chapter nine

Starch-based nanocomposites

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9.1 Introduction

In recent years there has been a growing effort to develop new biodegradable materials from environmentally friendly, biodegradable, and renewable resources whose feasibility in suiting their properties to a particular application can result in easily tailored composite materials. The utilization of natural polymers such as starch, lignin, cellulose, and proteins in the plastics industry is considered a viable approach to reduce surplus agricultural products and to develop biodegradable materials. Natural polymers derived from renewable resources have these environmental advantages when compared with petroleum-derived ones. Starch is one of the most studied and promising raw materials for the production of biodegradable materials because it is a widely abundant, relatively low-cost, and natural renewable polysaccharide obtained from a great variety of crops (Scott and Gilead, 1995; Chandra and Rustgi, 1998; Roper and Koch, 1990).

Composites have been used since ancient times. Archaeological evidence of the earliest civilizations reveals mud and straw "composites," bricks that are applied not unlike our modern composites today (Durant, 1963; Scherman, 2001). Natural composite materials range from wood to blood vessels (Shalaby and Latour, 1997), all of which show the advantage of reinforced structures. Modern nanocomposites advanced rapidly, in part when researchers from the automobile industry in the early 1990s created composites using nanostructured clay reinforcements (i.e., clay–polymer nanocomposites) that provided significant improvements in dimensional stability, stiffness, and heat distortion temperature relative to pure polymer. Nanocomposites utilize low levels of fillers, thereby minimizing the change in rheological properties during processing compared to traditional composites (Orts et al., 2005). Studies of characterization techniques and synthesis of new nanomaterials have opened up many research avenues, leading to a vast number of polymer matrices and fillers that can be used to produce nanocomposites.

One noteworthy example was introduced in the mid-1990s by Favier, Chanzy, and Cavaille (1995), who reported organic nanocomposites based on polymers reinforced with cellulose nanofibrils. In this research, crystalline cellulose needles (at 3–6% cellulose loadings) were dispersed in a copolymer acrylate latex film, increasing the dynamic storage modulus by more than threefold. Other researchers (Favier, Chanzy, and Cavaille, 1995; Greene and Imam, 1998) have continued work on natural cellulose nanoscale microfibrils highlighting advantages of these natural composites. Natural fibers such as wood are essentially cellulose-reinforced fibrils bound together by lignin and hemicellulose matrix, whereas bones,

the basic structure of all vertebrates, are collagen fibrils embedded in an inorganic apatite matrix (Chawla, 1998; Callister, 2006).

There are three significant distinctions between clay-reinforced and cellulose nanofibril-reinforced nanocomposites. First, clays are often flat platelets, whereas typical cellulosic nanofibrils are long crystalline "needles" usually ranging in size from 10–20 nm in width, with an average ratio of 20–100. Cellulose surfaces provide the potential for significant surface modification using well-established carbohydrate chemistry, some of which makes them ideally suited to interact with starch, a similar carbohydrate-based polymer. Sources of cellulose microfibrils, including wood, straw, bagasse, bacteria, and sea organisms, are widely diverse, providing a wide range of potential nanoparticle properties. The most-studied matrix for these cellulose-based nanocrystal composites has been starch, in part because starch is processed under aqueous conditions.

This chapter discusses these nanocomposites, the starch matrix and reinforcements—organic or inorganic materials—that have at least one of their dimensions in the range of 1–100 nm, the generally accepted definition of nanomaterials (Fishbine, 2002).

9.2 Nanocomposites

Nanotechnology principles and characterization techniques of materials have been revisited in search of new properties and applications. Nanocomposites not only exhibit enhancement in mechanical properties (tensile strength, elastic modulus, etc.) and physical properties (better barrier properties, reduced flammability, etc.), but they also show improved optical transparency when compared to traditional composites (Fischer, 2003). A low amount of added filler (less than 5% w/w) overcomes rheological implications, limiting the uses of many traditional composites (Sanadi et al., 1995; Bledzki and Gassan, 1999; Sanadi et al., 2001; Medeiros et al., 2005).

The nature and effectiveness of interactions at the interface phases are main variables acting on mechanical and physical properties of nanocomposites. Both interfacial region and particle dispersion play an important role in nanocomposite properties, mainly when fillers and reinforcements have a large contact surface area. Table 9.1 compares surface areas for several micro- and nanomaterials. A strong interface assures that any applied load can be easily transferred from the matrix to reinforcements, avoiding premature failure. A poor interface is also a drawback in situations other than external mechanical loading; for example, because of differential thermal expansions of reinforcement and matrix, premature failure can occur at a weak interface when the composite is subjected to thermal stress (Chawla, 1998; Callister, 2006).

Table 9.1 Surface Areas of Main Materials Used as Reinforcements and Fillers in Composites and Nanocomposites

Fibers/Fillers	Surface Area (m^2/g)
Natural fibers	0.5
Glass fibers	1
Paper fibers	4
Cellulose nanofibrils	250
Graphite	25–300
Fumed silica	100–400
Exfoliated clays	500
Carbon nanotubes	300–1000

Source: Dresselhaus, Dresselhaus and Avouris, 2001; Balaposzhinimaev, 2003; Bismarck, Mishra, and Lampke, 2005; Yang, Kim, and Lee, 2005; Simonsen, 2008.

