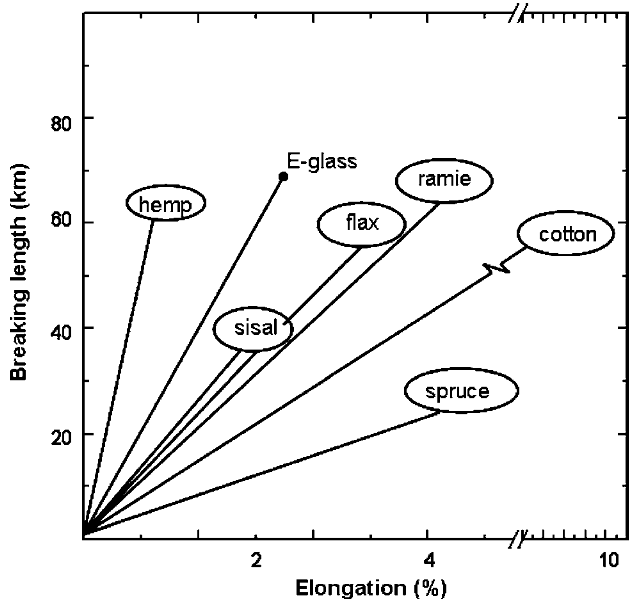


Fig. 13-7 Breaking length versus elongation of some natural fibers. (Reprinted from Herrmann et al., 1998, Construction materials based upon biologically renewable resources—from components to finished parts, *Polymer Degradation and Stability* 59:251–261. With permission from Elsevier.)

on these findings, flax fibers proved to be an appropriate fiber for the manufacture of composites compared with E-glass fibers.

13.3.1 Factors that Affect Fiber Mechanical Properties

As well the variability of natural fibers that depends on the quality (e.g., environmental growing conditions, maturity of plant at harvest), the mechanical properties of natural fibers can be affected by factors that may be introduced during manufacturing, during its service-life, and when subjected to different chemical treatments to improve their compatibility with polymeric matrices. These can alter the chemical structure or chemical composition of the fibers, which determine their strength. Such factors are vital and have been identified in order to make allowances for changes in the composites. Change in the chemical structure of the fibers can be brought about by thermal treatments, surface modifications of the fibers, and the effects of moisture. These are discussed in detail in the following.

13.3.1.1 Thermal Treatments During manufacture of fiber composites, it is often necessary to subject the thermoplastic matrix and fibers to heat to form the composites. Natural fibers are sensitive to thermal treatments as degradation can occur that weakens the fibers. The inherent moisture that is naturally bound to the hemicellulose component in the fibers can change depending on temperature and exposure time. Several publications have investigated these issues and have generally found that exposure to temperatures at or below 170°C did not have a significant effect on the strength of the fibers (Coutinho et al., 1999; Sharma et al., 1999; Gassan and Bledzki, 2001; Van de Velde and Baetens, 2001). However, exposure to higher temperatures (up to 247°C) can cause a significant reduction in the mechanical properties and change in chemical composition (Joffe et al., 2003). The strain was found to be more limited than the fiber strength. Removal of water by drying the fibers before fabrication of composites was sufficient to control the amount of moisture within the composites (Bledzki and Gassan, 1999).

The thermal stability of natural fibers is reported to depend on their structure and chemical composition. In general, the thermal stability of the individual components of natural fibers (in the absence of oxygen) is reported to show higher decomposition temperatures in the order lignin $<$ α-cellulose $<$ hemicellulose (Gassan and Bledzki, 2001). When the fibers are subjected to heat, the physical and/or chemical structural changes that can occur are depolymerization, hydrolysis, oxidation, dehydration, decarboxylation, and recrystallization (Gassan and Bledzki, 2001). Correlation of the degree of polymerization (X_n) and the degree of crystallinity (X_c) with the strength of flax and jute fibers (measured as tenacity) was presented in a study by Gassan and co-workers (Gassan and Bledzki, 2001). They concluded that when the fibers were exposed to temperatures below 170°C for a maximum of 120 min, a decrease in the X_n value resulted in a slight decrease in tenacity. For temperatures above 170°C, the tenacity showed a rapid decrease along with X_n, which depended on the exposure time and temperature. As jute fibers exhibited a lower value of X_n than flax, the decrease in tenacity was also greater.

It was found that chain scission of cellulose led to an increase in X_c upon heating of the fibers. It was thought that crystallization results from an increase in the size of preexisting crystallites by realignment of chains on the crystallite surface and at their ends, or by forming completely new crystallites within the amorphous regions of the fibers. However, an increase in X_c on exposure to high temperatures did not have any profound influence on the tenacity.

13.3.1.2 Effect of Moisture Removal of the moisture from the fibers before manufacture of composites is important for dimensional stability and elimination of voids within the composite, which would compromise its mechanical properties. However, exposure of fibers to mild humidity did not have a profound affect on the strength of the fibers as the moisture in fact had a plasticizing effect (Joffe et al., 2003). The effect of humidity on the fiber properties was found to be highly dependent on the exposure time, relative humidity, and any treatment of the fibers. Stamboulis and co-workers (Stamboulis et al., 2000, 2001) found that exposure of flax fibers up to a maximum humidity of 66% did indeed increase the strength of the fibers; this was attributed to plasticization due to "free" water molecules. It was thought that water was able penetrate into the cellulose network of the fiber in the capillaries and spaces between the fibrils. At relatively mild humidity, free water molecules force the cellulose molecules apart, destroying some rigidity of the cellulose structure. Due to this effect, cellulose molecules can move more freely because of plasticization and can reorientate to yield higher X_c and thus higher strength. However, at higher humidity, an increase in the absorbed bound water on the fibers and a decrease in free water molecules decreases the plasticizing effect, resulting in reduced fiber strength. On prolonged exposure, this may lead to degradation of the mechanical properties caused by fungus growth on the fiber surface.

Another explanation at a molecular level was presented by Stamboulis (Stamboulis et al., 2001). It was established that the strength was generally dependent on the spiral angle of the cellulose network. At high angles (flatter chains), the strength and modulus were reduced compared with a smaller angle. When water molecules penetrated into the fiber, the spiral angle was thought to be reduced (became steeper) resulting in higher tensile strength.

Along with marginal improvements in tensile strength with mild humidity, it is also important to note that the amorphous components of the fibers were dissolved, separating the filaments from the bundle. At high humidity, some damage to the fibers due to swelling resulted, which contributed to a reduction in strength. Swelling of the fibers resulted in formation of kink bands, determined to be defects along the fiber.

13.3.1.3 Surface Treatments of Fibers Surface treatments are often applied to fibers to enhance adhesion and durability under environmental conditions (temperature and moisture). As treatments usually change the fiber surface, they may alter the fiber strength. Surface treatments will be mentioned only briefly in this section as details will be discussed later.

Briefly, the mechanical properties of fibers after various treatments do not always produce an effect on the fiber strength. For example, acetylation of natural fibers brought about an increase in hydrophobicity so that compatibility with hydrophobic polymers was achieved. This was attained by reacting hydroxyl groups of the fiber constituents with acetyl groups through esterification (Zafeiropoulos et al., 2002). However, according to Joffe et al. (2003) no appreciable difference in the fiber strength was found upon acetylation of dew-retted flax, though for green flax a pronounced increase in the strength was observed. Treatment with stearic acid increased the hydrophobic nature of the fibers by reducing the number of free hydroxyl groups. Furthermore, the long hydrocarbon chain of stearic acid provided extra protection from moisture. The carboxyl groups of stearic acid reacted with the hydroxyl groups through esterification (Zafeiropoulos et al., 2002). This treatment was found to have no effect on the mechanical properties for low treatment times, but deterioration of the properties was observed with longer intervals. Ultimately, the effects on the mechanical properties depended on how the chemical or physical treatments changed the fiber structure and the chemical composition, so that no general trends can be given.

13.4 BIODEGRADABLE POLYMERS

There is a large range of biodegradable polymers that have been under extensive research. Most are produced synthetically from monomers of natural origin (biodegradable polymers) but some are produced by bacteria (biopolymers). These polymers have many potential applications, ranging from consumer packaging to medical applications (such as sutures, surgical implants) to automotive components. There are a number of types of biodegradable polymers and biopolymers and many kinds of classifications have been presented in the literature. In this study, these polymers are categorized by the origin of the monomers (synthetic or natural). A schematic representation of this classification is presented in Fig. 13-8.

The main function of the polymer in composites is to bind the fibers together, thus forming and stabilizing the shape of the composite structure. But most importantly, the matrix is responsible for transmitting the applied shear forces from the matrix to the fibers, resulting in high-strength composites. The selection of the matrix is important for the intended application in terms of the temperature range to which the composite will be subjected during use, the magnitudes of the mechanical loads, and the flexibility and stiffness required. From the range of biodegradable polymers available, the most promising for future use in place of synthetics such as poly (propylene) are the aliphatic polyesters. These are the most widely used polymers in the literature surveyed. As this study concerns the use of aliphatic polyesters as the matrices for biodegradable composites, their structure and synthesis and some properties of these polymers are presented.

As depicted in Fig. 13-8, the family of aliphatic polyesters can be produced from natural or synthetic monomers. From the category of natural monomers, these consists of poly(α-hydroxy acid)s and poly(β-hydroxyalkanoate)s. The classes of poly(ω-hydroxyalkanoate)s and poly(alkylene dicarboxylate)s are from synthetic monomers. These classes are summarized below.

13.4.1 Poly(α-Hydroxy Acid)s

Poly(lactic acid) and poly(glycolic acid) are two polymers from the class of poly(α-hydroxy acid)s. As poly(lactic acid) has been a primary concern in this study, it is discussed in detail.

Poly(lactic acid) (PLA) is a biodegradable, linear, aliphatic, thermoplastic polyester derived from completely renewable resources such as corn and sugar beets. It is a poly(α-hydroxy acid) and is also known as poly(lactate) or poly(lactide); its chemical structure is given in Fig. 13-9.

PLA exhibits good mechanical properties that are comparable with those of polystyrene (Martin and Averous, 2001). Its major drawback is its brittleness, but plasticization with various citrate esters (Labrecque et al., 1995, 1997; Martin and Averous, 2001; Ljungberg and Wesslen, 2002) or polyglycols (Sheth et al., 1997), and blending with other polymers (Kopinke and MacKenzie, 1997; Park et al., 2000; Ke and Sun, 2001) can improve its ductility. PLA is used primarily in medical applications such as sutures, drug delivery, and orthopedic implants because it is biocompatible (nontoxic for humans) (Labrecque et al., 1997). There is potential for large-scale uses in packaging and many consumer goods such as hygiene products.

PLA can be prepared by direct condensation of lactic acid and by ring-opening polymerization of the cyclic lactide dimer. Many different catalysts are employed such as complexes of aluminum, zinc, tin, and lanthanides. Stereochemically

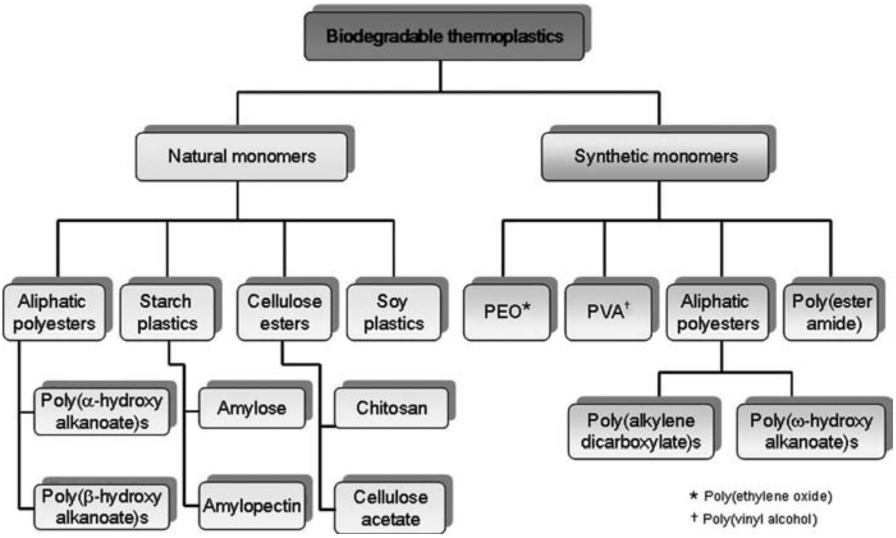


Fig. 13-8 Types of biodegradable thermoplastics from natural and synthetic monomers.

different PLAs can be produced from the two stereoisomers of lactide, L-lactide and D-lactide, and a third that exists as a mixture of D,L-lactide. The stereochemical compositions of the polymer have a dramatic affect on the melting temperature, the rate of crystallization, and the ultimate extent of crystallization. The glass transition temperature (T_g) is mainly affected by the molecular weight (M_w), which can range from "high" (425,000 g/mol) to "low" (12,000 g/mol) (Drumright et al., 2000).

The maximum melting temperature of stereochemically pure poly(lactide) (either D or L) is about 180°C with an enthalpy of melting of 40–50 J/g (Drumright et al., 2000). Higher enthalpy of melting in the range 76–78 J/g was reported (Perego et al., 1996). By introducing different stereochemical defects (D,L- or D-) into poly(L-lactic acid), reductions in the melting temperature, the rate of crystallization, and the magnitude of crystallinity can be observed with little effect on the T_g. The rate of crystallization is relatively slow even at the optimum crystallization temperature of 105–115°C for poly(L-lactic acid) (Drumright et al., 2000).

The properties of PLAs that make them suitable for many applications are good crease-retention and crimp properties, excellent grease and oil resistance, easy low-temperature heat sealability, and good barrier properties to flavors and aromas. They generally show a high modulus and strength but low toughness. The mechanical properties of PLA are largely dependent on the molecular weight and its processing conditions. After annealing of poly(L-lactic acid) (PLLA) with varying molecular weights, an increase in molecular weight showed only a slight increase in the tensile properties, but a more marked affect was noticed for the flexural properties. This was attributed to the crystallinity being lower at higher molecular weights as the lower-molecular-weight PLLA allowed crystallization to be more complete due to higher chain mobility (Perego et al., 1996). Another study, by Huda and coworkers (Huda et al., 2002), showed the importance of processing conditions for the dynamic mechanical properties. By using two different methods of processing—solution casting and heat pressing—the dynamic storage modulus (E'), which indicates the stiffness, they showed that the heat-pressed PLA retained its high stiffness to a higher temperature than did the solution cast sample.

Although PLA shows poor melt strength and is not very shear-sensitive, branching can be introduced by treating with peroxide or through addition of multifunctional initiators or monomers. Branching is proven to increase the viscosity even at low shear rates, making PLA applicable for use in extrusion coating, extrusion blow-molding, and foaming. Further modifications can make PLA suitable for injection molding, sheet extrusion, blow molding, thermoforming, film forming, or fiber spinning.

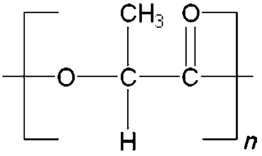


Fig. 13-9 Chemical structure of poly(lactic acid).

13.4.2 Poly(β-Hydroxyalkanoate)s

The polymers of poly(β-hydroxybutyrate) (PHB) and its copolymer, poly(β-hydroxybutyrate-*co*-hydoxyvalerate) (PHB-HV) come under the class of poly(β-hydroxyalkanoate)s. These are synthesized biochemically by microbial fermentation and bacteria accumulate them in granular form in their body as an energy storage material (Ha and Cho, 2002). PHB can be fermented from a variety of sources such as sugars and molasses or from hydrogen and carbon dioxide, depending on the bacteria used. Upon degradation under certain environmental conditions and with enzymes, these polymers become nontoxic residues of carbon dioxide and water.

Generally, poly(β-hydroxyalkanoate)s are linear polyesters that are semicrystalline, hydrophobic, and biocompatible and have good mechanical strength and modulus, resembling poly(propylene). Their structures are given in Fig. 13-10.

Pure PHB is highly crystalline (about 80%) (Janigova et al., 2002), resulting in its brittle nature and low elongations as drawing is not possible. PHB is frequently referred to as a hard, brittle plastic. It exhibits a narrow processing window as it readily undergoes degradation via chain-scission to form crotonic acid and oligomers (Kopinke and MacKenzie, 1997) along with a reduction in M_w and melt viscosity. Plasticizers such as glycerol, triacetin, citrate esters, and tributyrin are employed to reduce the processing temperature as well as the brittleness (El-Hadi et al., 2002; Janigova et al., 2002). The brittle nature of PHB comes from large volume-filling spherulites from few nuclei due to their high purity, accompanied by a number of interspherulitic cracks. Two types of cracks can be present, circular breaks around the center of the spherulite and splitting between the crystal interfaces. The crystallization rate depends on sample preparation but is generally faster with precipitation from solution than with solution casting. The mechanical properties of PHB depend largely on the crystallization process. It was found that during rapid cooling, the degree of crystallinity was reduced, producing smaller spherulites, which consequently exhibited better mechanical properties compared with PHB with high crystallinity and large spherulites. The T_g of PHB is around 0–5°C and it has a melting temperature (T_m) of about 178°C (Janigova et al., 2002). Young's modulus of PHB is usually about 3.5 GPa, which is comparable with poly(propylene) or poly (ethylene terephthalate) (Ha and Cho, 2002).

The copolymer of PHB with hydroxyvalerate (HV) units was produced in order to reduce the brittleness of PHB. The HV content in the copolymer can range from 0 to 95 mol% and the ductility depends on the relative content of HV. The Young's modulus generally decreases with greater HV content; thus properties from rigid

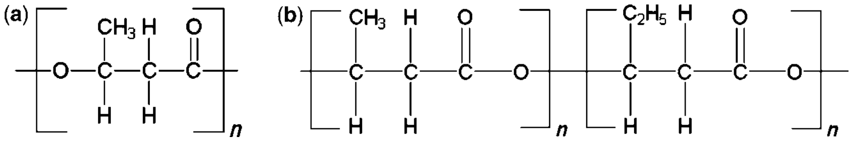


Fig. 13-10 Chemical structures of (a) poly(β-hydroxybutyrate) and (b) poly(β-hydroxybutyrate-*co*-hydroxyvalerate).

(with high crystallinity) to elastomeric can be obtained depending on the composition. The copolymers generally have lower crystallinity and thus reduced T_m compared with pure PHB. The T_m can be reduced to as low as 75°C with 40 mol% of HV and greater HV content results in a gradual increase in T_m to 108°C at 95 mol% HV (Mohanty et al., 2000b). The T_g of copolymers was reduced to about −10 to −20°C. The crystallization rate of copolymers was found to decrease with greater HV content and the HB and HV units cocrystallize.