9.2.1 Starch as matrix in nanocomposites

Several thermoplastic and elastomeric polymers have been used as matrices for nanocomposites (Giannellis, 1996; LeBaron, Wang, and Pinnavaia, 1999; Ajayan, Schadler, and Braun 2003; Gao, 2004). As in conventional composites, the matrix role is to support and protect the filler materials, transmitting and distributing the applied load between reinforcing agents (Giannellis, 1996; Chawla, 1998; LeBaron, Wang, and Pinnavaia, 1999; Callister, 2006). Because the range of particle sizes is on the nanoscale, the large surface area of the filler material makes the particle–matrix interfacial region even more important. Matrices support the filler surface by chemical reactions or adsorption, providing the strength of interfacial adhesion. In certain cases, the interface may be composed of an additional constituent such as bonding agents or interlayers between the two components of the composite.

The choice of a matrix depends on several factors such as application, compatibility between the components, processing, and costs. However, with the recent advances in development of biodegradable polymers, the search for biodegradable matrices such as starch, poly(lactic acid), poly(ε-caprolatones), polyhydroxybutyrate, poly(butylene succinate), and polyhydroxyalkanoates has received attention (Shalaby and Latour, 1997; Avérous, Fringant, and Moroa, 2001; Fischer, 2003; Ray and Okamoto, 2003; Okamoto, 2005). For many years starch has been considered a natural polymer with high potential for applications in biodegradable plastics because of its renewability, biodegradability, low cost, availability, and

mechanical properties (Avérous, Fringant, and Moroa, 2001; Corradini et al., 2006).Composites based on the opposite polysaccharide nanocrystals are often obtained by a casting/evaporation method. Increasing the affinity between the polysaccharide filler and the host matrix results in less favorable mechanical performance. This behavior is ascribed to the uniqueness of the reinforcing phenomenon of polysaccharide nanocrystals resulting from the formation of a percolating network due to hydrogen bonding forces (Dufresne, 2007).The microstructure of the matrix and the resulting competition between matrix–filler and filler–filler interactions also affect the mechanical behavior of the polysaccharide nanocrystal-reinforced nanocomposites. However, the major drawbacks associated with the use of starch-based materials in packaging applications are due to their hydrophilic nature, poor processability and brittleness, and postprocessing crystallization, resulting in poor mechanical properties (Whistler and Paschall, 1965, 1967; Aichholzer and Fritz, 1998; Rhim and Ng, 2007).

Significant research on starch as a matrix for nanocomposities has been done, with the matrix mechanical properties changing dramatically according to the starch botanical origin, plasticizier addition, and filler choice. Strong interactions between cellulose crystallites from cottonseed linters and glycerol plasticized starch matrix play a key role in reinforcing properties (Lu, Weng, and Cao, 2005). In natural rubber-based nanocomposites reinforced with starch nanocrystals (Angellier et al., 2005c), loss of mechanical properties is observed with adding reinforcement, a similar effect to that observed for unmodified or surface chemically modified chitin whiskers (Gopalan Nair et al., 2003). A transcrystallization resulting in a broader interphase and in a broadening of the main relaxation process of the matrix on plasticized starch reinforced with cellulose whiskers (Anglès and Dufresne, 2001) suggests that the strong loss of performance is due to the importance of the filler/filler interactions.

9.2.2 Nanocomposite classification

There are several methods to classify composites and nanocomposites, which are based on the nature and origin of the matrix, shape and size of the reinforcements, and uses of the obtained material (Chawla, 1998; Callister, 2006). According to filler particle shape, nanocomposites can be classified into particulate, elongated particle, and layered nanocomposites.

Particulate nanocomposites generally use isodimensional particles as reinforcement. The reinforcing effect is moderate and the general purpose of using these reinforcements is to enhance composite resistance to flammability or to decrease permeability or costs.

Elongated particle nanocomposites are composed of reinforcement particles, such as cellulose nanofibrils and carbon nanotubes. These

nanocomposites present better mechanical properties due to the particles' higher aspect ratio.

Layered particle-reinforced polymer nanocomposites, also known as layered polymer nanocomposites (LPN), are classified into three subcategories according to how the particles are dispersed in the matrix. *Intercalated nanocomposites* are formed by intercalated polymer chains on sheets of layered nanoparticles, *exfoliated nanocomposites* are obtained by separation of individual layers, and *flocculated* or *phase-separated nanocomposites* present no separation between the layers due to particle–particle interactions. This last class of composites is often called microcomposites because the individual laminas do not separate, thus acting as microparticles dispersed in the polymeric matrix. Their mechanical and physical properties are poorer than those of exfoliated and intercalated nanocomposites (Ajayan, Schadler, and Braun, 2003; Ray and Okamoto, 2003; Orts et al., 2005). Figure 9.1 shows a schematic drawing of the structure of layered nanocomposites.