13.4.3 Poly(ω-Hydroxyalkanoate)s

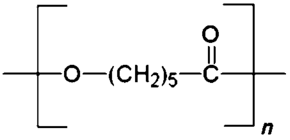
Poly(ε-caprolactone) (PCL) is a typical poly(ω-hydroxyalkanoate) that is a partially crystalline linear polyester with a very low T_g of −60°C and a low T_m of 60°C (Mohanty et al., 2000b). PCL is produced from the cyclic ester lactone monomer by ring-opening reactions with stannous octanoate as a catalyst in the presence of an initiator with an active hydrogen atom. Its structure is shown in Fig. 13-11.

PCL is described as a tough and semirigid polymer at room temperature, exhibiting a tensile modulus between 520 and 600 MPa depending on its molecular weight (Corden et al., 1999). The molecular weights can range from 200 to 100,000 g/mol and the polymers exist from liquids to hard waxes. PCL is flexible at room temperature due to its low T_g. The crystallinity of PCL is quite high (about 45–60%) as its T_g is significantly low, which allows crystallization to proceed easily. It is miscible with a range of polymers and organic materials and therefore is widely used as a compatabilizer. From the literature surveyed, PCL is not used as a polymeric matrix for composites because the mechanical properties are generally lower than those of the other types of aliphatic polyesters. PCLs are mainly used in blend formulations as a plasticizer for other brittle polymers to enhance their mechanical properties.

13.4.4 Poly(Alkylene Dicarboxylate)s

The types of polyesters known as poly(alkylene dicarboxylate)s include poly(butylene succinate) (PBS), poly(butylene succinate-*co*-butylene adipate) (PBSBA), and poly(ethylene succinate) (PES). These are produced through polycondensation reactions of glycols (e.g., ethylene glycol and 1,4-butanediol) with aliphatic dicarboxylic acids (such as succinic acid and adipic acid). The general structure of poly(alkylene dicarboxylate)s is depicted in Fig. 13-12.

The average molecular weights of poly(alkylene dicarboxylate)s range from 40,000 to 1,000,000 g/mol (Fujimaki, 1998). Their T_m values are about 116°C but



$$\left[-O-(CH_2)_5-\overset{O}{\overset{\|}{C}}- \right]_n$$

Fig. 13-11 Chemical structure of poly(ε-caprolactone).

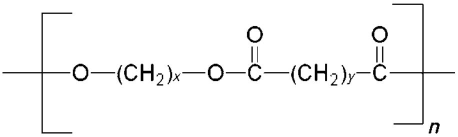


Fig. 13-12 Chemical structure of poly(alkylene dicarboxylate)s.

T_m values of their copolymers are slightly lower and their T_g values range from -45 to -10°C. The tensile modulus for PBS is 0.54 MPa with a yield strength of 32.9 MPa and a large elongation of 560%. The tensile modulus of PES is similar to that of PBS but its elongation and yield strength are lower than for PBS (200% and 20.5 MPa, respectively) (Fujimaki, 1998). Depending on the polymer structure, these polymers are suitable for processing with conventional methods and equipment. The linear types are suitable for injection molding and fabrication of filaments, while the comb types with short branching are applicable to film casting, foaming, and sheet extrusion. The star types with few long branches are suitable for tubular films, foamed fibrils, and manufacture of bottles. Like PCL, aliphatic polyesters of this type are not used for manufacture of natural fiber composites because of their low mechanical properties relative to the poly(α-hydroxy acid)s and poly(β-hydroxyalkanoate)s.

13.5 MAJOR PROBLEMS ASSOCIATED WITH HIGH-STRENGTH COMPOSITES

The problem of adhesion between fibers and matrices is well recognized in the field of composites. It is highly desirable to have a strong fiber–matrix interface as it is thought that the composite strength stems from the ability of the matrix to transfer its stress to the fibers. The fiber–matrix interface is generally the weakest part of the composite. The degree of interaction between the fibers and the matrix is often called the "interfacial bonding" and is related to the "interfacial strength." Many studies have found that good interfacial bonding is crucial for high-strength and high-modulus composites.

In natural fiber composites the polymers used as the matrix are often hydrophobic (nonpolar), while the natural fibers are hydrophilic (polar). This leads to limited compatibility and gives inherently inferior mechanical properties. The presence of natural waxy compounds on the fiber surface also limits the fiber–matrix bonding due to poor surface wetting.

The importance of the interfacial bonding for the mechanical properties was revealed in a study by Lui and co-workers (Lui and Netravali, 1999). This entailed unidirectional biocomposites comprised of pineapple fibers and poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHB-HV). The variables of interest were fiber loading and fiber orientation. It was found that as the fiber loading increased, the tensile and flexural strength and modulus increased accordingly in the longitudinal direction compared with the pure polymer. An increase in tensile strength from 26 MPa (pure polymer) to 80 MPa was exhibited with 29% volume of fibers. However, the tensile and flexural strength of the composites in the transverse direction decreased as a function of fiber content. A reduction in tensile strength from 26 MPa (pure polymer) to 8 MPa resulted with the inclusion of 29% volume of fibers. The fractured surfaces of these composites revealed that failure was initiated at the fiber–matrix interface, as observed by SEM. No polymer was observed on the fiber surface and fiber pull-out from the matrix was evident, indicative of poor interfacial adhesion. Further evidence of poor adhesion between the fibers and the matrix was implied in the crystallization kinetics. No change in the kinetics during crystallization of PHBV was detected regardless of the fiber loading. Accordingly, the melting temperature and enthalpy remained constant. If there is interaction between the matrix and the fiber existed, the fiber surface would be expected to act as a nucleating agent, affecting the crystallization kinetics.

Various physical and chemical methods have been investigated to improve the interfacial bonding and gain some improved levels of adhesion. These methods usually alter the surface energy of the fibers and can alter the surface structure. The ultimate interfacial bonding is complex and is difficult to achieve as there are many parameters that contribute to the interfacial properties. These include the surface energies of the fibers and matrix, matrix morphology, fiber surface condition, presence of residual stresses, moduli of the fiber and the matrix, and the presence of reactive functionalities (Gao and Kim, 2000). Roughness of the fiber surface is thought to contribute to a good interface as it can cause mechanical interlocking between the matrix and the fiber.

Pathways to improvement of the interface have taken directions toward the use of physical methods to alter the fiber surface (with no change to chemical composition) as well as chemical methods such as chemical surface modification and the use of additives (i.e., coupling agents). Chemical methods have proved to be the most popular and convenient for chemists. The various methods are summarized in sections 13.5.1 and 13.5.2 with particular emphasis on the use of additives.

13.5.1 Physical Modification of Natural Fibers

Physical methods do not involve changes in the chemical composition of the fibers. Some of these methods include stretching, calendering, thermal treatment, and production of hybrid yarns, all of which change the structural and surface properties of the fibers and influence the mechanical bonding between the fibers and the polymer.

Electric discharge methods (corona and cold plasma) are physical treatments. Corona treatment is effectively surface oxidation and it has been found to alter the surface energy of cellulose fibers (Bledzki and Gassan, 1999). Cold plasma treatment basically functions the same way as the corona discharge method. Depending on the choice of gases, a variety of surface modifications could be achieved such as surface crosslinking, increasing or decreasing the surface energies, and production of reactive free radicals and groups. Electric discharge methods are very effective for use with polymer substrates that are "nonactive" such as polystyrene, polyethylene, and polypropylene and they have been found to be successful with cellulose-based fibers.

13.5.2 Chemical Modifications of Natural Fibers

Chemical modifications are applied to natural fibers in an attempt to improve the matrix–fiber adhesion by bringing about changes in the chemical composition of the fibers as well as the surface properties. Some chemical modifications could lead to reduced water absorption. Since the use of natural fibers as reinforcements was introduced, numerous chemical modifications have been published in the literature such as dewaxing (Gassan and Bledzki, 1999; Mohanty et al., 2000a), alkalization (mercerization) (Gassan and Bledzki, 1999; Mwaikambo and Ansell, 1999; Mohanty et al., 2000a; Ray and Sarkar, 2001), acetylation (Mwaikambo and Ansell, 1999; Hill and Abdul Khalil, 2000; Singh et al., 2000), coating with coupling agents (Singh et al., 2000; Rozman et al., 2001), cyanoethylation (Mohanty et al., 2000a; Rout et al., 2001), esterification and etherification (Kazayawoko et al., 1997; Baiardo et al., 2002), and grafting (acrylonitrile and methyl methacrylate) (Samal, 1994, 1997; Saha et al., 2000; Mishra et al., 2001). Other modifications include crosslinking with formaldehyde, *p*-phenylenediamine, and phthalic anhydride; nitration; dinitrophenylation; benzoylation; and transesterification (Samal, 1995, 1997, 2001).

Schematic presentations of some of these chemical reactions are shown in Fig. 13-13.

As there are many chemical modification methods, only the most popular methods, alkalization, acetylation, treatment with anhydrides, and the use of silane coupling agents are discussed in detail. Some novel innovations that have been developed recently are also presented. Excellent review papers on the other surface treatments of natural fibers can be found in Bledzki and Gassan (1999) and Mohanty et al. (2001).

13.5.2.1 Alkalization Alkalization (mercerization) is commonly used as a pretreatment to improve the polymer–fiber composite properties through treatment of the fibers with an alkali (KOH, LiOH, and NaOH). The most effective and commonest alkali used is NaOH. The chemical reaction is shown as reaction (1) in Fig. 13-13. The use of an alkali produce a change to a new cellulose form, from cellulose I to cellulose II, partial dissolution of noncellulosic components (such as hemicellulose, lignin, and pectin), and a rougher surface topography. All these factors combined lead to polymer–fiber composites with improved modulus and strength compared with their untreated counterparts. However, careful consideration must be exercised toward the alkali concentration and treatment times as extremely harsh treatments will degrade the cellulose crystal structure and inhibit maximum conversion of cellulose I to cellulose II forms.

Native cellulose found in flax and other natural fibers exhibits a monoclinic crystalline lattice of cellulose I (Van de Weyenberg et al., 2006). When subjected to NaOH, the cellulose fiber swells, widening the small pores between the lattice plane, and NaOH penetrates into them. Sodium ions displace hydrogen ions on the hydroxyl groups, forming Na-cellulose I. After removal of the excess NaOH by

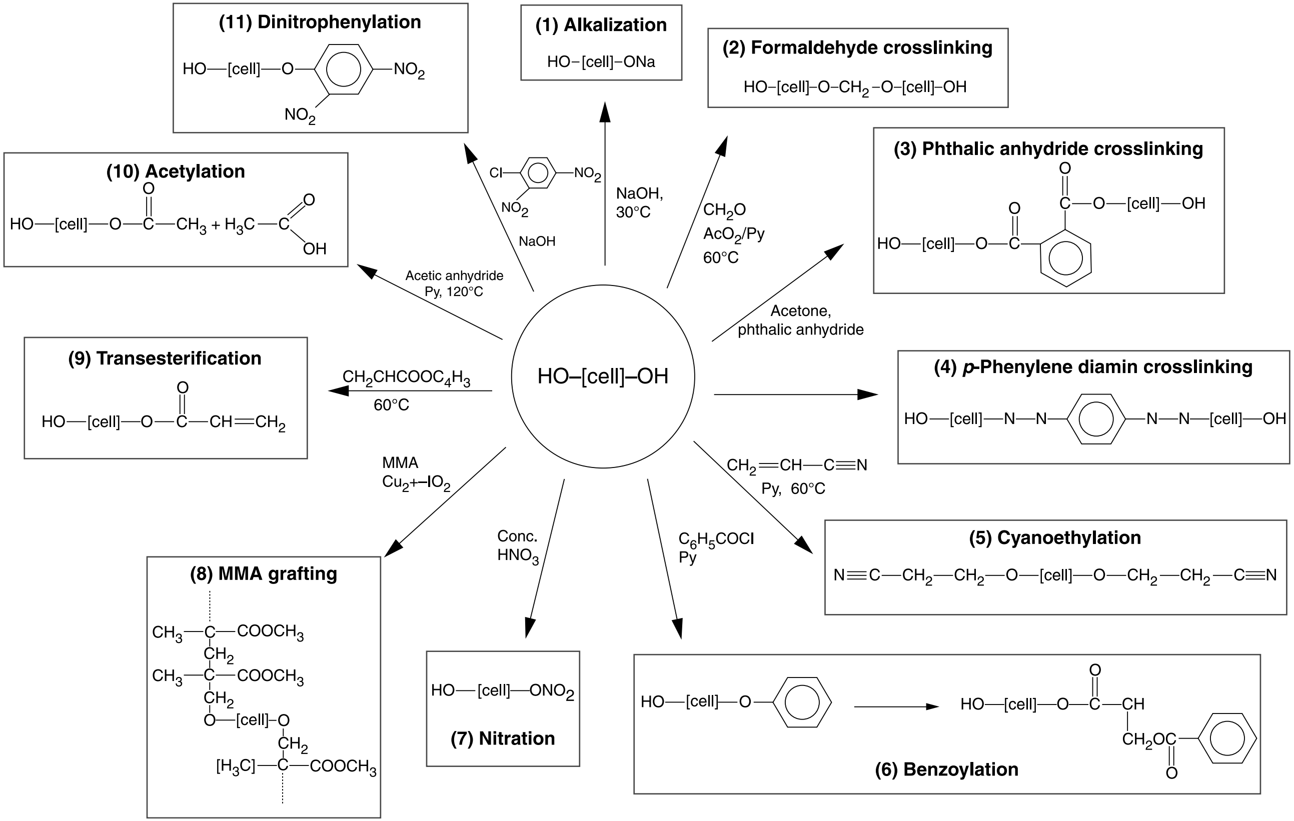


Fig. 13-13 Schematic presentation of chemical modifications of natural fibers.

washing with distilled water, sodium ions are removed and conversion occurs from cellulose I to cellulose II, which is more thermodynamically stable. Subsequent to caustic treatment, it was found that the crystallinity increased along with improved crystalline packing due to the removal of noncellulosic components (Mwaikambo and Ansell, 1999; Das and Chakraborty, 2006; Van de Weyenberg et al., 2006). The dissolution of the noncellulosic constituents allowed the cellulose fibrils to rearrange, exhibiting a reduced spiral angle (the angle between the fibrils and fiber axis) and increased the molecular orientation. Ray and Sarkar (2001) showed that after alkali treatment of coir fibers, the fiber modulus and the tenacity increased while the strain at break was reduced.

The partial removal of noncellulosic components (hemicellulose, pectin, and lignin) caused the fiber bundles to separate into technical and elementary fibers of smaller diameters. This led to an increase in the fiber aspect ratio (the ratio of length of the fiber to the diameter) and accordingly to surface area. The surface topography was markedly altered, whereby the surface roughness was greatly enhanced. A number of large holes or pits on the fiber surface were visible (Fig. 13-14). Rout and co-workers attributed those holes to the removal of fatty deposits of tyloses that lie hidden inside the surface of the untreated fiber. The increasing surface roughness was thought to be responsible for better fiber–matrix adhesion, giving rise to additional sites for mechanical interlocking (Rout et al., 2001).

Shrinkage of jute fibers upon alkalization was reported by Gassan and co-workers (Gassan and Bledzki, 1999), which led to a beneficial change in the mechanical properties. It was found that the higher the alkali concentration (up to 28%), the greater the degree of shrinkage from a greater loss of lignin and hemicellulose. As a result, improved yarn modulus and strength were observed due to removal of hemicellulose, which caused a change in the orientation of the amorphous cellulose and some regions of the crystalline cellulose.

Composites comprised of alkali-treated jute fibers and poly(3-hydroxybutyrate-*co*-8%-3-hydroxyvalerate) (tradename Biopol®) were studied by Mohanty and

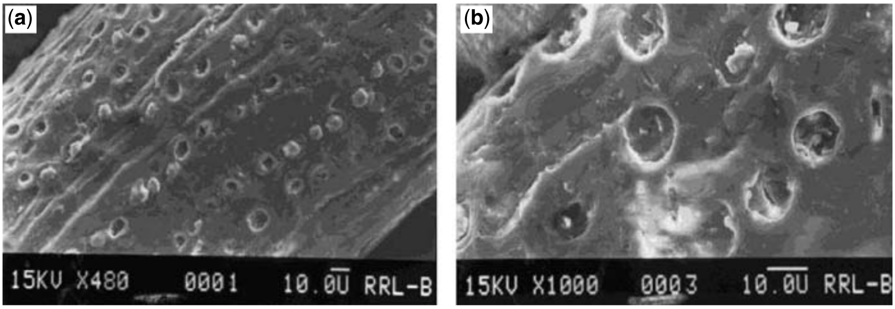


Fig. 13-14 SEM images of coir fibers before (a) and after (b) alkali treatment. Scale bar given in 10 μm. (Reprinted from Rout et al., 2001, Scanning electron microscopy study of chemically modified coir fibers, *Journal of Applied Polymer Science* 79, 1169–1177. Copyright 2001 John Wiley & Sons. Reprinted with permission of John Wiley & Sons, Inc.)

co-workers (Mohanty et al., 2000c). The fibers were oriented and were prepared by a prepreg method. For the composites tested in the parallel direction to the fiber orientation, the tensile, flexural, and impact strengths were significantly improved relative to the pure polymer and to those comprised of defatted fibers (surface waxes removed with a solution of 1 : 2 alcohol and benzene).

The tensile strength of the alkali-treated composite was about 2.4 times greater than that of the pure polymer, while that of the defatted fiber composite was about 1.9 times higher than that of the pure polymer. Similar incremental improvements in flexural strength were obtained of 1.5 times and 1.25 times for alkali and defatted composites, respectively. The authors attributed the improved composite properties seen in the alkali fiber composites to the rough fiber surface topography, enabling mechanical interlocking. Fiber fibrillation increased the effective contact surface area between the fiber and the matrix, and was suspected to contribute to the enhanced mechanical properties.

13.5.2.2 *Acetylation* Acetylation involves replacing the hydroxyl groups of the natural fibers with acetyl moieties. It is done to plasticize the fibers, improve the dimensional stability, and improve dispersion of fibers into polymeric matrices, traditionally nonbiodegradable polymers such as polyalkenes. After acetylation, the moisture regain was considerably reduced as the fibers became more hydrophobic due to the substitution of hydroxyl groups with acetyl groups (Khalil et al., 1997). It has been found that acetylation of hydroxyl groups from lignin and hemicellulose occurs more readily than of those from cellulose due to the tightly packed, hydrogen-bonded crystalline nature of cellulose (Tserki et al., 2005). Acetylated fibers were obtained by immersing the plant fibers in acetic anhydride as illustrated in Fig. 13-13, reaction (10) in the presence of pyridine (Bauer and Owen, 1988). Any unreacted reagents and acid by-products were removed by Soxhlet extraction with acetone. Alternatively, acetylation could occur in the presence or absence of an acid catalyst. In the presence of a catalyst, the untreated fibers were initially soaked in acetic acid to cause them to swell so that a faster reaction could occur before acetylation with acetic anhydride (Mwaikambo and Ansell, 1999).

Interestingly, the type of natural fibers has proved to be paramount to the degree of acetylation. Because the substitution of hydroxyl groups with acetyl moieties occurs mostly within lignin and hemicellulose, fibers that contain greater amounts of these components generally show greater degrees of esterification. The reactivity of acetic anhydride is greatest with lignin, followed by hemicellulose and lastly cellulose. Teserki and co-workers quantified the ester content after acetylation of flax, hemp, and wood fibers for various reaction times (Tserki et al., 2005). Wood fibers that are rich in lignin and hemicellulose resulted in the greatest ester content (17.2 wt%) after 120 min of treatment. Flax and hemp fibers that are abundant in cellulose displayed lower ester content of 6.9 and 5.8 wt%, respectively.

The effect of acetylation on the surface topography of the fibers was inspected by SEM (Fig. 13-15). For all untreated fibers, uneven layers of wax on the surface can be clearly seen. Upon acetylation, the esterified fibers were smooth compared with the untreated fibers. This indicated that some of the waxy surface substances

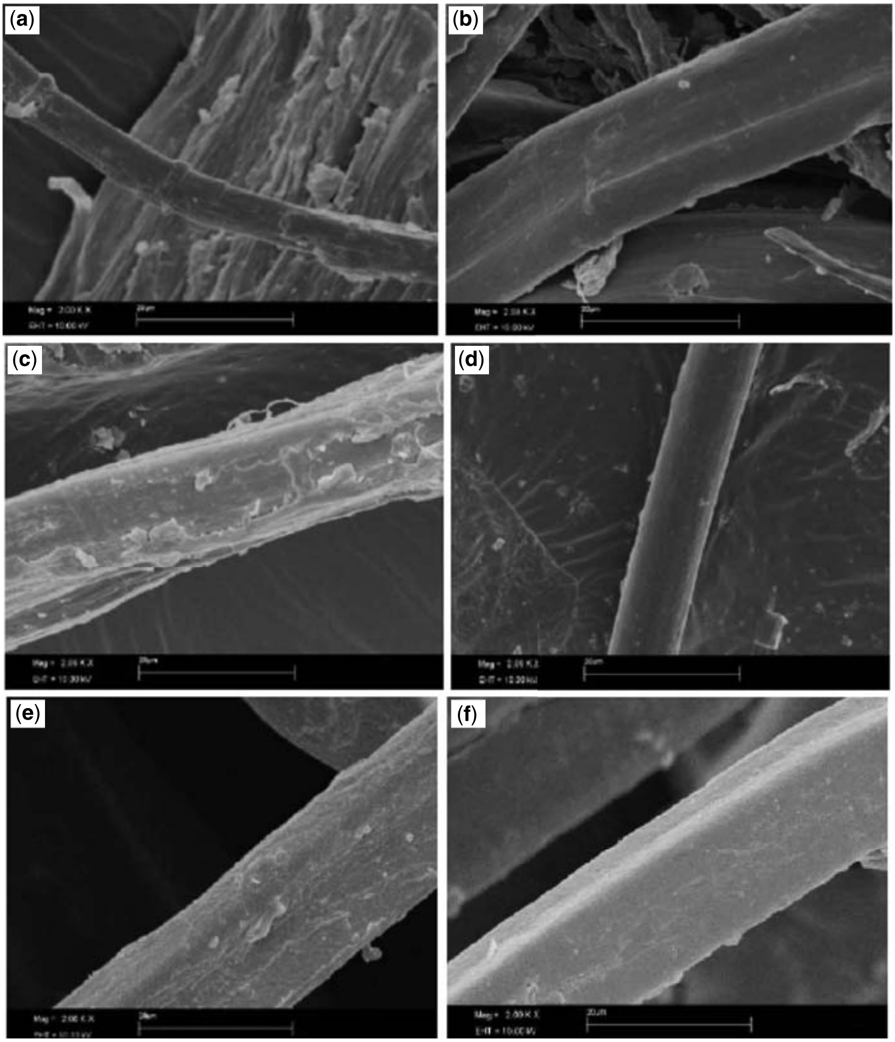


Fig. 13-15 SEM images of untreated (a) and acetylated (b) flax fiber, untreated (c) and acetylated (d) hemp fiber and untreated (e) and acetylated (f) of wood fiber. (Reprinted from Tserki et al., 2005, A study of the effect of acetylation and propionylation surface treatments on natural fibers, *Composites Part A: Applied Science and Manufacturing* 36(8):1110–1118. Reproduced with permission from Elsevier.)

were removed and it was postulated that a smooth fiber surface resulted from the acetyl groups.

Acetylated fibers have proved to be effective in many nonbiodegradable polymeric matrices. The tensile strength and modulus of acetylated fiber/polyester composites were found to be higher, probably due to better resin wetting. Compared with the untreated fiber composites, the increase in hydrophobicity of the acetylated fibers prevented debonding at the interface as covalent bonds could be formed between the matrix and the fibers. The interfacial shear strength (IFSS) (a measure of adhesion) of oil palm acetylated fibers with polystyrene was higher than that of unmodified fibers as the matrix had a greater ability to wet the fiber surface, increasing the work of adhesion. Similar results were found with various commercial epoxy resins. Overall, the improvement in the IFSS was attributed to an increase in compatible surface energies and formation of chemical, physical, and mechanical bonds.

Zini and co-workers studied the effects of acetylation of flax fibers on the tensile properties in poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (P[3HB-*co*-3HH]) composites. In the unmodified short fiber composite, the tensile strength was lower than in the pure polymer (1.3 GPa and 1.4 GPa, respectively). This was thought to be due to a lack of adhesion between the fibers and the polymer (Zini et al., 2007).

The tensile strength of the resultant composite was greater than that of the unmodified composite upon acetylation of the fibers. The tensile strength increased from 1.3 GPa to 1.8 GPa. With the aid of SEM (Fig. 13-16), a strong interface was observed between the acetylated fibers and the matrix compared with the unmodified fiber system.

It can be clearly seen that large cavities at the interface were present in the unmodified composite, indicative of inferior bonding between the fibers and the matrix. This resulted in poor transfer of stress from the fibers to the matrix, giving lower strength than the pure polymer. Conversely, no cavities were observed at the interface of the acetylated composite, as consequence of a stronger interface.

Due to the difference in surface morphology after acetylation, polarized optical microscopy revealed that transcrystallinity—the phenomenon whereby the fiber behaves as a nucleating agent, inducing spherulite growth along the perpendicular of the fiber—was absent during isothermal crystallization compared with the unmodified fiber. The authors could not definitively explain why transcrystallinity did not develop. However, they did note that their results supported earlier findings that transcrystallinity did not enhance the strength of the fiber composites as the acetylated composites displayed improved strength (without transcrystallinity) compared with the unmodified composites, which exhibited transcrystallization.

13.5.2.3 Treatment with Anhydrides

Anhydrides used in composites are by definition considered as organic coupling agents. Coupling agents are described as "substances that are used in small quantities to treat a surface so that bonding occurs between it and another surface" (Lu et al., 2000). Anhydrides that have been successfully used as coupling agents are acetic anhydride (AA), alkyl succinic anhydride (ASA), succinic anhydride (SA), phthalic anhydride (PA), butyric anhydride (BA) and maleic anhydride (MA). The most common of this variety is MA. The carboxylate groups in AA, SA and PA can covalently bond to cellulose through esterification or through hydrogen bonding. The reaction is shown in Fig. 13-17.

MA on the other hand is an α,β-unsaturated carbonyl compound with one carbon–carbon double bond and two carboxylate groups. The conjugated structure significantly enhanced the reactivity of the carbon–carbon double bond with the

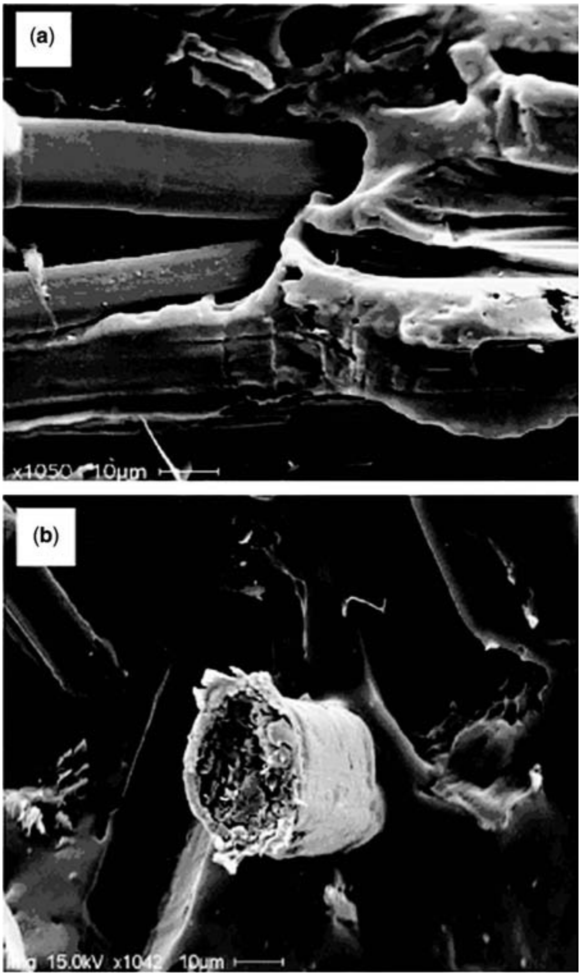


Fig. 13-16 SEM images of fractured surfaces of (a) unmodified fiber composite and (b) acetylated fiber composite. (Reprinted from Zini et al., 2007, Biocomposite of bacterial poly(3-hydroxybutyrate-*co*-3-hydroxybutyrate) reinforced with vegetable fibers, *Composite Science and Technology*, 67(10):2085–2094. Reproduced with permission from Elsevier.)

polymeric matrix using a radical initiator. Crosslinking that occurred caused a strong adhesion at the interface.

BA was used to treat abaca leaf fibers in PHB-HV composites (Shibata et al., 2002). The level of fiber loading ranged from 0 to 20%wt and was randomly orientated. Fibers

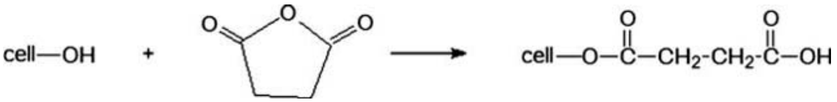


Fig. 13-17 Reaction between cellulose fibers and succinic anhydride (SA).

were treated by soaking in a solution of BA and pyridine (molar ratio of 1 : 1) at room temperature for various prescribed times (0.5 to 24 h). In this study, an improvement in flexural strength and modulus was observed relative to the unmodified composite, but no improvements in the tensile properties were detected.

As expected, an increase in the fiber loading (up to 20 %wt) of the treated fibers in the composites resulted in a substantial rise in the flexural modulus and flexural strength compared with the pure polymer and the untreated composites. The authors of the study found that the anhydride treated fiber composites were comparable with PHB-HV/glass fiber composites at the same fiber loading. The length of the anhydride treatment times of the fibers did not display a significant effect on the flexural properties. The composites with fibers that were treated for 5 h exhibited a marginal rise in flexural strength and modulus compared with the composites with 12 h treatment.

On SEM it was found that there were no appreciable differences in surface topography between the unmodified and the anhydride-treated fibers. The treated fiber surface was only marginally rougher than that of the unmodified fibers, implying that the improvement in flexural properties was not due to a physical effect. However, micrographs of the fractured surface of the unmodified composite and the treated fiber composite revealed that strong fiber–matrix adhesiveness was attained, as was implied by the absence of cavities between the fiber–matrix interfaces in the anhydride-treated composite.

Grafting of anhydrides onto polymers can be effective for enhancing the compatibility between polymeric matrices and natural fibers. It is well known that maleated polypropylene (PP-*g*-MA) is very effective in polypropylene/natural fiber composites. The mechanism of PP-*g*-MA is similar to that of anhydrides with cellulose. The reaction scheme is presented in Fig. 13-18. A covalent bond is formed between the cellulose fiber and PP-*g*-MA, while the PP chain can form chain entanglements with the matrix to give strong adhesion (Mohanty et al., 2001).

In recent publications it was revealed that anhydride grafting onto PHB-HV can be achieved by reactive blending and is an effective coupling agent in natural fiber composites (Avella et al., 2007). The anhydride group can bond with the hydroxyl group of cellulose, like the PP-*g*-MA, and have the same surface energy/polarity of PHB-HV to enhance the interfacial strength.

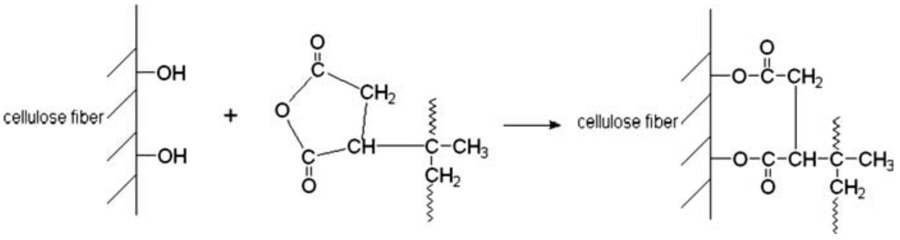


Fig. 13-18 Esterification of cellulose and PP-*g*-MA.

Anhydride grafting onto PHB-HV involved dibenzoyl peroxide (DBPO), PHB-HV and maleic anhydride mixed in a Brabender-like apparatus at 170°C. Details of the synthesis of maleated PHB are given in Chen et al. (2003). The reaction is shown in Fig. 13-19.

Different amounts of maleic anhydride (3, 5, and 7 wt%) were grafted onto PHB-HV through thermal decomposition of DBPO. It was found that attachment of MA mainly occurred onto the hydroxybutyrate units rather than hydroxyvalerate. It is speculated that this was due to steric hindrance of the ethyl group on the β-carbon of the hydroxyvalerate unit. The reduced acidity from the presence of the ethyl group could also reduce the availability of hydrogen to radical attack.

Maleated PHB-HV was used at 5 wt% in PHB-HV/kenaf fiber composites (Avella et al., 2007). Dynamic mechanical analysis showed that for these composites, the storage modulus (*E*′) was higher than for the uncompatibilized composites and the pure PHB-HV. That is, the stiffness or hardness of the maleated composites is high and can be subjected to higher stress before permanent deformation. The damping factor (tan δ), which is the ratio of the loss modulus (viscous flow component or energy loss) to the storage modulus, was influenced by the presence of maleated PHB-HV. The damping factor of composites with maleated PHB-HV was significantly reduced compared with the unmodified composites with identical fiber loading. An increase in fiber loading also resulted in a decline in the damping factor. A reduction in tan δ indicated that the polymer chains were immobilized to some degree, which in this case could be due to the maleated PHB-HV in composites of the same fiber loading. A reduction in the damping factor also coincided with a rise in the glass transition temperature (T_g), which was measured from the maximum of the damping factor. The increase in T_g supported the idea that the PHB-HV matrix chains were immobilized in the presence of the fibers and even further with maleated PHB-HV.

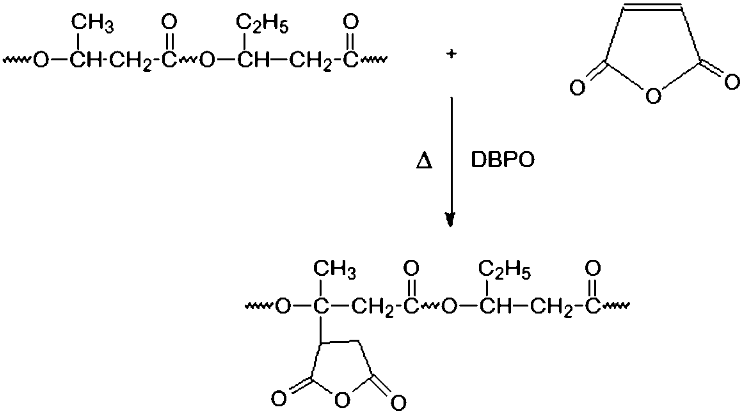


Fig. 13-19 Reaction between PHB-HV and maleic anhydride during reactive blending.

To quantify the strength of the interfacial adhesion, Avella et al. (2007) proposed an adhesion parameter, A, for the fiber–matrix interface, using the T_g values measured from the damping factor:

$$A = \frac{1}{1 - V_f} \frac{\tan \delta_c(T)}{\tan \delta_m(T)} - 1 \tag{13.1}$$

where V_f is the volume fraction of fillers in the composite, and tan $\delta_c(T)$ and tan $\delta_m(T)$ are the tan δ values measured at temperatures T of the composite and the pure matrix, respectively. With a higher fiber loading, with and without maleated PHB-HV, A was found to increase, indicating that the interface was weaker. The authors explained this observation by considering that at 20 wt% of kenaf fibers, the maximum surface contact between the matrix and the fibers may be reached; thus higher fiber content did not promote higher adhesion. In the presence of maleated PHB-HV, A was reduced compared with the composites of the same fiber content, implying that the interface was much improved.

Aside from the tensile properties, the flexural and impact properties also increased in a corresponding manner. With the incorporation of kenaf fibers alone, the flexural modulus increased as much as 108% compared with the pure PHB-HV (at 30 vol% fiber loading). Further improvements were observed for composites with maleated PHB-HV due to a stronger interface. An increase as great as 161% was observed at 30 vol% fiber loading. In a corresponding manner, the maximum flexural stress increased by 39% upon incorporation of unmodified kenaf fibers. In the presence of maleated PHB-HV, the composites increased by 46% compared with the pure PHB-HV. A similar rise in the impact strength was observed.

13.5.2.4 Treatment with Silane Coupling Agents

Silanes are classified as organic–inorganic coupling agent and were introduced primarily for use with glass fiber-reinforced composites, but they have been found also to be effective with natural fibers. They can couple with virtually any polymer or mineral in composites. Of all modification techniques, the use of silanes to improve the interfacial adhesion of natural fibers and polyolefins is by far the most popular. Fiber surface silanization is thought to enhance the interfacial adhesion thus the interfacial load transfer efficiency by improving the chemical affinity of the fibers with the polymer matrix. The other positive aspects brought about by silanization are enhanced tensile strengths of the composites, reduced effects of moisture on the composite properties, and composite strength.

For most coupling agents, the chemical structure can be represented by the formula $R\text{-}(CH_2)_n\text{-}Si(OR')_3$, where $n = 0$ to 3, OR′ is the hydrolyzable alkoxy group, and R is the functional organic group. Some common silanes are vinyltris(2-methoxyethoxy) silane (A-172), γ-methacryloxypropyltrimethoxysilane (A-174), and (3,4-epoxycyclohexyl)ethyltrimethoxysilane (A-187). The organo functional group is responsible for bonding with the polymer via copolymerization and/or formation of an interpenetrating network. The attachment of the silane onto the fiber is accomplished after hydrolyzing the silane as depicted in Fig. 13-20.