9.2.3 Fillers

Fillers are generally defined as organic or inorganic particulate material (spheres, plates, flakes, sheets, fibers, fibrils, and whiskers) used in composites to reduce costs. As such, they are generally the least expensive of the major ingredients. In addition, they often modify mechanical or physical properties, such as processability, flammability, conductivity, shrinkage, weight, or visual appearance. Depending on the application, fillers are given specific terms, such as smoke suppressors, nucleating agents, and UV stabilizers among others (Shalaby and Latour, 1997; Chawla, 1998; Medeiros et al., 2001, 2002; Ray and Okamoto, 2003). Nanocomposite fillers can provide multiple advantages even if added in small amounts.

Fillers can also be classified into three major categories, according to their particle size and shape. *Isodimensional* or *zero-dimensional particles* have the same size in all directions (examples include spherical silica, nanoclusters, metallic nanoparticles, carbon black, and fullerenes) and their aspect ratio is usually close to unity (L/D ~1). The second category of particles, also known as *cellulose nanofibrils, microcrystalline cellulose, cellulose nanocrystals,* or *nanowhiskers,* consists of elongated particles or fibrils with diameter between 1 and 100 and length of several hundreds of nanometers. The third category is comprised of particles shaped in a lamina or sheet, with width and thickness ranging from a few angstroms to several hundreds of nanometers and length of thousands of nanometers, called layered particles. These particles are composed of stacks of laminas; usually found in nature, they can also be produced synthetically (Grim, 1962, 1988; Ajayan, Schadler, and Braun, 2003).

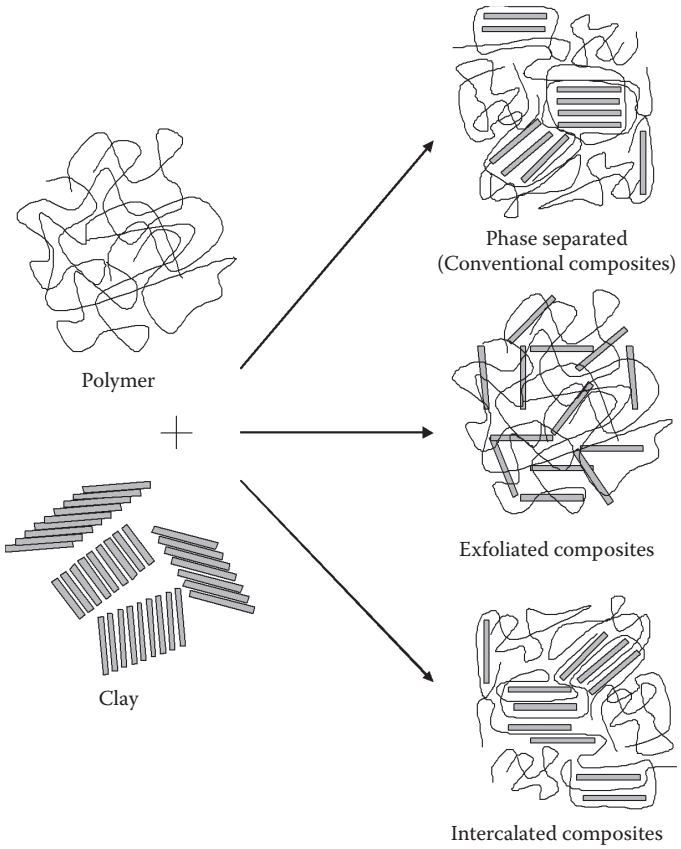


Figure 9.1 Different types of nanocomposites from polymers and clays. Conventional composites are also known as microcomposites.

Due to their high aspect ratio, which confers a higher enhancement of the mechanical properties of the nanocomposites, nanomaterials of the last two categories are the most popular. The most common fillers used to obtain nanocomposites are carbon nanotubes, carbon black, fumed silica and clays (inorganic fillers), and cellulose-based fibrils (organic fillers). Carbon nanotubes are molecular-scale tubes formed by rolled-up graphene sheets with outstanding mechanical and electrical properties, with the stiffest and strongest fibers (Balaposzhinimaev, 2003; Popov, 2004).