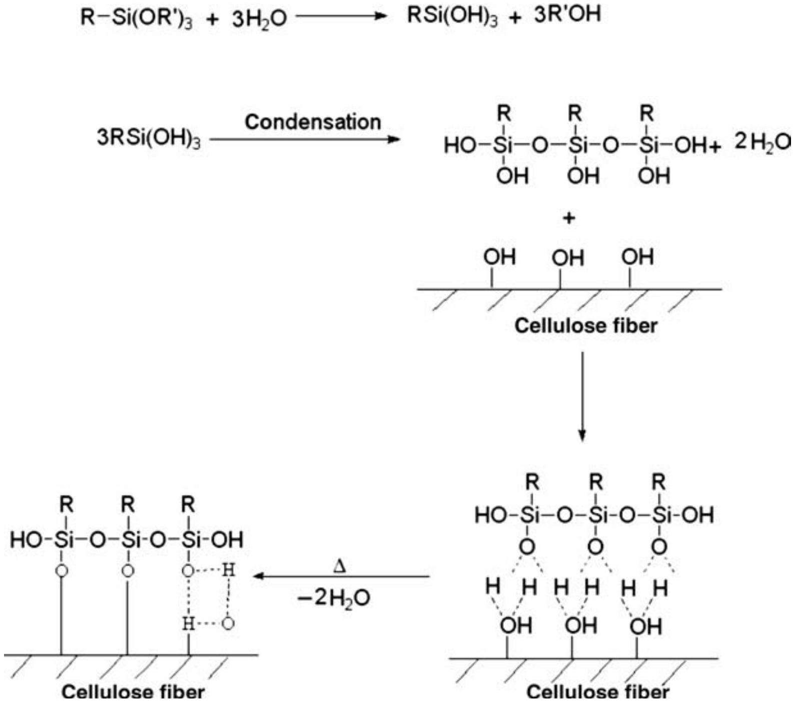


Fig. 13-20 Reaction of silane with cellulose.

From the above reactions, the alkoxysilanes first undergo hydrolysis, followed by condensation, and finally formation of bonds. Along with the bond formation, polysiloxanes could be formed. Valandex-Gozalez et al. (1999) found that the presence of polysiloxanes inhibited the adsorption of silanes on the fiber. In the same study, the efficiency of silane treatments on the fiber–polyester composite was found to be better for fibers that had been pretreated with alkali than for those with no pretreatment. The adsorption of silane on alkalized fibers was much greater than on the untreated fibers as there were a larger amounts of exposed cellulose on the surface due to partial removal of lignin, waxes, and hemicellulose. For fibers that were rich in lignin and waxes, the silane had to diffuse through these compounds before it could interact with cellulose, which had a limiting effect on the adsorption. Upon alkalization, the fiber surface became rougher, which increased the effective surface area for adsorption.

Silane coupling agents in anisotropic composites comprised of flax fibers and PHB and copolymers (PHB-HV) were used with some success (Shanks et al., 2004). Flax fibers were treated with an aqueous solution of trimethoxymethacrylsilane prior to composite fabrication. The dynamic mechanical and thermal properties were investigated. Interestingly, it was found in this study that for the untreated fiber composites, the introduction of hydroxyvalerate units into the PHB matrix had indeed increased the stiffness, as indicated by E'. Hydroxyvalerate units are usually introduced into PHB polymers to reduce its brittle nature; it could therefore be expected that the copolymer composites would be less brittle than the PHB composite if no interactions existed between the fibers and the matrix. In agreement with the rise in storage modulus, the T_g values detected by the loss modulus (E'') of the copolymer-unmodified composites were generally greater than for the PHB composites. This suggested that even without the use of silanes, the hydroxyvalerate units provided better chemical affinity between the matrix and the fibers. This was supported by optical microscopy, whereby nucleation of the matrix along the fiber surface was observed.

The storage moduli of silane-treated composites generally exhibited higher values compared with their untreated equivalents, indicating that a greater stiffness was attained, possibly due to greater interfacial strength. The increase in fiber–matrix adhesion observed was in parallel with the enhanced nucleating ability of the fibers, which was observed by optical microscopy. For the silane-treated fibers, many sporadic crystalline regions nucleated from the fiber surface were observed. This was most evident when PHB was the matrix, as there was no crystal growth from the fiber surface for the untreated fibers but such phenomena occurred with silane-treated fibers.

13.5.2.5 Modification of Natural Fibers by Plasticizer Absorption A novel technique to overcome the problem of moisture variability in natural fibers was presented by absorption of plasticizers into the fibers after removal of water (Wong et al., 2002). It was anticipated that fabricated composites would result in better interfacial adhesion by enhancing the compatibility between the hydrophilic fibers with the hydrophobic matrix. It was expected that the dimensional stability of the fibers and composites under different humidity levels would show less variability due to the fiber treatments with less hydrophilic liquids.

The plasticizers chosen in this study were mostly derived from natural sources, such as tributyl citrate (TBC) and glyceryl triacetate (GTA) and one that was commonly used to treat wood, poly(ethylene glycol) (PEG). The plasticizers were introduced into the fibers by impregnation at elevated temperatures after removal of water. Excess plasticizer was removed by washing with acetone and then dried prior to composite fabrication with PHB. The amount of plasticizer present was determined to be between 7 and 8 vol%, which was similar to 8 vol% of moisture typically present in flax. The fiber loading was fixed at 50 vol%.

Dynamic flexural testing was performed to determine the mechanical properties. The storage modulus (G') values of pure PHB and the composites of interest are shown in Fig. 13-21. Upon the addition of unmodified fibers, the stiffness, as indicated by G' was significantly reduced relative to the pure PHB below temperatures of about 70°C. This showed that flax fibers in the unmodified form failed to act as reinforcement to the PHB matrix. Conversely, the composites containing GTA- and PEG-treated fibers displayed higher stiffness throughout the entire temperature range tested, while those treated with TBC exhibited higher G' only below about 0°C. This enhancement in the presence of GTA and PEG (and to a limited degree

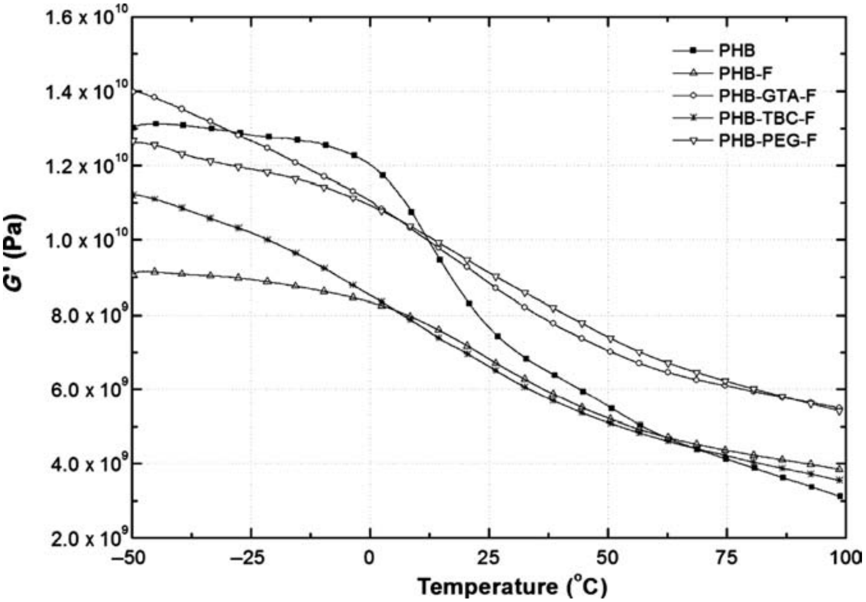


Fig. 13-21 Storage moduli (G') of PHB and composites.

with TBC) was suspected to be due to stronger interfacial adhesion, as suggested by the damping factor tan δ, shown in Fig. 13-22.

The tan δ peak intensity can indirectly indicate the magnitude of the interfacial adhesion in composites. A lower intensity generally indicates that the mobility of the polymer chains is hindered, most probably from the interactions with the fibers or fillers. In this case, the intensity of the unmodified PHB composite relative to pure PHB was much greater, indicating that the motion of the polymer chains was not affected by the fibers (little to no interactions). The reduced degree of crystallinity (i.e., larger amount of the amorphous phase), as measured by DSC, would certainly contribute to the higher tan δ intensity.

The composites containing GTA and PEG generally displayed the lowest tan δ intensity throughout the temperature range investigated. Their degree of crystallinity (as determined by DSC) was lower than that of the unmodified composite, hence the decline in the intensity could be due to greater interfacial adhesion. The adhesion parameter A, as proposed by Avella et al. (2007), was calculated for each of the composites at three temperatures that were most applicable to the service temperature, shown in Table 13-3 (see equation 13.1 above).

At all three temperatures of interest, A was lowest for the composite treated with GTA followed by PEG, as anticipated. Lower values of A correspond to a higher degree of adhesion. It appeared that the presence of TBC had a negligible effect on the interfacial adhesion as the value was not significantly different from that of the unmodified composite. Interestingly, it appeared that the degree of interfacial adhesion was a function of temperature, as A for any composite was observed to

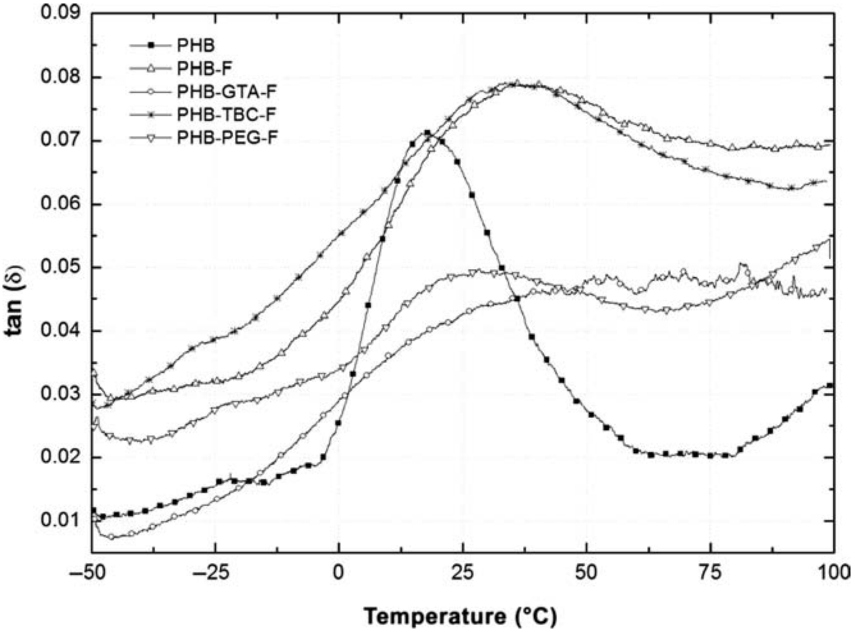


Fig. 13-22 Damping factor (tan δ) of PHB and composites.

be the lowest at 25°C regardless of the fiber treatment. At 0°C, the adhesion was reduced by as much as 3 times. At 50°C, the adhesion was most adversely affected, showing a reduction as great as 7 times relative to that at room temperature. As the systems are complex, a definitive reason cannot easily be determined but it would most likely involve the temperature-sensitive nature of PHB and surface energetic; the situation is further complicated by the presence of plasticizers.

Further evidence to support the effectiveness of GTA and PEG in improving the interfacial adhesion was provided by SEM on inspection of the cross-sections of the fractured composites. These are shown in Fig. 13-23.

The most obvious feature between the different composites was the magnitude of the cavities located at the interface. The largest cavities were seen for the unmodified composite and that with TBC (Fig. 13-23a and c, respectively), these exhibiting

TABLE 13-3 Adhesion Parameter *A* of Various PHB Composites at Three Temperatures

	A Value at Temperature		
Composite	0°C	25°C	50°C
PHB-flax	2.49	1.28	4.56
PHB-GTA-flax	1.28	0.31	2.47
PHB-PEG-flax	1.67	0.50	2.32
PHB-TBC-flax	3.32	1.33	4.43

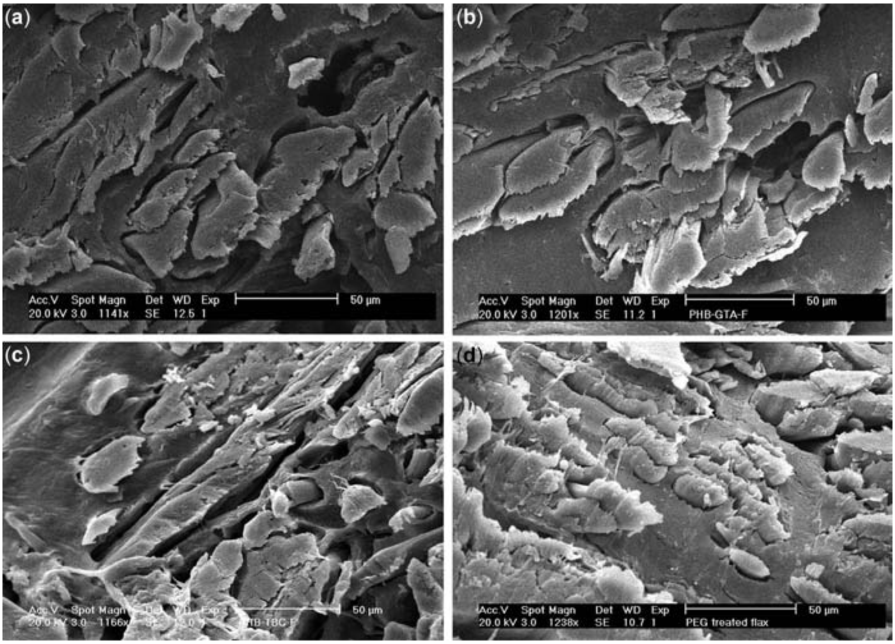


Fig. 13-23 SEM images of PHB–plasticizer–flax systems: (a) PHB–flax, (b) PHB–GTA–flax, (c) PHB–TBC–flax, and (d) PHB–PEG–flax. (Reprinted from Wong et al., 2002, Properties of poly(3-hydroxybutyric acid) composites with flax fibers modified by plasticiser absorption, *Macromolecular Materials and Engineering* 287:647–655. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

higher A and lower G' values. Conversely, the composites with GTA and PEG showed smaller cavities, corresponding to lower A and higher G' values.

Polarized optical microscopy was employed to observe the nucleating ability of the fibers in the PHB matrix with various treatments (Fig. 13-24). A dense transcrystalline layer resulted from the untreated fibers, whereas lower-density transcrystals were attained in the presence of the plasticizers. Plasticizer located at the fiber surface would inhibit nucleation at the fiber surface, hence the density of transcrystallinity. Coincidently, a lower degree of transcrystallinity corresponded to a reduced degree of crystallinity as measured by DSC.

13.5.2.6 Novel Dihydric Phenols as Interfacial Bonding Additives

Another novel approach to improving the interfacial bonding to yield stable composites with high mechanical strength was the use of hydrogen-bonding additives. A suitable dihydric phenol is 4,4′-thiodiphenol (TDP). It has been shown with Fourier transform infrared (FT-IR) spectroscopy that hydrogen bonding existed between the hydroxyl groups of cellulose and the hydroxyl and carbonyl groups of aliphatic polyesters (Wong et al., 2004). Another advantage of such

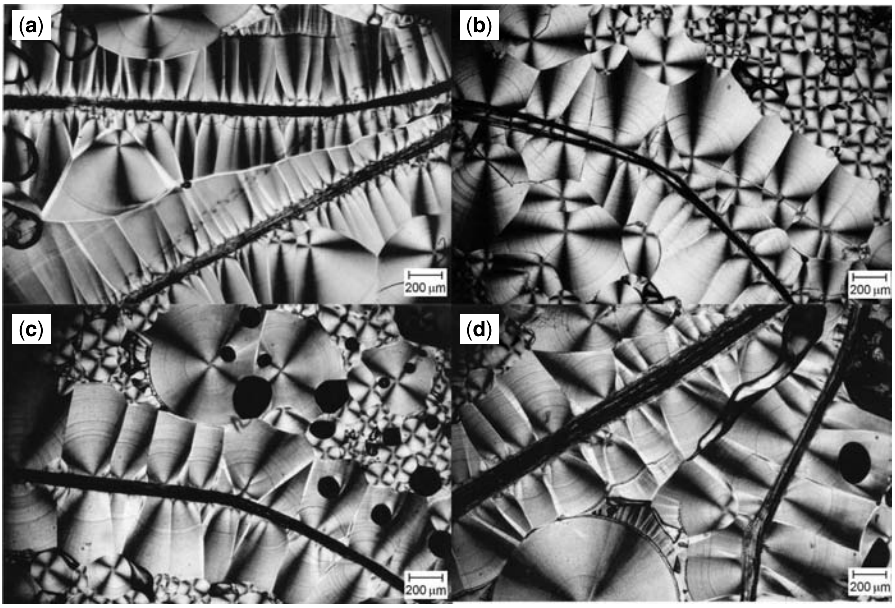


Fig. 13-24 Optical micrographs of PHB–plasticiser–flax systems: (a) PHB–flax, (b) PHB–GTA-flax, (c) PHB–TBC–flax, and (d) PHB–PEG–flax. (Reprinted from Wong et al., 2002, Properties of poly(3-hydroxybutyric acid) composites with flax fibers modified by plasticiser absorption, *Macromolecular Materials and Engineering* 287:647–655. Copyright Wiley-VCH Verlag GmBH & Co. KGaA. Reproduced with permission.)

treatment of the fibers was a noticeable increase in the fiber thermal stability. It was postulated that during processing of TDP and flax fibers, a more ordered cellulose structure could have been obtained due to some disruption of hydrogen bonds of cellulose.

The fibers were pre-treated by dewaxing with acetone via Soxhlet extraction for 24 h prior treatment with TDP. This was intended to remove the surface waxes to maximize the amount of TDP bonding onto the fiber surface. The success of dewaxing was observed via SEM as the presence of fibers with a rugged surface. After drying of any residual solvent and moisture, the washed fibers were immersed in a solution of TDP dissolved in 1,4-dioxane and the solvent was evaporated to leave a "coating" of TDP onto the fibers. The TDP concentration was varied from 0 to 20 vol% based on the fibers at 5% increments. The fiber loadings of the composites were fixed at 50 vol% and the fibers were randomly orientated.

Dynamic mechanical analysis in 3-point bend mode was performed on the composites to observe the improvement in the mechanical properties. The values of storage modulus G' are depicted in Fig. 13-25.