9.2.3.1 Clays

Clays are constituted of colloidal fragments of primary silicates, also known as clay minerals. The structure of clay minerals is made up of tetrahedral and octahedral sheets of small cations, such as aluminum or

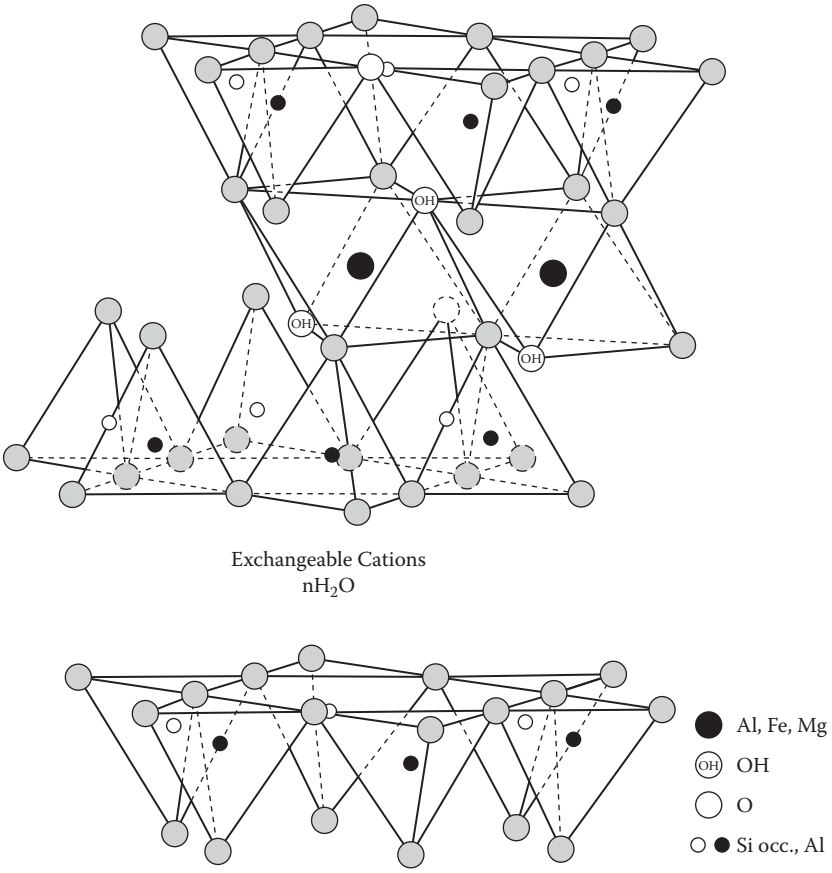
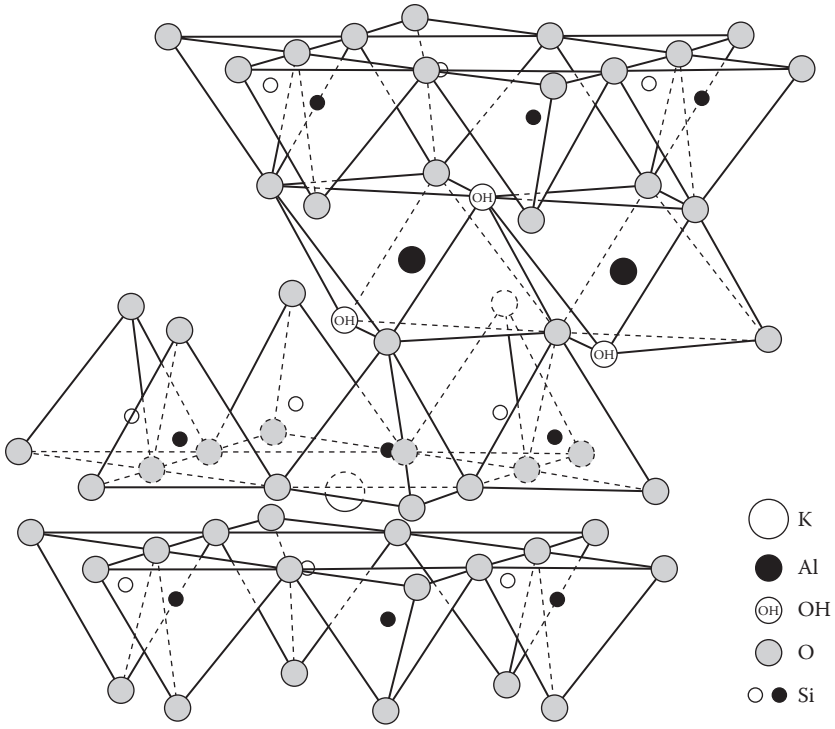


Figure 9.2 Structure of some of the clay minerals used as fillers in nanocomposites: (a) montmorillonite, (b) muscovite, (c) kaolinite. Note the layered structure composed of tetrahedrons and octahedrons with atoms positioned at both interstitial and corner positions (Grim, 1962).

magnesium coordinated by oxygen atoms. Clays are classified based on the way that tetrahedral (n) and octahedral (m) sheets are packaged into layers as n:m clays. For example, 1:1 clays are formed by one tetrahedral and one octahedral group in each layer. Figure 9.2 shows the tetrahedral–octahedral structure of some of the clay minerals used in nanocomposites. One important feature of clays is that the space between layers contains hydrated cations such as Na^+ or K^+ that can undergo exchange reaction with organic as well as inorganic cations (Grim, 1962, 1988). Addition of clay (as sodium montmorillonite) to a matrix of plasticized starch and glycerol results in improved properties when compared with the starch



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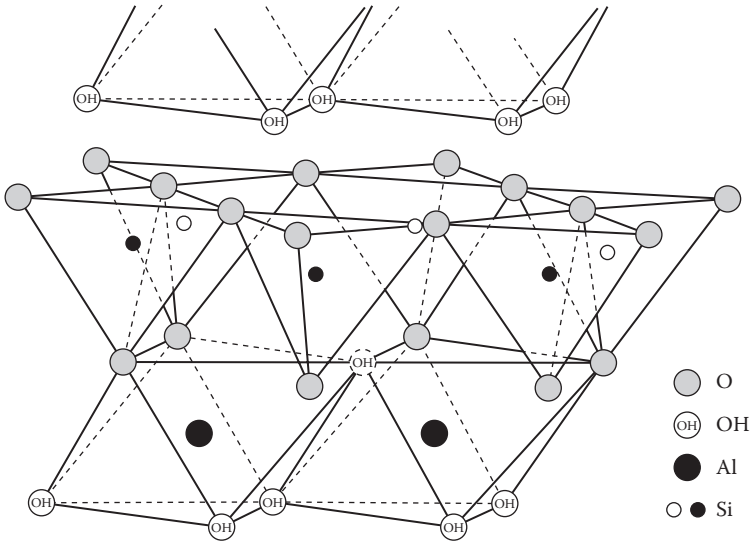

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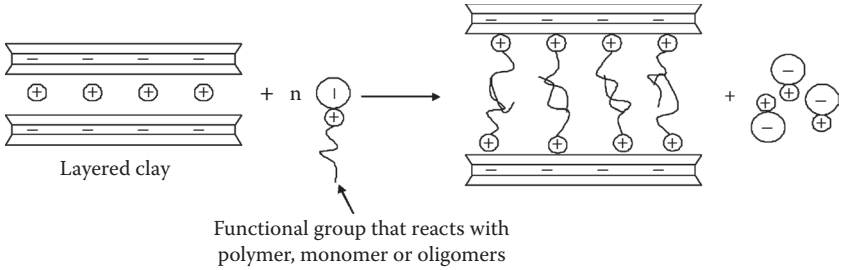

Figure 9.3 (a) Cation exchange reaction to produce organically modified clays; (b) compounding with a polymer matrix to make nanocomposites.

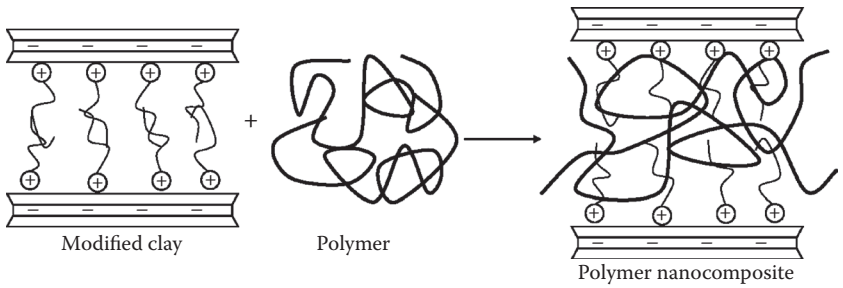

Figure 9.3 (Continued.)

matrix (Chen and Evans, 2005; Park et al., 2003; Qiao, Jiang, and Sun, 2005; Chiou et al., 2007; Magalhães and Andrade, 2009).

Cation exchange reactions in clays are very important to impart functionality and compatibility with polymers as shown schematically in Figure 9.3 (Fischer, 2003; Ray and Okamoto, 2003).

9.2.3.2 Cellulose

Cellulose is the most abundant organic polymer in nature with an estimated annual production of 1.5×10^{12} ton (Crawford, 1981). Chemically, cellulose is a linear polymer made up of several hundred to over 10,000 repeating units of β(1→4) linked D-glucose (see Figure 9.4) (Klemm et al., 2005). Physically, cellulose is found in the form of microfibrils constituted of amorphous and crystalline domains in combination with other substances such as lignin, hemicelluloses, and proteins making up the basic structural unit of plant cell walls as shown schematically in Figure 9.5. Cotton, wood, leaves, and stalks are examples of raw materials from plants that can be a source of cellulose, but it can also be produced by bacteria, algae, and fungi (Klemm et al., 2005).

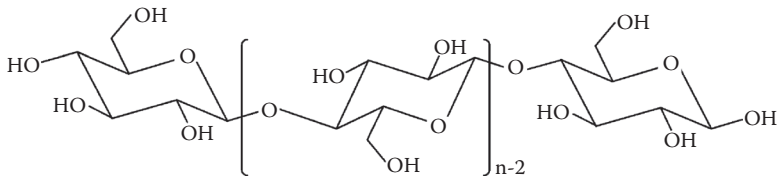

Figure 9.4 Chemical structure of cellulose.

Crystalline cellulose can be isolated by treatment of cotton, sisal, and wood with strong acids such as hydrochloric and sulfuric acid in order to remove the amorphous parts, yielding fibrils with diameters in the range of 5 to 20 nm and aspect ratio of about 1 to 100 times (Figure 9.6) (Klemm et al., 2005).