Upon addition of unmodified fibers (no TDP) to PHB, the stiffness markedly reduced due to poor interfacial adhesion arising from the difference in polarity of the constituents. For all TDP-treated composites, the stiffness showed higher

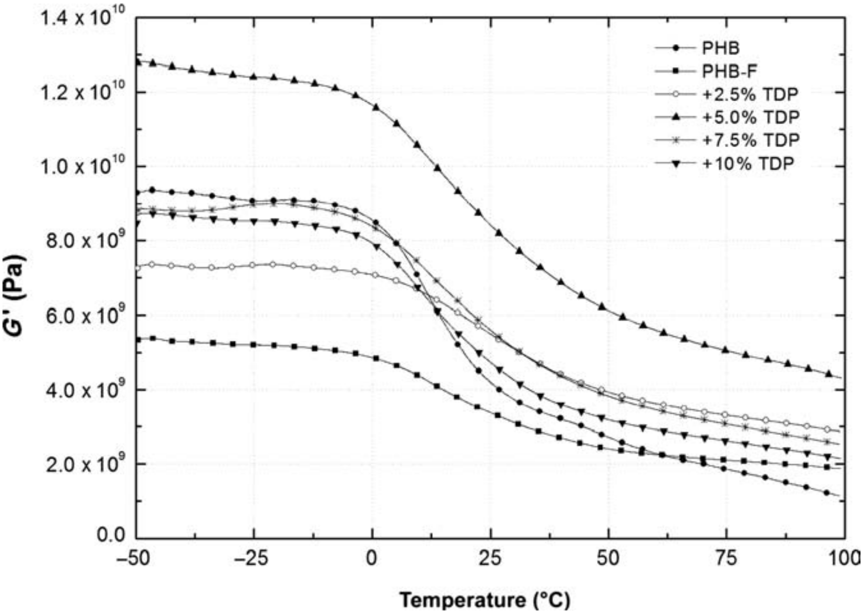


Fig. 13-25 Storage moduli of PHB composites with varying TDP concentrations.

values than the unmodified PHB composite, even after the glass–rubber transition. The stiffness of the composites increased as the concentration of TDP increased from 2.5% to 5.0%. Thereafter, the G' values were greater than for the unmodified PHB composite but lower than that with 5% TDP. Wong et al., attributed the phenomenon to the TDP migrating to the matrix when "excessive" amounts are present, which may cause the matrix to exhibit lower mechanical properties. A reduction in crystallinity, as determined by DSC, corresponded with a diminution of modulus.

The damping factor, tan δ was used to indicate the level of interfacial adhesion of the composites (Fig. 13-26). It can clearly be seen that the intensity of the damping factor was higher in the presence of the unmodified fibers, indicative of lower interfacial interactions. With an increase in TDP level up to 5%, the intensity of the damping factor diminished, implying that interfacial interaction is greater, most likely due to hydrogen bonding at the interface provided by TDP. The interaction parameter, *A* first introduced by Avella et al. (2007) was used to quantify the level of adhesion; the results are tabulated in Table 13-4. The calculated *A* values illustrated that the optimal TDP level for maximum adhesion was attained at 5%. Above and below this level, the adhesion was lower but was still better than that of the unmodified composite.

Further evidence to support the improved level of adhesion was observed from the cross-section of the fractured composites with SEM.

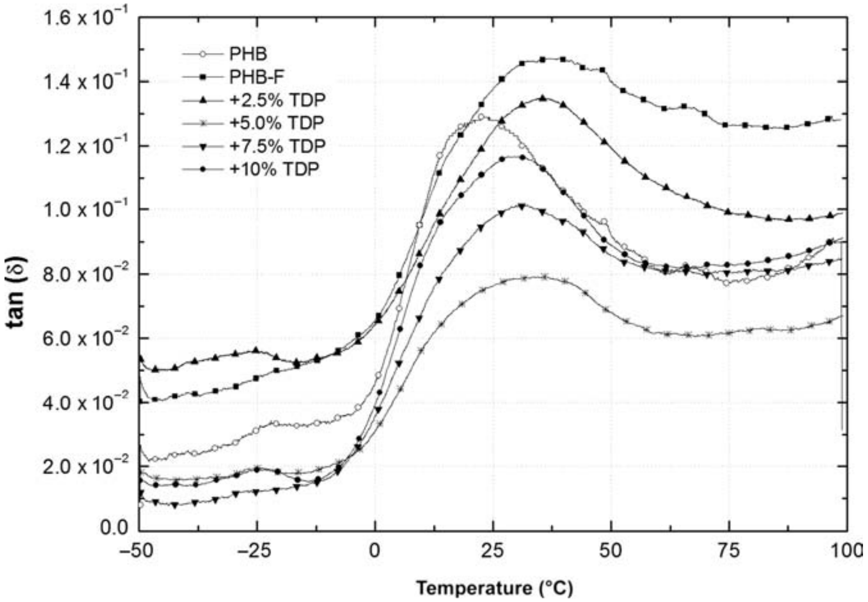


Fig. 13-26 Damping factor (tan δ) of PHB composites with varying TDP concentration.

All composites (Fig. 13-27) showed reasonable dispersion of the fibers within the PHB matrix as no fiber segregation was observed. However, it is evident that there is some limitation on their compatibility as cavities are seen surrounding the fibers in all composites. With TDP, the number of cavities as well as their size was reduced compared with the unmodified composite. Along with the closer contact between the fibers and the matrix with TDP, optical microscopy (Fig. 13-28) showed that the density of the transcrystalline regions was lower than in the unmodified composite. The effect of transcrystallinity on the performance of composites has been investigated extensively and the results are contradictory in the published literature. Some authors concluded that transcrystallinity was beneficial to the mechanical properties by preventing debonding at the fiber–matrix interface (Zhang et al., 1996).

TABLE 13-4 Adhesion Parameter *A* of PHB Composites with Varying TDP Levels

	A Value at Temperature		
Composite	0°C	25°C	50°C
PHB-F	1.85	1.15	2.04
+2.5% TDP	1.80	0.94	1.59
+5% TDP	0.35	0.19	0.48
+7.5% TDP	0.55	0.52	0.86
+10% TDP	0.71	0.77	0.93

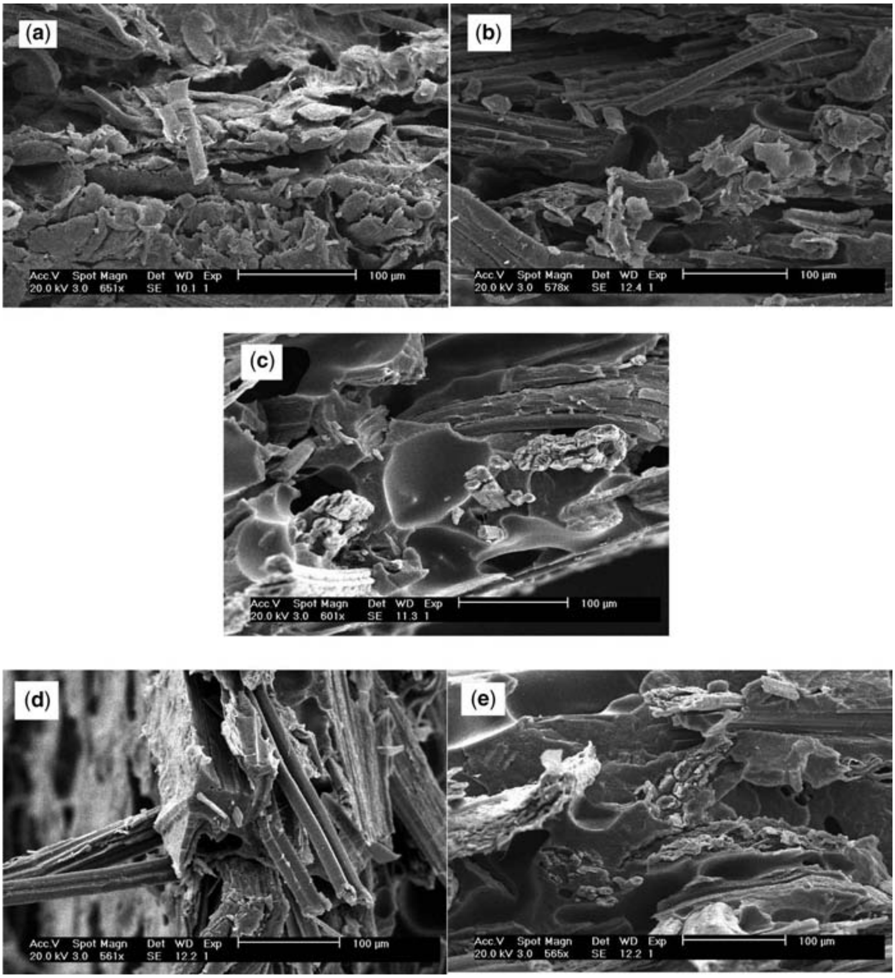


Fig. 13-27 SEM images of the cross-section of (a) unmodified PHB composite, and composites with (b) 2.5% TDP, (c) 5% TDP, (d) 7.5% TDP, and (e) 10% TDP. (Reprinted from Wong et al., 2004, Interfacial improvements in poly(3-hydroxybutyrate)–flax fiber composites with hydrogen bonding additives, *Composites Science and Technology* 64(9):1321–1330. Reproduced with permission from Elsevier.)

Others argue that a transcrystalline region caused a reduction in the mechanical properties by premature brittle failure occurring at the zone where the growing transcrystalline layers meet (Teishev and Maron, 1995). In this study, with the decrease in the density of the transcrystalline regions and induction of hydrogen bonding at the interface, higher G' values were attained compared with the unmodified composite. But at higher levels TDP migrated to the matrix, weakening the matrix by lowering the crystallinity, resulting in lower G' values than those at lower concentrations.

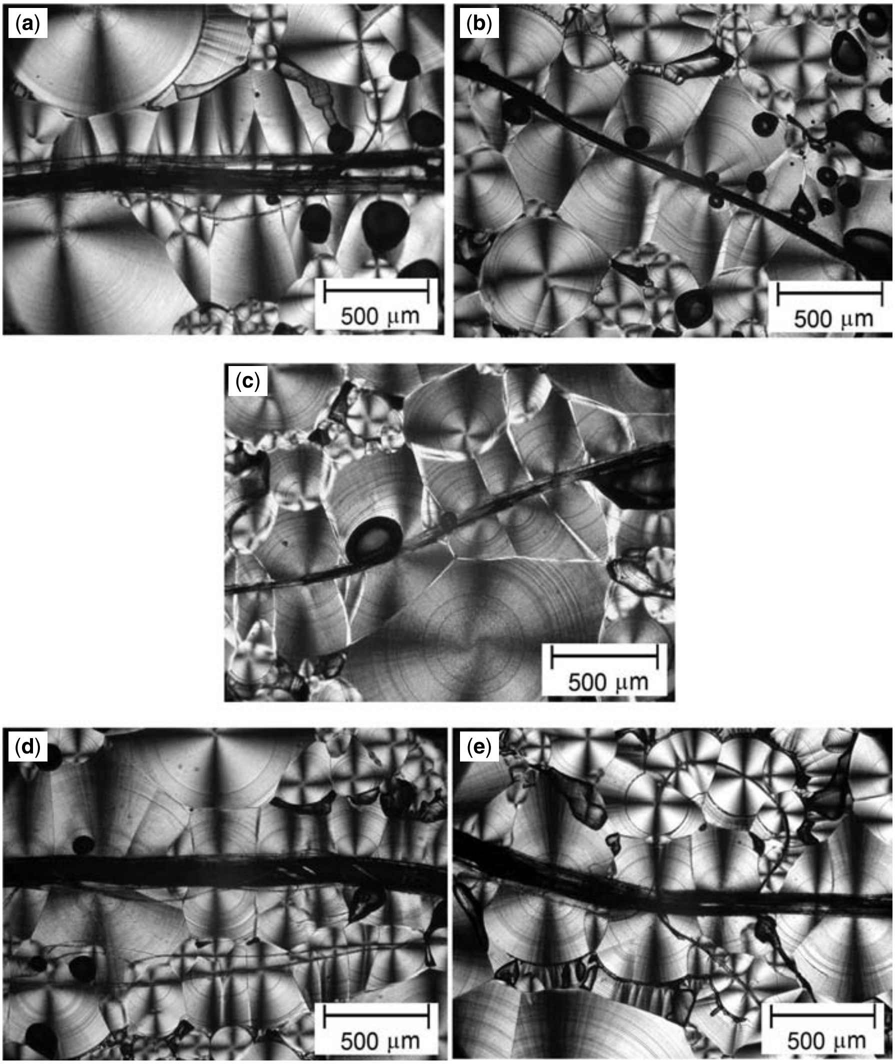


Fig. 13-28 Optical micrographs of (a) unmodified PHB composite, and composites with (b) 2.5% TDP, (c) 5% TDP, (d) 7.5% TDP, and (e) 10% TDP. (Reprinted from Wong et al., 2004, Interfacial improvements in poly(3-hydroxybutyrate)–flax fiber composites with hydrogen bonding additives, *Composites Science and Technology* 64(9): 1321–1330. Reproduced with permission from Elsevier.)

13.6 SUMMARY

Composites comprised of natural fibers and biodegradable thermoplastics can be used as alternative materials to traditional composites that are made of nonbiodegradable constituents such as glass or carbon fibers with polypropylene or epoxy resins.

The use of natural fibers offers the advantages of low density, good mechanical and manufacturing properties, and overall reduction in costs. However, even with these advantages, the use of natural fibers in composites is limited by the lower composite properties compared with those of traditional composites. The lower mechanical behavior was found to be due to two main problems that can be effectively resolved through modifications to the constituents.

The first problem is the incompatibility arising from the hydrophobic polymeric matrices and the hydrophilic nature of the natural fibers. The limited fiber–matrix interactions usually lead to reduced mechanical properties due to inefficient stress transfer from the matrix to the fibers. The second problem is the hydrophilic nature of the fibers as a result of which they absorb moisture. This not only contributes to lower mechanical properties but also affects the dimensional stability. The undesirable variability of moisture content in the composites under different environmental conditions can lead to erratic properties during their service life.

The use of additives and fiber surface treatments in the composites can address these problems and help improve the mechanical behavior of the composites. These effectively introduce a stronger fiber–matrix interface either by altering the fiber surface chemistry to reduce the incompatibility between the constituents or by forming chemical bonds between the components. For some fiber treatments and additives, the composites can be less moisture-sensitive and hence they possess improved dimensional stability. Since there are a range of treatments and additives available, this offers a window of flexibility for composite manufacturers to use appropriate methods without dramatic changes to processing equipment.

REFERENCES

Avella M, Bogoeva-Gaceva G, et al. 2007. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)-based biocomposites reinforced with kenaf fibres. *Journal of Applied Polymer Science* 104:3192–3200.

Baiardo MF, Scandola M, Licciardello A. 2002. Surface chemical modification of natural cellulose fibres. *Journal of Applied Polymer Science* 83:38–45.

Bauer H, Owen AJ. 1988. Some structural and mechanical properties of bacterially produced poly-beat-hydroxybutyrate-co-beta-hydroxyvalerate. *Colloid and Polymer Science* 266:241–247.

Bledzki AK, Gassan J. 1999. Composites reinforced with cellulose based fibres. *Progress in Polymer Science* 24:221–274.

Brouwer WD. 2000. Natural fibre composites: where can flax compete with glass? *SAMPE Journal* 36:18–23.

Chen C, Peng S, Fei B, et al. 2003. Synthesis and characterisation of maleated poly(3-hydroxybutyrate). *Journal of Applied Polymer Science* 88:659–668.

Corden TJ, Jone A, Rudd CD, Christian P, Downes S. 1999. Initial development into a novel technique for manufacturing a long fibre thermoplastic bioabsorbable composite: in-situ polymerisation of poly(epsilon-caprolactone). *Composites Part A: Applied Science and Manufacturing* 30:737–755.

Coutinho FMB, Costa THS, Carvalho DL, Gorelova MM, de Santa Maria LC. 1999. Thermal behaviour of modified wood fibres. *Polymer Testing* 17:299–310.

Das M, Chakraborty D. 2006. Influence of alkali treatment on the fine structure and morphology of bamboo fibres. *Journal of Applied Polymer Science* 102:5050–5056.

Drumright DE, Gruber PR, Heton DE. 2000. Polylactic acid technology. *Advanced Materials* 12:1841–1846.

El-Hadi A, Schnabel R, Straube E, Muller G, Henning S. 2002. Correlation between degree of crystallinity, morphology, glass temperature, mechanical properties and biodegradation of poly(3-hydroxyalkanoate) PHAs and their blends. *Polymer Testing* 21:665–674.

Fujimaki T. 1998. Processibility and properties of aliphatic polyesters, "Bionelle," synthesised by polycondensation reaction. *Polymer Degradation and Stability* 59:209–214.

Gao SL, Kim JK. 2000. Cooling rate influences in carbon fibre/PEEK composites. Part 1. Crystallinity and interface adhesion. *Composites Part A: Applied Science and Manufacturing* 31:517–530.

Gassan J, Bledzki AK. 1999. Possibilities for improving the mechanical properties of jute/epoxy composites by alkali treatment of fibres. *Composites Science and Technology* 59:1303–1309.

Gassan J, Bledzki AK. 2001. Thermal degradation of flax and jute fibres. *Journal of Applied Polymer Science* 82:1417–1422.

Ha CS, Cho WJ. 2002. Miscibility, properties, and biodegradability of microbial polyester containing blends. *Progress in Polymer Science* 27:759–809.

Herrmann AS, Nickel J, Riedel U. 1998. Construction materials based upon biologically renewable resources—from components to finished parts. *Polymer Degradation and Stability* 59:251–261.

Hill CAS, Abdul Khalil HPS. 2000. Effect of fibre treatments on the mechanical properties of coir or oil palm fibre reinforced polyester composites. *Journal of Applied Polymer Science* 78:1685–1697.

Huda M, Yasui M, Mohri N, Fujimura T, Kimura Y. 2002. Dynamic mechanical properties of solution-cast poly(L-lactide) films. *Materials Science and Engineering* 333:98–105.

Janigova I, Lacik I, Chodak I. 2002. Thermal degradation of plasticised poly(3-hydroxybutyrate) investigated by DSC. *Polymer Degradation and Stability* 77:35–41.

Joffe R, Janis A, Wallstron L. 2003. Strength and adhesion characteristics of elementary flax fibres with different surface treatments. *Composites Part A: Applied Science and Manufacturing* 34:603–612.

Karus MK, Kaup M. 1999. Use of Natural fibres in the German automotive industry. *Journal of the International Hemp Association* 6:72–74.

Kazayawoko M, Balatinecz JJ, Woodhams RT. 1997. Diffuse reflectance fourier transform infrared spectra of wood fibres treated with maleated polypropylenes. *Journal of Applied Polymer Science* 66:1163–1173.

Ke T, Sun X. 2001. Thermal and mechanical properties of poly(lactic acid) and starch blends with various plasticisers. *Transactions of the ASAE* 44:939–944.

Khalil AR, Mitra BC, Lawther M, Banerjee AN. 1997. Studies of acetylation of jute using simplified procedure and its characterisation. *Polymer Plastics Technology and Engineering* 39:757–781.