As a result of the acid treatment used to obtain cellulose, nanofibrils often have electronegative surface charges on their surface. Particle–particle or particle–solvent–particle interactions form three-dimensional networks giving rise to a rheological behavior reminiscent of clay nanocomposite behavior (Crawford, 1981; Lima and Borsali, 2002; Klemm et al., 2005). However, acid hydrolysis also decreases thermal stability of nanofibrils, which determines the range of starch processing temperatures (Tadmor and Gogos, 1979; Morton-Jones, 1989; Glasser et al., 1999). The thermal stability can be recovered to a certain extent by modifying the extraction process, such as by the use of low acid concentrations, low acid-to-cellulose ratio, and short reaction times (Roman and Winter, 2004), or postextraction processes such as restabilization by partly neutralizing the sulfuric acid groups with strong bases such as sodium hydroxide (Wang, Ding, and Cheng, 2007).

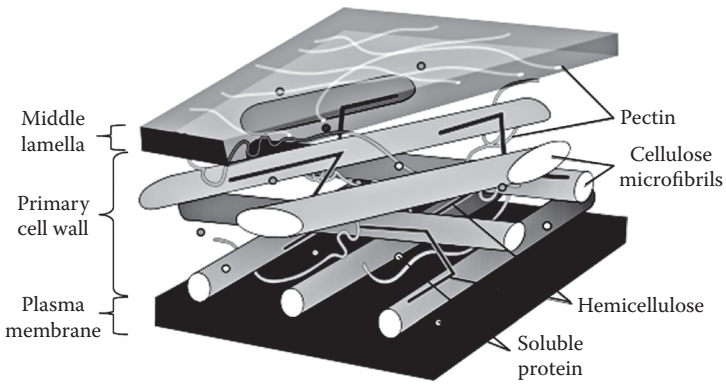

Figure 9.5 Physical structure of cellulose showing the location and arrangement of cellulose microfibrils in plant cell walls (Wikipedia, 2008).

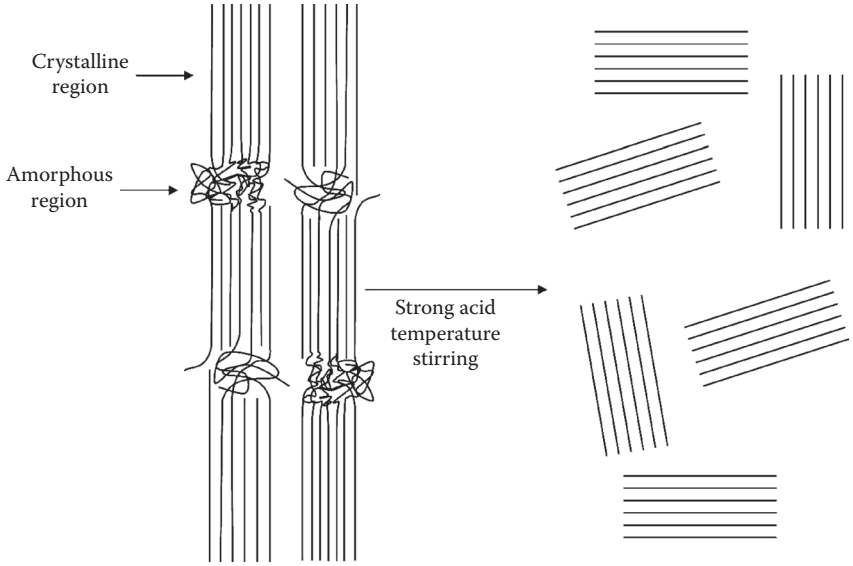

Figure 9.6 Isolation of cellulose nanofibers: (a) schematic representation of the isolation process used to obtain cellulose microfibrils; (b) disintegration of microfibrils by acid attack forming nanofibrils (Rosa et al., 2008).

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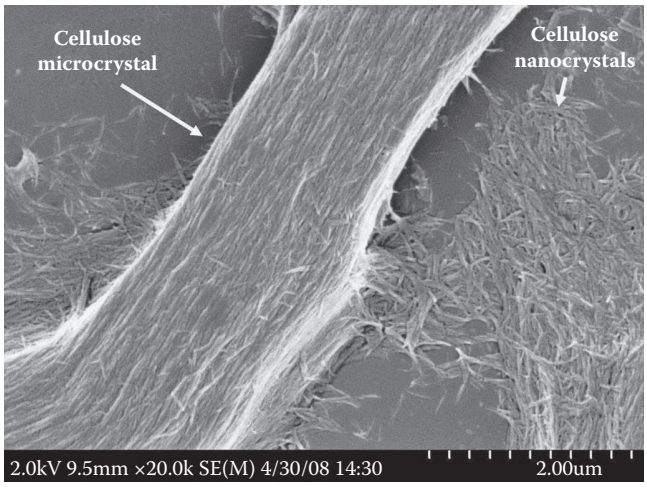

Figure 9.6 (Continued.)