Kopinke F, MacKenzie K. 1997. Mechanistic aspects of the thermal degradation of poly(lactic acid) and poly(beta-hydroxybutyric acid). *Journal of Analytical and Applied Pyrolysis* 40–41:43–53.

Labrecque LV, Dave V, Gross RA, McCarthy SP. 1995. Citrate esters as biodegradable plasticisers for poly(lactic acid). ANTEC '95.

Labrecque LV, Dave V, Gross RA, McCarthy SP. 1997. Citrate esters as plasticisers for poly(lactic acid). *Journal of Applied Polymer Science* 66:1507–1513.

Li Y, Mai YW, Lin Y. 2000. Sisal fibre and its composites: a review of recent developments. *Composites Science and Technology* 60:2037–2055.

Ljungberg N, Wesslen B. 2002. The effects of plasticisers on the dynamic mechanical and thermal properties of poly(lactic acid). *Journal of Applied Polymer Science* 86:1227–1234.

Lu JZ, Wu Q, McNabb HS. 2000. Chemical coupling in wood fibre and *polymer composites*: a review of coupling agents and treatments. *Wood and Fibre Science* 32:88–104.

Lui S, Netravali AN. 1999. Mechanical and thermal properties of environment-friendly "green" composites made from pineapple leaf fibres and poly(hydroxybutyrate-co-valerate) resin. *Polymer Composites* 20:367–378.

Martin O, Averous L. 2001. Poly(lactic acid): plasticisation and properties of biodegradable multiphase systems. *Polymer* 42:6209–6219.

Mishra S, Misra M, Tripathy SS, Nayak SK, Mohanty AK. 2001. Graft copolymerisation of acrylonitrile of chemically modified sisal fibres. *Macromolecular Materials and Engineering* 286:107–113.

Mohanty A, Khan MA, Hinrichsen G. 2000a. Influence of chemical surface modification on the properties of biodegradable jute fabrics–polyester amide composites. *Composites Part A: Applied Science and Manufacturing* 31:143–150.

Mohanty A, Misra M, Hinrichsen G. 2000b. Biofibres, Biodegradable Polymers and Biocomposites: An Overview. *Macromolecular Materials and Engineering* 276/277:1–24.

Mohanty AK, Khan MA, Sahoo S, Hinrichsen G. 2000c. Effect of chemical modification on the performance of biodegradable jute yarn–biopol composites. *Journal of Materials Science* 35:2589–2595.

Mohanty A, Misra M, Drzal LT. 2001. Surface modifications of natural fibres and performance of the resulting biocomposites: an overview. *Composite Interfaces* 8:313–343.

Mwaikambo LY, Ansell MP. 1999. The effect of chemical treatment on the properties of hemp, sisal, jute and kapok for composite reinforcement. *Die Angewante Makromolekulare Chemie* 272:108–116.

Park JW, Im SS, Kim SH, Kim YH. 2000. Biodegradable polymer blends of poly(L-lactic acid) and gelatinized starch. *Polymer Engineering and Science* 40:2539–2550.

Perego G, Cella GD, Bastioli C. 1996. Effect of molecular weight and crystallinity on poly (lactic acid) mechancial properties. *Journal of Analytical and Applied Pyrolysis* 59:37–43.

Pou JB, Quintero QF, Lusquinos F, Soto R, Perez-Amor L. 2001. Comparative study of the cutting of car interior trim panels reinforced by natural fibres. *Journal of Laser Applications* 13:90–95.

Ray D, Sarkar BK. 2001. Characterisation of alkali-treated jute fibres for physical and mechanical properties. *Journal of Applied Polymer Science* 80:1013–1020.

Rong M, Zhang MQ, Lui Y, Yang GC, Zeng HM. 2001. The effect of fibre treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites. *Composites Science and Technology* 61:1437–1447.

Rouette HK 2001. Flax stem structure. In: *Encyclopedia of Textile Finishing*. Cambridge, UK: Woodhead Publishing. p. 74.

Rout JT, Misra M, Nayak SK, Mohanty AK. 2001. Scanning electron microscopy study of chemically modified coir fibres. *Journal of Applied Polymer Science* 79:1169–1177.

Rozman JT, Misra S, Nayak M, Mohanty AK. 2001. Preliminary studies on the use of modified ALCELL lignin as a coupling agent in the biofibre composites. *Journal of Applied Polymer Science* 81:1333–1340.

Saha AK, Das S, Basak K, Bhatta D, Mitra BC. 2000. Improvement of functional properties of jute-based composite by acrylonitrile pretreatment. *Journal of Applied Polymer Science* 78:495–506.

Samal RK. 1994. Chemical modification of lignocellulosic fibres I. Functionality changes and graft copolymerisation of acrylonitrile onto pineapple leaf fibres; their characterisation and behaviour. *Journal of Applied Polymer Science* 52:1675–1685.

Samal RK, Ray MC. 1997. Effect of chemical modifications on FTIR spectra II. Physicochemical behaviour of pineapple leaf fibre (PALF). *Journal of Applied Polymer Science* 64:2119–2125.

Samal RK, Mohanty AK, Ray MC. 2001. FTIR spectra and physico-chemical behaviour of vinyl ester participated transesterification and curing of jute. *Journal of Applied Polymer Science* 79:575–581.

Samal RK, Rout SK, Mohanty AK. 1995. Effect of chemical modification on FTIR spectra I. Physical and chemical behaviour of coir. *Journal of Applied Polymer Science* 58:745–752.

Shanks R, Hodzic A, Wong S. 2004. Thermoplastic biopolyester natural fibre composites. *Journal of Applied Polymer Science* 91:2114–2121.

Sharma HSS, Gaughey G, Lyons G. 1999. Comparsion of physical, chemical, and thermal chanracteristics of water-, dew-, and enzyme-retted flax fibres. *Journal of Applied Polymer Science* 74:139–143.

Sheth M, Kumar A, Dave V, Gross RA, McCarthy SP. 1997. Biodegradable polymer blends of poly(lactic acid) and poly(ethylene glycol). *Journal of Applied Polymer Science* 66:1495–1505.

Shibata M, Takachiyo KI, Ozawa K, Yosomiya R, Takeishi H. 2002. Biodegradable polyester composites reinforced with short abaca fibre. *Journal of Applied Polymer Science* 85:129–138.

Singh BS, Verma M, Tyagi OS. 2000. FTIR microscopic studies on coupling agents: treated natural fibres. *Polymer International* 49:1444–1451.

Singleton A, Ballie CA, Beaumont PWR, Peijs T. 2003. On the mechanical properties, deformation and fracture of a natural fibre/recycled polymer composites. *Composites Part B: Engineering* 34:519–526.

Stamboulis AB, Baillie CA, Garkhail SK, van Melick HBH, Peijs T. 2000. Environmental durability of flax fibres and their composites based on polypropylene matrix. *Applied Composite Materials* 7:273–294.

Stamboulis AB, Baillie CA, Peijs T. 2001. Effects of enviromental conditions on mechanical and physical properties of flax fibres. *Composites Part A: Applied Science and Manufacturing* 32:1105–1115.

Teishev A, Maron G. 1995. The effect of transcrystallinity on the transverse mechanical properties of single-polymer polyethylene composites. *Journal of Applied Polymer Science* 56:959–966.

Tserki V, Zafeiropoulos NE, Simon F, Panayiotou C. 2005. A study of the effect of acetylation and propionylation surface treatments on natural fibres. *Composites Part A: Applied Science and Manufacturing* 36:1110–1118.

Valadex-Gozalez A, Cervantes JM, Olayo R, Herrera-Franco PJ. 1999. Chemical modification of henequen fibres with an organosilane coupling agent. *Composites Part B: Engineering* 30:321–331.

Van de Velde K, Baetens E. 2001. Thermal and mechanical properties of flax fibres as potential composite reinforcement *Macromolecular Materials and Engineering* 286:342–349.

Van de Weyenberg I, Truong TC, Vangrimde B, Verpoest I. 2006. Improving the properties of UD flax fibre reinforced composites by applying an alkaline fibre treatment. *Composites Part A: Applied Science and Manufacturing* 37:1368–1376.

Van Den Oever MJA, Bos HL, Van Kemenade MJJM. 2000. Influence of the physical structure of flax fibres on the mechanical properties of flax fibre reinforced polypropylene composites. *Applied Composite Materials* 7:387–402.

Wong S, Shanks RA, Hodzic A. 2002. Properties of poly(3-hydroxybutyric acid) composites with flax fibres modified by plasticiser absorption. *Macromolecular Materials and Engineering* 287:647–655.

Wong S, Shanks RA, Hodzic A. 2004. Interfacial improvements in poly(3-hydroxybutyrate)–flax fibre composites with hydrogen bonding additives. *Composites Science and Technology* 64:1321–1330.

Zafeiropoulos NE, Williams DR, Baillie CA, Matthews FL. 2002. Engineering and characterisation of the interface in flax fibre/polypropylene composite materials. Part I. Development and investigation of surface treatments. *Composites Part A: Applied Science and Manufacturing* 33:1083–1093.

Zhang M, Xu J, Zeng H, Xiong X. 1996. Effect of transcrystallinity on tensile behaviour of discontinuous carbon fibre reinforced semicrystalline thermoplastic composites. *Polymer* 37:5151–5158.

Zini E, Focarete ML, Noda I, Scandola M. 2007. Bio-composite of bacterial poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) reinforced with vegetable fibres. *Composites Science and Technology* 67:2085–2094.

CHAPTER 14

Starch–Fiber Composites

MILFORD A. HANNA and YIXIANG XU

Industrial Agricultural Products Center, University of Nebraska, Lincoln, NE 68583–0730, USA

14.1 INTRODUCTION

Plastic products have occupied a dominant position since the 1950s when the petroleum industry grew rapidly (Xu and Hanna, 2005). Almost every product we buy and most of the food we eat comes encased in plastic, due to its easy processing, light weight, durability, and low cost (Australian Academy of Science, 2002). While we enjoy the convenience offered by plastic products, the side-effects of the excessive use of synthetic plastics have also become more obvious. Municipal solid wastes consist of 7.2% by weight, or 18% by volume, of plastics (Thiebaud et al., 1997). Serious environmental problems are associated with disposal of used plastic products, attributable to their nondegradability and long-term survival in landfills, resulting in overburdening of landfills and harming of wildlife. For example, it was found that 1 in 30 cetaceans had choked on plastic debris in the oceans (Demicheli, 1996).

Biodegradable Polymer Blends and Composites from Renewable Resources. Edited by Long Yu

In addition to the ecological problems, the pressure on fossil energy resources and growing awareness of their finiteness have triggered interest in reduced dependence on these petroleum-derived plastics. Accordingly, during the past two decades, many research efforts have been put forth to develop environmentally compatible biodegradable products. The potential advantages of such materials are their biodegradability and biocompatibility; they can be easily and naturally decomposed by microbial action after use rather than accumulating in landfills and waterways (Dufresne et al., 2000).

In general, biodegradable polymers can be classified into two categories: natural biopolymers such as starch and cellulose, and synthetic biopolymers including poly(lactic acid), polycaprolactone, poly(hydroxyalkanoate)s, and poly(vinyl alcohol) (Jang et al., 2001). Although these synthetic biopolymers possess excellent mechanical properties, they are expensive, which reduces their competitiveness with their traditional counterparts. More attention has therefore been paid to renewable natural biopolymers from agricultural sources, because of their low cost and availability, and their being totally biodegraded after usage. However, the intrinsic deficiencies of natural biopolymers, including poor mechanical properties, poor water resistance, and difficult processability, limit their wide use. Consequently, the development of biocomposites has become a subject of increasing research interest. Biocomposites, consisting of biodegradable polymers as the matrix material and biodegradable fillers, are expected to fully biodegradable since both components are biodegradable (Averous and Boquillon, 2004). In this chapter, we focus on the preparation and characterization of starch–natural fiber composites.

14.2 STARCH-BASED BIOPOLYMERS

14.2.1 Starch Composition, Structure, and Properties

Starch is a natural and renewable polysaccharide and exists in the form of fine white granules. Starch granules are composed of amylose and amylopectin with the basic composite unit of glucose (Fig. 14-1). Linear amylose, consisting of α-1,4 linked D-glucose, has an average molecular weight of 2×10^5 and is responsible for the amorphous region. Amylopectin, a branched chain with both α-1,4 and α-1,6-linked glucopyranose, has an average molecular weight of 2×10^8 and forms the double helix crystalline structure in starch molecules (Andersen et al., 1999; Xu et al., 2004). The discrete and partially crystalline microscopic granules are held together by intra- and inter-molecular hydrogen bonds (Dufresne and Vignon, 1998).

Although starch granules are insoluble in cold water, they form a high-viscosity paste when heated in the presence of water. This physical change of form of starch granules in hot water is termed gelatinization. Starch gelatinization is a process whereby the intermolecular bonds of starch molecules are broken down in the presence of water and heat, resulting in the collapse of the crystalline structures of starch granules. Starch gelatinization is a slow process. During initial heating of starch, the granules do not change their appearance. When a critical temperature is

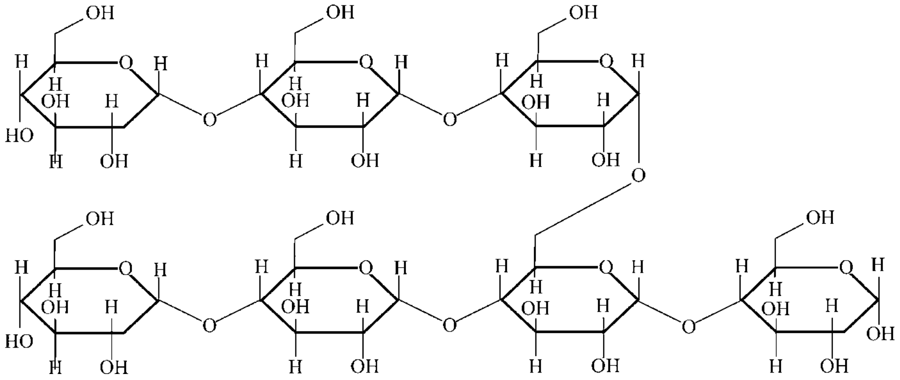


Fig. 14-1 Illustration of starch molecular structure.

reached and the granules swell up and absorb water, starch chains lose their ability to hold together. Increasing temperature further leads to all chains pulling out or away from each other. The gelatinized stage is reached with the formation of a viscous solution (Torres et al., 2007). Gelatinization plays an important role in industrial application of starch. However, gelatinized starch retrogrades with cooling or standing, caused by alignment of the molecules and recrystallization of amylose.

Starch granules are found in various sites of plants, such as roots (sweet potatoes, tapioca), tubers (potatoes), stems (sago palm), cereal grains (corn, rice, wheat, barley, oat, sorghum), and legume seeds (peas and beans) (Swinkels, 1985). Tapioca, potatoes, corn, rice, wheat, and peas are the most widely commercially available starch sources (Dufresne and Vignon, 1998). The shape, composition, and properties of the individual starches vary considerably, depending on the sources as shown in Table 14-1.

TABLE 14-1 Shape, Composition and Properties of Six Commercial Starches

Starch Type	Shape	Diameter (μm)	Amylose Content (%)	Amylopectin Content (%)	Pasting Temperature (°C)
Tapioca	Round, oval[a]	4–35[a]	16–17[b]	83–84[b]	65–70[a]
Potato	Oval, spherical[a]	5–100[a]	20–21[b]	79–80[b]	60–65[a]
Corn	Round, polygonal[a]	2–30[a]	25–28[b]	72–75[b]	75–80[a]
Rice	Polyhedral[e]	3–5[e]	17–30[b]	70–83[b]	79–86[b]
Wheat	Round, lenticular[a]	1–45[a]	25–30[b]	70–75[b]	80–85[a]
Pea[c]	Round, oval[d]	5–20[d]	33–49[d]	51–67[d]	60–67[d]

[a] Swinkels (1985).
[b] Gregorová et al. (2006).
[c] Refers to smooth pea.
[d] Ratnayake et al. (2002).
[e] Champagne (1996).

14.2.2 Starch-Based Biopolymers

There has been increasing interest in the use of starch as a biodegradable thermoplastic polymer and particulate filler because of its abundance, availability, and low cost. However, starch, by itself, is not a good alternative for synthetic polymers because of various inherent drawbacks. Starch is not truly thermoplastic and degrades, under high temperature, to form products with low molecular weight (Dufresne and Vignon, 1998). However, starch can be plasticized by disruption and plasticization of native starch in the presence of water and other plasticizers with high boiling-points, such as triethylene glycol, glycerol, and oleic acid, by injection, extrusion, or blow molding (Cinelli et al., 2003; Corradini et al., 2006). The resultant thermoplastic starch melts and flows under milder conditions. Thus, the use of starch to produce biodegradable plastics has become popular.

Starch-Based Biopolymers Type and Processing Method

Starch-Based Films Starch-based films and coatings have been used mainly for protecting food and pharmaceuticals from oxygen and moisture, and for encapsulating active ingredients for controlled release (Liu and Han, 2005). The functional properties of starch films and coatings, such as tensile strength, elongation at break, water vapor permeability, and oxygen permeability, are highly dependent on their compositions and processing conditions. In general, starch films, in the absence of any plasticizer, are very brittle and are readily broken into fragments. They are good barriers to oxygen but have poor water resistance, owing to their hydrophilicity. The films are very sensitive to the humidity of environments where they are used and stored. Plasticizers, including glycerol, sorbitol, and poly(ethylene glycerol) (PEG), contain many hydroxyl groups and are compatible with starch film-forming solutions to give homogeneous mixtures without phase separation (Zhang and Han, 2006). Addition of plasticizers can enhance the flexibility and extensibility of the films by reducing intermolecular interaction between starch molecules and increasing the mobility of the chains. However, these improvements are related to the type of plasticizer. Glycerol generally gives the greatest effects on the functional properties of the films, resulting in significant decreases in water vapor permeability and tensile strength but increasing elongation. PEG had the most pronounced effect on oxygen permeability (Laohakunjit and Noomhorm, 2004). Furthermore, the functional properties also are dependent on the amylose content. Strong and flexible films were obtained from starch with high amylose content (Palviainen et al., 2001).

Generally, solvent casting and thermoplastic processing (extrusion and injection molding) have been used to prepare starch films. In the solvent casting method, starch and plasticizer are dissolved in water and heated until the starch gelatinizes. After cooling, the film-forming solution is poured onto a plate and dried at ambient conditions to obtain a film. The advantages of thermoplastic processing over solvent casting include that no preprocessing steps, such as gelatinization and destruction of granular starch, are required, and its environmentally benign character due to the absence of solvents other than water.

Starch-Based Foams Starch is a good alternative for expanded polystyrene as loose-fill packaging materials to protect fragile products by absorbing or isolating impact energy during transportation and handling (Altieri and Lacourse, 1990; Wang and Shogren, 1997; Fang and Hanna, 2000a). A foam having a dense outer skin and a less dense rigid interior with large, mostly open cells is formed by thermal processing (extrusion), which consists of swelling, gelatinization if the starch and network building in the presence of a blowing agent, such as water, sodium bicarbonate, and citric acid and a nucleating agent such as talcum, calcium carbonate, barium sulfate, aluminum oxide, and silicon dioxide (Parra et al., 2006). Unfortunately, the low elastic modulus (strength) and high hydrophilicity of these native starch-based products do not meet the requirements of some applications. Strategies adopted to overcome these problems include chain modification and blending with other polymers.

Starch Modification Chemical modification of starch involves replacing the starch's hydroxyl groups (OH) with ester or ether groups to produce hydrophobic thermoplastic materials (Sagar and Merrill, 1995; Shogren, 1996; Jantas, 1997; Bayazeed et al., 1998; Aburto et al., 1999; Miladinov and Hanna, 2000; Sitohy et al., 2000; Xu et al., 2004). After substitution of the hydrophilic hydroxyl groups of starch by ester and ether groups, starch's water resistance and miscibilities with other hydrophobic synthetic polymers are improved. In addition, these substituted groups also function as plasticizers, inhibiting the strong hydrogen-bonding networks between starch molecules, thus enhancing the toughness and thermal stability.

Currently, hydroxypropylated starch is being used in the preparation of commercial packaging material. At the same time, there is a great deal of interest in starch acetylation because of its relative ease. During acetylation, three free hydroxyl groups located on C-2, C-3, and C-6 of the starch molecule are substituted with acetyl groups, resulting in a theoretical maximum degree of substitution of 3. Although starch acetate has excellent functional properties, the biggest hurdle which limits its wide application is its production cost—on average 10 times higher than for native potato starch (Chen et al., 2006).

Mixtures with Other Polymers Starch has been added, as a natural filler, to synthetic polymer matrixes to accelerate the deterioration of plastics under bioenvironmental conditions (Goheen and Wool, 1991; Matzions et al., 2001). It has also been blended with synthetic polymers such as polystyrene and poly(ethylene-vinyl alcohol) to strengthen the mechanical properties of starch biopolymers (Simmons and Thomas, 1995; Fang and Hanna, 2000b; Kalambur and Rizvi, 2006). However, whichever of the above methods was used, increasing the amount of starch in the matrix caused decreases in the mechanical and physical properties. This was attributed mainly to phase separation caused by immiscibility of starch and hydrophobic polymers at the molecular level.

Attempts have been made to improve the compatibility of starch and hydrophobic polymers, including grafting of functional groups such as carboxylic acid, anhydride, epoxy, urethane, or oxazoline on the polymers. These functional groups react with the

OH groups on starch to form hydrogen bonds, which result in a stable morphology (Shogren et al., 1991; Jang et al., 2001; Wu, 2003). However, some functional groups were found to inhibit the rate of starch biodegradation (Bikiaris and Panayiotou, 1998). Other methods to improve miscibility between starch and other hydrophobic polymers include chemical modifications of starch, as discussed above.

To preserve renewability and biodegradability, starch also has been blended with natural polymers including proteins, chitosan, and natural fibers (Dufresne and Vignon, 1998; Jagannath et al., 2003; Xu et al., 2005a). In this chapter, we focus on starch–natural fiber blends.

14.3 NATURAL FIBERS

14.3.1 Natural Fiber Composition, Structure, and Properties

Natural fibers originate mainly from plant materials. They are three-dimensional biopolymers and are composed of a variety of chemical substances including cellulose, hemicellulose, lignin, pectin, and small amounts of waxes and fats (Parra et al., 2006). Among these components, cellulose, hemicellulose, and lignin can serve as reinforcement (Guan and Hanna, 2004). The chemical compositions and physical properties of fibers vary with different sources as summarized in Table 14-2.

Cellulose is the most abundant ingredient in all fibers and the content varies with different sources, ranging from 26–43% for bamboo to 87–91% for ramie. Cellulose is a linear polysaccharide polymer consisting of β-(1,4)-linked D-glucose units (Fig. 14-2), with an average molecular weight ranging from 10,000 to 150,000 (Rowell et al., 2000).

The formation of intra- and intermolecular hydrogen bonds results in a highly crystalline structure, with a 80% crystalline region for most plants (Rowell et al., 2000). At the same time, the large numbers of hydroxyl groups make cellulose hydrophilic. In contrast, hemicellulose usually contains more than one sugar. The reason the term "pentosan," instead of "hemicellulose," appears in Table 14-2 is that part of the hemicellulose fraction is composed of five-carbon sugars, namely D-xylose and L-arabinose (Rowell et al., 2000).

14.3.2 Natural Fiber Applications and Modifications

Natural fibers have been used primarily as animal feed. In recent years, interest in the use of natural fibers as reinforcement in both thermoplastic and thermoset polymers has grown. This is attributed to the intrinsic virtues of natural fibers including low cost, abundance and renewability, low density, good mechanical properties, and significant processing advantages such as being less abrasive to processing equipment. They also benefit our ecosystem since CO_2 is emitted (Romhány et al., 2003). Notwithstanding these attractive properties, the mechanical properties of a fiber-reinforced polymer composite depend on many factors, including fiber source, volume fraction, orientation, aspect ratio, and fiber–matrix adhesion (Parra et al., 2006).

TABLE 14-2 Chemical Composition and Physical Properties of Several Common Natural Fibers[a]

	Chemical Composition (%)				Physical Properties			
					Fiber Length (mm)		Fiber Width (mm)	
Type of Fiber	Cellulose	Lignin	Pentosan	Ash	Avg	Range	Avg	Range
k fiber								
Rice	28–48	12–16	23–28	15–20	1.4	0.4–3.4	8	4–16
Wheat	29–51	16–21	26–32	4.5–9	1.4	0.4–3.2	15	8–34
Cane fiber								
Bagasse	32–48	19–24	27–32	1.5–5	1.7	0.8–2.8	20	10–34
Bamboo	26–43	21–31	15–26	1.7–5	2.7	1.5–4.4	14	7–27
Grass fiber								
Esparto	33–38	17–19	27–32	6–8	1.2	0.2–3.3	13	6–22
Sabai	–	22	24	6	2.1	0.5–4.9	9	4–28
Reed fiber								
Communis	44–46	22–24	20	3	2.0	1.0–3.0	16	10–20
Bast fiber								
Seed flax	43–47	21–23	24–26	5	33	9–70	19	5–38
Kenaf	44–57	15–19	22–23	2–5	5	2–6	21	14–33
Jute	45–63	21–26	18–21	0.5–2	2	2–5	20	10–25
Hemp	57–77	9–13	14–17	0.8	25	5–55	25	10–51
Ramie	87–91	–	5–8	–	120	60–250	50	11–80
Leaf fiber								
Abaca	56–63	7–9	15–17	1–3	6	2–12	24	16–32
Sisal (agave)	43–62	7–9	21–24	0.6–1	3	1–8	20	8–41
Seed hull fiber								
Cotton	85–96	0.7–1.6	1–3	0.8–2	18	10–40	20	12–38
Wood fiber								
Coniferous	40–45	26–34	7–14	<1	–	–	–	–
Deciduous	38–49	23–30	19–26	<1	–	–	–	–

Note: – indicates no available data.

[a] From Rowell et al. (2000).

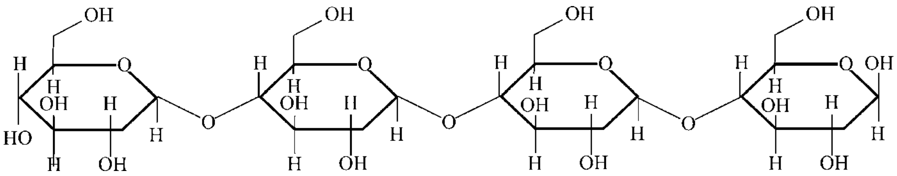


Fig. 14-2 Illustration of cellulose molecular structure.

The inherent polar and hydrophilic nature of cellulose makes it difficult to disperse in nonpolar and hydrophobic thermoplastic polymers, resulting in composites of poor performance (Dufresne et al., 2000).

Strategies to enhance the compatibility between hydrophobic thermoplastic polymers and hydrophilic cellulose fiber include modification of the polymeric matrices or fiber surfaces (Vallo et al., 2004). Alkaline treatment is the most commonly used chemical method to partially remove lignin and hemicellulose from natural fibers. The treatment is at high temperature and for long times. Consequently, the amount of crystalline cellulose increases and a rough surface topography is formed (Alvarez et al., 2003). FT-IR spectra showed that alkali treated fiber had an increased intensity of OH peak, along with disappearance of the C=O stretching of carboxylic group, compared to untreated group. The crystal structure of cellulose changes from the parallel polymer chains of cellulose I to aligned antiparallel cellulose II. This leads to higher exposure and concentration of OH groups to interact with groups on the polymer matrix (Vallo et al., 2004). Furthermore, the fiber density, elastic modulus, and fibrillation increased with treatment (Cyras et al., 2001). All of these factors improved the physical and mechanical properties of the composites.

14.4 STARCH-NATURAL FIBER BLENDS

The use of natural fibers as reinforcement opens a window of opportunity for starch-based composite developments because of the fibers' outstanding properties.

14.4.1 Preparation Methods

The preparation methods for starch and natural fiber blends include compound molding and solvent casting. Compound molding usually involves a premix process. Starch, fiber, and other additives are mixed vigorously at a high speed until no major fiber clumps are observed. This intensive premixing is not only efficient in separating the bundles of fibers to ensure a good dispersion, but it also results in a considerable reduction of fiber length and diameter and in a higher aspect ratio (Alvarez et al., 2004). The mixture is then transformed by different compounding techniques, including injection molding, compression, and extrusion. An injection mold typically consists of two parts, a core and a cavity, held together by a clamp (Fig. 14-3).

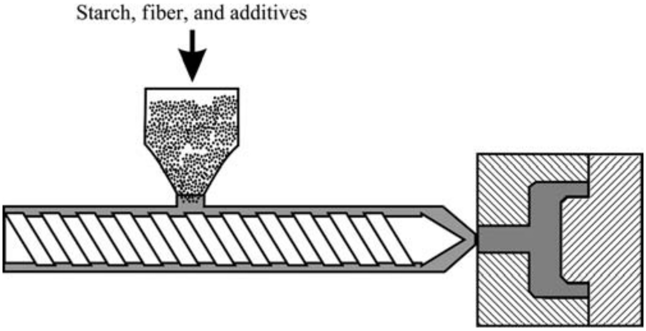


Fig. 14-3 A schematic representation of injection molding.

Compression molding is achieved by applying top pressure, usually from a hydraulic press, to force preheated material into a hot mold to cure (Fig. 14-4).

The effects of these two processing techniques on the properties of fiber composites were investigated by Alvarez et al. (2004). The results showed that complex viscosity varied as a function of frequency and temperature, and compression-molded samples had higher viscosity than injection-molded ones, implying that compression-molded material is more difficult to process than injected materials.

Extrusion is another popular composite polymer processing technique, and is used to produce expanded foams, films, and pellets. The premixed starch and fiber mixtures are compounded either with a single-screw or a twin-screw extruder (Fig. 14-5).

Selection of processing parameters for thermal compounding molding depends on the starch gelatinization temperature and thermal degradation temperatures of the starch and the fibers.

In addition, starch/fiber composites also can be prepared by the methods of filming stacking. In this method, no previous mixing is involved, and the thermoplastic starch film and a layer of fiber are placed on one another alternately, with fibers oriented either unidirectionally or cross-ply. Pressing is performed at a prescribed pressure and temperature in a matched tool (Romhány et al., 2003).

For solvent casting, a fiber suspension is mixed with a gelatinized starch solution. The mixture is homogenized and then cast into a Teflon mold and dried at ambient temperature (Dufresne and Vignon, 1998).

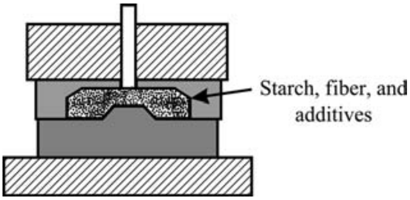


Fig. 14-4 A schematic representation of compression molding.

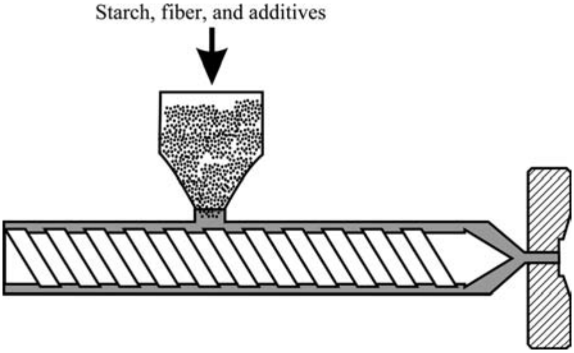


Fig. 14-5 A schematic representation of extrusion molding.

The maximum fiber content that can be introduced into the polymer depends on the selected processing method, with a maximum of 40 wt%. Above 40 wt%, fiber cannot be wetted totally by starch (Romhány et al., 2003). In thermal compounding, the fiber content is governed by viscosity. The viscosity increases with increase in fiber content and the great increase in viscosity at higher fiber contents makes processing difficult (Wollerdorfer and Bader, 1998).

14.4.2 Characterization of Starch–Fiber Blends

Morphology of Starch–Fiber Blends The morphology of starch–fiber blends can be observed by scanning electron microscopy (SEM) to investigate fiber dispersion and interaction between the starch matrix and the fibers after processing. A typical micrograph of the fractured surface of a fiber-filled thermoplastic starch composite is shown in Fig. 14-6.

It can be seen clearly that there was good adhesion of fiber in the starch matrix. Also, the fiber's surface was covered by starch, further indicating a strong adhesion between the starch and fiber (Curvelo et al., 2001). This good adhesion between starch and fiber can be attributed to the chemical structural similarities of starch and fiber. Both of them are polysaccharides, polar, and hydrophilic; as a result, there is an interaction between these two components.

Transparency of Starch–Fiber Films The influence of addition of fibers on the transparency of starch-based films was investigated by Ban et al. (2006). The decrease in film transparency with increases in fiber content was ascribed to the light–product interaction and to mixture structure. Film transparency is controlled by light diffusion and transmission: the higher the light diffusion at the interface, the lower the light transmission and transparency. In starch–fiber blends, although fibers can be dispersed in the starch matrix, they cannot be dissolved completely in a starch solution. Instead, the blends produce a discontinuous phase after drying.

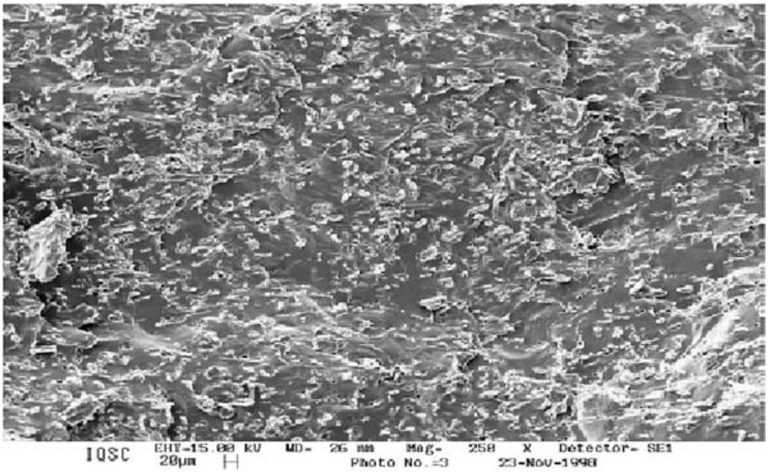


Fig. 14-6 SEM image of a fragile fracture surface of 16% fiber-filled thermoplastic starch (30% glycerin) composite (250× magnification). (From Curvelo et al., 2001.)

As a result, the increase in light diffusion at the starch–fiber interface reduces the light transmission, resulting in low transparency of the film.

Water Absorption High water absorbency is one of the most limiting factors to many practical applications of pure starch products. The strong hydrophilicity of starch products is ascribed to its high number of hydroxyl groups in the molecules and amorphous structure. Many efforts, including blending of starch with protein and chitosan, have been proposed to improve the water resistance of starch products (Jagannath et al., 2003; Xu et al., 2005a). The water resistance of these products is also enhanced significantly by incorporation of small amounts of fiber (Funke et al., 1998). In fact, cellulose, like starch, is a hydrophilic polymer, owing to high numbers of hydroxyl groups in the molecules. However, differently from starch, high crystallinity and tight microfibril structure in the fiber render it more hydrophobic than starch (Ban et al., 2006). The improvement in water resistance of starch products with addition of fiber is controlled by various factors, including fiber content, fiber modification, the presence of glycerine, and environmental relative humidity. Water sensitivity is generally expressed by water uptake rate, and is measured as a function of time. Water uptake rate decreases dramatically with increasing fiber content. Ban et al. (2006) reported that a 6.7% fiber addition in the starch film resulted in approximately 40% reduction in total water absorbency, while the film water absorbency was reduced further to more than 50% when the cellulosic fiber content was 12.5%. No further improvement was observed at higher fiber contents. Alkaline treatment changes the structure of cellulose from type I to type II. Cellulose II is more hydrophilic than its type I counterpart. Therefore, a starch and alkaline-treated fiber blend has a higher water uptake rate than the blends with untreated fiber (Alvarez et al., 2003). Glycerin acts as a plasticizer in a starch film, and the plasticized starch is more sensitive to water uptake rate than an unplasticized one. Dufresne and Vignon (1998) found that addition of fiber resulted in a more pronounced reduction in water uptake for plasticized starch film than for unplasticized film. A 30% reduction was achieved with a glycerol-plasticized film compared with less than 20% for its unplasticized counterpart, when 40% fiber was added. Starch film is more hydrophilic at high relative humidity, irrespective of the fiber content.

Gas Permeation Gas permeability is an important functional property of starch-based films. Ban et al. (2006) found that incorporation of cellulose prohibited CO_2 permeation. The CO_2 concentration in a vial covered by a pure starch film reached almost the same level as that in air after 10 min. However, the CO_2 concentration increased 50% when using a film with 19% cellulosic fiber content. Further, the permeation rate of CO_2 decreased as the cellulosic fiber content of the starch-based film increased.

Mechanical Properties Mechanical properties, including Young's modulus, ultimate tensile strength, elongation at break, compression, and spring index, are important characteristics of starch-based films and foams. Of these properties, the first three are mainly film properties, while the last two are foam properties. Young's modulus, often referred to as tensile modulus, measures the stiffness of a material, and is expressed as the ratio of the change rate of stress with strain. Ultimate tensile strength is the maximum tensile stress a material can withstand before it breaks. Elongation at break is measured as percentage elongation of sample at the point of rupture to its initial length. Compressibility describes the cushioning ability of a foam material and is related to its relative softness or hardness. Spring index relates to resiliency and refers to the ability of a foam material to recover its original shape after it has been deformed. Poor mechanical properties of neat starch products limit their wide use in diverse commercial applications. In general, the addition of fiber into a starch matrix appreciably improves the mechanical properties. Ban et al. (2006) found that increases in film tensile strength of as much as fivefold were achieved by incorporating up to 22% fiber into these films. However, the extent of fiber enhancement of starch products is influenced by many factors.