Although cellulose nanofibrils have been studied and used industrially since the 1960s (Battista, 1975), recently these nanostructures have gained more scientific attention due to the application of nanomaterials from renewable resources. These nanofibrils possess several advantages in engineering material, such as low cost and density, renewability, biodegradability, nontoxicity, formation of stable aqueous suspension, and remarkable mechanical properties, being capable of improving the mechanical performance of polymers at quite low fiber concentrations (Orts et al., 2005; Marcovich et al., 2006). Consequently, crystalline cellulose has a modulus rivaling steel, therefore representing an appropriate material for nanocomposites. With the above-mentioned benefits, cellulose-based nanocomposites are organic alternatives to clay-based particulates, with the added advantage of applying well-understood cellulose chemistry. Moreover, due to cellulose polyfunctionality, chemical reactions can be carried out on the surface of the nanofibrils, enhancing their interaction with a vast number of polymeric matrices (Klemm et al., 2005; Orts et al., 2007).

9.2.4 Preparation, processing, and characterization of nanocomposites

9.2.4.1 Preparation

One of the most important steps in the preparation of polymer nanocomposites is the mixing process. In order for the properties of a compatible filler to be fully exploited, it has to be well distributed and well dispersed, as shown in Figure 9.7. This is important in nanocomposites because filler content is low and because high surface area nanoparticles have a natural

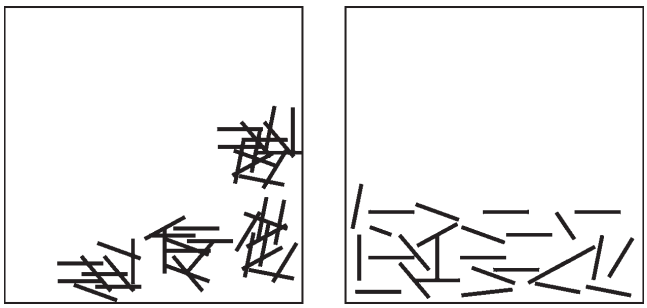

Figure 9.7 Degrees of dispersion and distribution of fibrillar reinforcements in a polymeric matrix: (a) poorly distributed and poorly dispersed; (b) poorly distributed and well dispersed; (c) poorly dispersed and well distributed; and (d) well dispersed and well distributed.

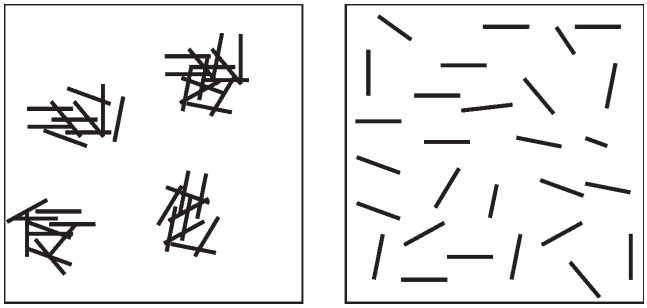

Figure 9.7 (Continued.)

tendency to agglomerate rather than disperse in the matrix (Tadmor and Gogos, 1979; Morton-Jones, 1989; Fischer, 2003; Ray and Okamoto, 2003,).

Nanocomposites are basically prepared by solution and melt dispersion (Ray and Okamoto, 2003), sol-gel synthesis (Ajayan, Schadler, and Braun, 2003), in situ polymerization, and self-assembly (Decher and Schlenoff, 2002; Medeiros, Paterno, and Mattoso, 2006).

Solution dispersion is a process whereby the filler is dispersed in an organic solvent, followed by swelling. Meanwhile, the polymer is dissolved in the same solvent for further mixing. Both the mixing intensity and duration are critical to ensure a good distribution and dispersion of filler particles. The major limitations of these processes are that the polymer needs to be soluble in the same solvent used to disperse and swell the filler, and the solvent removal is an additional step which limits large-scale industrial processing.

Melt dispersion is probably the most practical process of nanocomposite preparation, inasmuch as traditional methods of composite mixing such as twin- and single-screw extruders, rheometers, and mixers can be used, providing a good mixing efficiency (Tadmor and Gogos, 1979; Morton-Jones, 1989). Melt dispersion consists of mixing the filler with a polymer melt to assure a good dispersion by high shear and temperature. Shear prevents the filler particles from aggregating and higher temperatures promote polymer chain diffusion between separated particles. The thermodynamical driving forces change according to the polarity of the fillers, chemical compatibility with the polymeric matrix, processing temperature, and polymer molecular weight (Giannellis, 1996; LeBaron, Wang, and Pinnavaia, 1999).

In situ polymerization comprises filler dispersion in a liquid monomer or a monomer dissolved in a suitable solvent, allowing monomers to diffuse between the layers. Upon further addition of initiator or exposure

of appropriate source of light or heat, the polymerization takes place in situ producing the nanocomposite.