Type of Fibers Chemical composition and physical properties of the fibers vary with type. Generally, fibers containing high cellulose contents offer larger enhancement in mechanical properties owing to the intrinsic characteristics of cellulose. Averous and Boquillon (2004) compared cellulose fiber and lignocellulose fiber. The surface properties of these two fibers were found to vary according to the fiber nature. Cellulose fibers had more polar components and greater surface tensions than lignocellulose fibers. The presence of less polar lignins on the surface of lignocellulose fibers decreases the adhesion between fiber and starch, thereby producing lower mechanical properties. Corradini et al. (2006) reported higher Young's modulus and ultimate tensile strength values for matrices with sisal fiber incorporated than for those with coconut and jute fibers, owing to sisal's high cellulose content (67–78% for sisal fiber, 61–71.5% for jute fiber, and 36–43% for coconut).

Torres et al. (2007) confirmed that sisal fibers gave the highest tensile strengths compared with jute and cabuya fibers. The tensile strength increased almost 100% for potato starch with a 10% sisal content with respect to the unreinforced matrix, while improvements were 54% and 15%, respectively, for matrices with additions of jute and cabuya fiber.

Chemical Treatment of Fiber The goal of chemical treatment of fiber is to change the surface morphology to improve the compatibility between matrix and fiber. Corradini et al. (2006) reported higher Young's modulus and ultimate tensile strength values for composites reinforced with mercerized coconut and jute fibers than for those reinforced with nonmercerized fibers. Mohanty et al. (2000) observed that alkali-treated fabrics had better tensile strengths than dewaxed samples, although dewaxing of fiber also helps improve the fabric–matrix interaction. Alkali treatment of fiber not only produces a rough surface topography to improve the adhesive characteristics of fiber surface by removing natural and artificial impurities, but also fibrillates fiber bundles into smaller fibers, thus increasing the effective surface area available for contact with matrix polymers. The high values of the aspect ratio and rough surface have favorable effects on mechanical properties (Vallo et al., 2004).

Fiber Content Fibers act as reinforcement for a starch matrix. In general, an increase in mechanical properties of starch/fiber composites is observed with fiber content, irrespective of fiber orientation and damage that may occur during mixing (Alvarez et al., 2003). The fiber content is often expressed by fiber volume fraction, and a composite's Young's modulus and ultimate tensile strength are functions of fiber volume fraction, having an increasing trend with increase in fiber volume fraction (Alvarez et al., 2006). Elongation decreases with fiber content (Averous and Boquillon, 2004). The improvement of the mechanical properties suggests that there is good fiber–starch matrix adhesion. Starch and natural fiber are polysaccharides and have the same unit structure. The intrinsic chemical similarities between these two components enhance compatibility. Torres et al. (2007) found that the ultimate tensile strength of the unreinforced potato starch matrix increased from 4.15 MPa to 6.5 MPa when 5 wt% of sisal fiber was added. However, when fiber content was above 10 wt%, fiber dispersion in the composites became difficult, resulting in fiber clumps and voids in the specimens, thereby decreasing the tensile strength of specimens and increasing the standard deviations. Lawton et al. (2004) showed that trays with a fiber content of 15–30% had the best performance at all humidities. Tray strength declined with fiber contents above 30%.

Fiber Length Investigations of the effects of different fiber lengths on the strength of starch films indicated that short fiber reinforced the tensile properties of the film, since an effective load transfer from the matrix to the fiber provided a strong fiber–matrix interfacial bond (Alvarez et al., 2005). On the other hand, long fibers result in reduced film uniformity. Takagi and Ichihara (2004) indicated that 15 mm was a critical fiber length. The negative effect of long fibers on mechanical properties may be attributable to entanglement from long fiber–long fiber interactions, difficulty in uniformly dispersing such fibers in a starch matrix, and the occurrence of fiber pullout (Ban et al., 2006).

Fiber Alignment Fiber direction in a starch matrix plays a critical role in the reinforcement effect. Reinforcement is relatively low when fibers are laid transverse to the direction of loading. This can be explained by the fact that the fibers loaded in the transverse direction act as barriers that prevent the distribution of stress throughout the matrix (Alvarez et al., 2006). In contrast, when the fibers are aligned in the direction of loading, the strength of starch composites is double that of the neat matrix (Romhány et al., 2003).

Foam Compression resistance and flexibility are the most commonly used parameters in evaluating the mechanical properties of starch-based foams. Parra et al. (2006) prepared cassava starch foam with addition of cassava and wheat fibers. Foam with 1% cassava fiber had the higher compression resistance, and compression resistance decreased with increasing fiber content up to 3%. The flexibility of the cassava starch increased with fiber content up to 2%, followed by a decrease with further increases in fiber content to 3%.

Thermal Behavior Thermal characteristics, including phase transitions, melting, and thermal degradability play important roles in determining thermal processing conditions for starch-fiber composites.

Differential scanning calorimetry (DSC) is an accepted method for determining the thermal transition of starch polymer and its fiber blends. Samples sealed in stainless steel DSC pans are heated from 20 to 250°C at a heating rate of 10°C/min in a nitrogen atmosphere. The glass transition temperature and melting temperature are taken as the inflection point of the increment of specific heat capacity and as the peak value of the endothermal process in the DSC curves, respectively. Starch has a semicrystalline structure, showing a glass transition temperature and melting temperature on a DSC heating curve, with the presence of water or other plasticizers. Addition of fiber into the starch matrix increases its glass transition temperature (Curvelo et al., 2001). This is attributed to the interaction between the fiber and the plasticizer, leading to less-plasticized starch.

Measurements of the thermal stability of starch and its fiber composites are carried out by thermogravimetric analysis (TGA). Samples of 3–6 mg are placed in the balance system and heated from 50 to 650°C at a heating rate of 20°C/min in a nitrogen atmosphere. Degradation temperatures are determined as the peak maxima (Averous and Boquillon, 2004). Initial degradation of pure starch began at 297°C and ended at 326°C with a weight loss of 70.7% (Xu et al., 2005b). The decomposition of starch can be explained by inter- or intramolecular dehydration reactions of the starch molecules, with water as the main product of decomposition (Thiebaud et al., 1997). For fibers, two thermal decomposition temperatures are observed. The first at 300°C, corresponding to hemicellulose and glucosidic link depolymerization, overlaps with that of starch, while the second one at 360°C has been assigned to the thermal degradation of the α-cellulose in the fiber

(Alvarez and Vázquez, 2004). Addition of fiber into the starch matrix has a beneficial effect on the thermal stability of the starch matrix, with the maximum onset of degradation temperature shifting to a higher value and the mass loss decreasing. The improvement in the thermal stability of a starch–fiber blend, compared with an unfilled starch matrix, was attributed to overall low water content in the composite. In addition, diverse interactions between starch, fiber, and plasticizer reduce original water sites on thermoplastic starch (Averous and Boquillon, 2004).

14.5 SUMMARY

Starch-based films and foams have limited commercial applications because of their lack of flexibility and water resistance, among other characteristics. The addition of fiber into starch matrices enhances functional properties, that is, it decreases the water absorption and CO_2 permeability and increases Young's modulus and tensile strength. These improvements in functional properties extend the use of starch-based products in new applications that are moisture sensitive, including gas-selective membranes and ion channels. In addition, starches and natural fibers low cost and are natural and renewable polysaccharides from agricultural resources, which means that starch–natural fiber composites are fully biodegradable. The potential of these "green" composites to share the market with petroleum-based packaging becomes evident with stricter waste disposal regulations.

REFERENCES

Aburto J, Alric I, Thiebaud S, et al. 1999. Synthesis, characterization, and biodegradability of fatty-acid ester of amylose and starch. *J Appl Polym Sci* 74:1440–1451.

Altieri PA, Lacourse NL. 1990. Starch-based protective loose-fill material. *Proceedings of the Corn Utilization Conference III*, June 20–21, St. Louis, MO. National Corn Growers Association. Section 2, p. 1–4.

Alvarez VA, Vázquez A. 2004. Thermal degradation of cellulose derivatives/starch blends and sisal fiber biocomposites. *Polym Degrad Stab* 84:13–21.

Alvarez VA, Ruscekaite RA, Vázquez A. 2003. Mechanical properties and water adsorption behavior of composites made from a biodegradable matrix and alkaline-treated sisal fibers. *J Compos Mater* 37(17):1575–1588.

Alvarez VA, Rerenzi A, Kenny JM, Vázquez A. 2004. Melt rheological behavior of starch-based matrix composites reinforced with short sisal fibers. *Polym Eng Sci* 44(10):1907–1914.

Alvarez V, Vázquez A, Bernal C. 2005. Fracture behavior of sisal fiber-reinforced starch-based composites. *Polym Compos* 26:316–323.

Alvarez V, Vázquez A, Bernal C. 2006. Effect of microstructure on the tensile and fracture properties of sisal fiber/starch-based composites. *J Compos Mater* 40(1):21–35.

Andersen PJ, Kumar A, Hodson SK. 1999. Inorganically filled starch based fiber reinforced composite foam materials for food packaging. *Mater Res Innov* 3:2–8.

Australian Academy of Science. 2002. Making packaging greener—biodegradable plastics. http://www.science.org.au/nova/061/061key.htm (accessed August 28, 2007).

Averous L, Boquillon N. 2004. Biocomposites based on plasticized starch: thermal and mechanical behaviours. *Carbohydr Polym* 56:111–122.

Ban WP, Song JG, Argyropoulos DS, Lucia LA. 2006. Improved the physical and chemical functionality of starch-derived films with biopolymers. *J Appl Polym Sci* 100:2542–2548.

Bayazeed A, Farag S, Shaarawy S, Hebeish A. 1998. Chemical modification of starch via etherification with methyl methacrylate. *Starch/Staerke* 50:89–93.

Bikiaris D, Panayiotou C. 1998. LDPE/starch blends compatibilized with PE-*g*-MA copolymers. *J Appl Polym Sci* 70:1503–1521.

Champagne ET. 1996. Rice starch composition and characteristics. *Cereal Food World* 41(11):833–838.

Chen Y, Ishikawa Y, Maekawa T, Zhang Z. 2006. Preparation of acetylated starch/bagasse fiber composite by extrusion. *Trans ASAE* 49(1):85–90.

Cinelli P, Chiellini E, Gordon SH, Imam SH. 2003. Characteristics and degradation of hybrid composite films prepared from PVA, starch and lignocellulosics. *Macromol Symp* 197:143–155.

Corradini E, de Morais LC, Rosa MdF, Mazzetto SE, Mattoso LHC, Agnelli JAM. 2006. A preliminary study for the use of natural fibers as reinforcement in starch-gluten-glycerol matrix. *Macromol Symp* 246:558–564.

Curvelo AAS, de Carvalho AJF, Agnelli JAM. 2001. Thermoplastic starch–cellulosic fiber composites: preliminary result. *Carbohydr Polym* 45:183–188.

Cyras VP, Iannace S, Kenny JM, Vazquez A. 2001. Relationship between processing and properties of biodegradable composites based on PLC/starch matrix and sisal fibers. *Polym Compos* 22(1):104–110.

Demicheli M. 1996. Biodegradable plastics from renewable sources. http://www.jrc.es/iptsreport/vol10/english/Env1E106.htm#Contacts (accessed by Sep. 20, 2003).

Dufresne A, Vignon MR. 1998. Improvement of starch film performances using cellulose microfibrils. *Macromolecules* 31:2693–2696.

Dufresne A, Dupeyre D, Vignon MR. 2000. Cellulose microfibrils from potato tuber cells: processing and characterization of starch–cellulose microfibril composites. *J Appl Polym Sci* 76:2080–2092.

Fang Q, Hanna MA. 2000a. Mechanical properties of starch-based foams as affected by ingredient formulation and foam physical characteristics. *Trans ASAE* 43:1715–1723.

Fang Q, Hanna MA. 2000b. Functional properties of polylactic acid starch-based loose fill packaging foams. *Cereal Chem* 77(6):779–783.

Funke U, Bergthaller W, Lindhauer MG. 1998. Processing and characterization of biodegradable products based on starch. *Polym Degrad Stab* 59:293–296.

Goheen SM, Wool RP. 1991. Degradation of polyethylene-starch blends in soil. *J Appl Polym Sci* 42:2691–2701.

Gregorová E, Pabst W, Bohačenko I. 2006. Characterization of different starch types for their application in ceramic processing. *J Eur Ceram Soc* 26:1301–1309.

Guan JJ, Hanna MA. 2004. Functional properties of extruded foam composites of starch acetate and corn cob fiber. *Ind Crops Prod* 19:255–269.

Jagannath JH, Nanjappa C, Das Gupta DK, Bawa AS. 2003. Mechanical and barrier properties of edible starch-protein-based films. *J Appl Polym Sci* 88:64–71.

Jang BC, Huh SY, Jang JG, Bae YC. 2001. Mechanical properties and morphology of the modified HDPE/starch reactive blend. *J Appl Polym Sci* 82:3313–3320.

Jantas R. 1997. Synthesis and characterization of acryloyloxystarch. *J Appl Polym Sci* 65:2123–2129.

Kalambur S, Rizvi SSH. 2006. An overview of starch-based plastic blends from reactive extrusion. *J Plast Film Sheet* 22:39–57.

Laohakunjit N, Noomhorm A. 2004. Effects of plasticizers on mechanical and barrier properties of rice starch film. *Starch/Staerke* 56:348–356.

Lawton JW, Shogren RL, Tiefenbacher KF. 2004. Aspen fiber addition improves the mechanical properties of baked cornstarch foams. *Ind Crops Prod* 19:41–48.

Liu Z, Han JH. 2005. Film-forming characteristics of starches. *J Food Sci* 70(1):E31–36.

Matzions P, Bikiaris D, Kokkou S, Panayiotou C. 2001. Processing and characterization of LDPE/starch products. *J Appl Polym Sci* 79:2548–2557.

Miladinov VD, Hanna MA. 2000. Starch esterification by reactive extrusion. *Ind Crops Prod* 11:51–57.

Mohanty AK, Khan MA, Hinrichsen G. 2000. Surface modification of jute and its influence on performance of biodegradable jute-fabric/Biopol composites. *Compos Sci Technol* 60:1115–1124.

Palviainen P, Heinamaki J, Myllarinen P, Lahtinen R, Yliruusi J, Forssell P. 2001. Corn starches as film former in aqueous-based film coating. *Pharm Dev Technol* 6(3):353–361.

Parra DF, Carr LG, Ponce P, Tadini CC, Lugao AB. 2006. Biodegradable foams made of cassava starch and fibers: influence in the mechanical properties. *Proceedings of the 2nd CIGR Section VI International Symposium on Future of Food Engineering*, April 26–28, Warsaw, Poland.

Ratnayake WS, Hoover R, Warkentin T. 2002. Pea starch: composition, structure and properties—a review. *Starch/Staerke* 54:217–234.

Romhány G, Karger-Kocsis J, Czigány T. 2003. Tensile fracture and failure behavior of thermoplastic starch with unidirectional and cross-ply flax fiber reinforcements. *Macromol Mater Eng* 288:699–707.

Rowell RM, Han JS, Rowell JS. 2000. Characterization and factors effecting fiber properties. In: Frollini E, Leão AL, Mattoso LHC, editors. *Natural Polymers and Agrofibers Composites*. Brazil: Embrapa Instrumentação Agropecuária. p. 115–134.

Sagar AD, Merrill EW. 1995. Properties of fatty-acid esters of starch. *J Appl Polym Sci* 58:1647–1656.

Shogren RL. 1996. Preparation, thermal properties, and extrusion of high-amylose starch acetate. *Carbohydr Polym* 29:57–62.

Shogren RL, Thompson AR, Greene RV, Gordon SH, Cote G. 1991. Complexes of starch polysacchrides and poly (ethylene co-acrylic acid): structural characterization in the solid state. *J Appl Polym Sci* 47:2279–2286.

Simmnons S, Thomas EL. 1995. Structural characteristics of biodegradable thermoplastic starch/poly (ethylene-vinyl alcohol) blends. *J Appl Polym Sci* 58:2259–2285.

Sitohy MZ, Labib SM, El-Saadany SS, Ramadan MF. 2000. Optimizing the conditions for starch dry phosphorylation with sodium mono- and dihydrogen orthophosphate under heat and vacuum. *Starch/Staerke* 4:95–100.

Swinkels J.J.M. 1985. Composition and properties of commercial native starches. *Starch/Staerke* 37:1–5.

Takagi H, Ichihara Y. 2004. Effect of fiber length on mechanical properties of "green" composites using a starch-based resin and short bamboo fibers. *JSME International Journal, Series A* 47(4):551–555.

Thiebaud S, Aburto J, Alric L, et al. 1997. Properties of fatty-acid esters of starch and their blends with LDPE. *J Appl Polym Sci* 65:705–721.

Torres FG, Arroyo OH, Gomez C. 2007. Processing and mechanical properties of natural fiber reinforced thermoplastic starch biocomposites. *J Thermoplast Compos Mater* 20:207–223.

Vallo C, Kenny JM, Vazquez A, Cyras VP. 2004. Effect of chemical treatment on the mechanical properties of starch-based blends reinforced with sisal fiber. *J Compos Mater* 38(16):1387–1399.

Wang L, Shogren RL. 1997. Preparation and properties of corn-based loose fill foams. In *Proceedings of the 6th Annual Meeting of the Bio/Environmentally Degradable Polymer Society*, St. Paul, MN.

Wollerdorfer M, Bader H. 1998. Influence of natural fibers on the mechanical properties of biodegradable polymers. *Ind Crops Prod* 8:105–112.

Wu CS. 2003. Physical properties and biodegradability of maleated-polycaprolactone/starch composite. *Polym Degrad Stab* 80:127–134.

Xu YX, Hanna MA. 2005. Physical, mechanical, and morphological characteristics of extruded starch acetate foams. *J Polym Environ* 13(3):221–230.

Xu YX, Miladinov V, Hanna MA. 2004. Synthesis and characterization of starch acetates with high degree of substitution. *Cereal Chem* 81(6):735–740.

Xu YX, Kim KM, Hanna MA, Nag D. 2005a. Chitosan-starch composite film: Preparation and characterization. *Ind Crops Prod* 21(2):185–192.

Xu YX, Dzenis YA, Hanna MA. 2005b. Water absorption, thermal, and biodegradability of starch acetates foams. *Ind Crops Prod* 21(3):361–368.

Zhang Y, Han JH. 2006. Mechanical and thermal characteristics of pea starch films plasticized with monosaccharides and polyols. *J Food Sci* 71(2):E109–118.