9.2.4.2 Processing

Although they can be carried out separately, mixing and processing generally take place at the same time to reduce costs and time. The quality of final products depends strongly on this step, because it can impart defects, inefficient dispersion, and undesired orientation of the reinforcement; resulting in premature failure and other environmental stress cracking processes (Tadmor and Gogos, 1979; Morton-Jones, 1989; Chawla, 1998; Shackelford, 1999; Callister, 2006).

The nature of the matrix (thermoplastic, thermoset, or elastomeric), the nature of the fillers, and their thermal resistance should be the main factors considered when choosing a process. The most common methods are extrusion, injection molding, casting, and compression molding; reactive extrusion is a potential option (Tadmor and Gogos, 1979; Fischer, 2003; Ray and Okamoto, 2003). More information on polymer processing operations can be found in the specialized literature (Tadmor and Gogos, 1979; Morton-Jones, 1989; Rosato, 1997; Begishev and Malkin, 1999; Brydson, 1999; Crawford, 1999).

9.2.4.3 Characterization of nanocomposites

Actually, there are several techniques of nanocomposite characterization (Brundle, Evans, and Wilson, 1992). The choice of the most appropriate technique to characterize nanocomposites depends strongly on the nature of the materials and their applications.

Particle size, distribution and dispersion, degree of interaction, and the filler–matrix interface are some parameters evaluated by direct or indirect techniques. Direct techniques include microscopic observations (scanning electron microscopy, transmission electron microscopy, scanning probe microscopy, and X-ray diffraction). Indirect techniques provide data about nanocomposite characterization correlating with their mechanical, physical, rheological, thermal, and thermomechanical properties; they include rheometric and calorimetric analysis.

Wide angle X-ray diffraction (WAXD) is used most broadly in nanocomposite characterization. This technique, which is based on changes in the Bragg peaks, provides details about the crystalline orientation and interplanar spaces. WAXD is especially useful for polymer-layered nanocomposites to evaluate the exfoliation degree on clays and the interplanar expansion after chemical surface treatments. WAXD has been used in cellulose nanocomposites to study changes in crystalline degree and structure of cellulose nanofibrils and polymeric matrices after fiber extraction and composite formation or processing (Edgar and Gray, 2003; Nishino, Matsuda, and Hirao 2004; Huang et al., 2005). Figure 9.8 illustrates

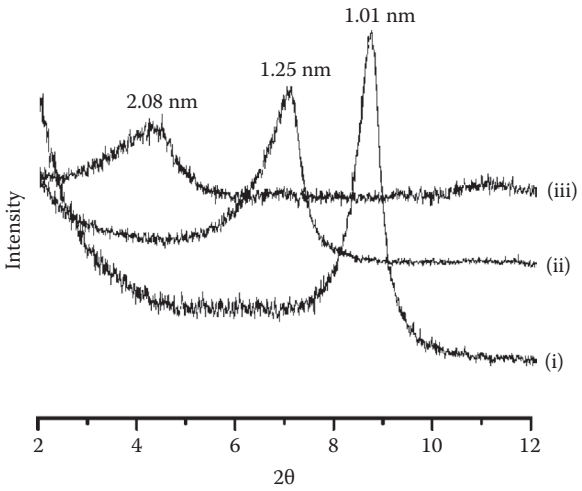

Figure 9.8 (a) WADS patterns of (i) untreated montmorillonite (MMT), (ii) activated montmorillonite (EMMT), and (iii) thermoplastic starch/activated montmorillonite nanocomposites (TPS/EMMT) (Huang, 2005); and (b) schematic representation showing the changes in the interplanar spacing of montmorillonite (d_1) with activation (d_2), and intercalation (d_3).

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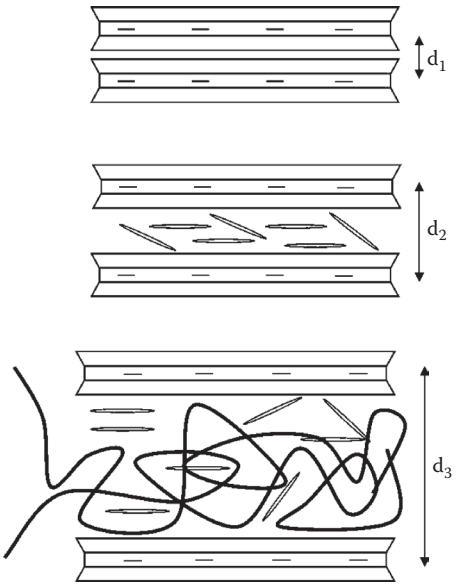

Figure 9.8 009x008b.eps

application of WAXD on samples of starch/montmorillonite composites from 1.01 to 1.25 and 2.08 nm.

Transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), and scanning electron microscopy (SEM) are the most commonly used microscopy methods. Details about microscopy in characterization of starch and starch-based materials are provided in Chapter 2. Figure 9.9 compares ranges of sizes of structures that can be analyzed by microscopic techniques. Transmission electron microscopy is by far the most used imaging technique in nanocomposite characterization. It provides spatial distribution of the various phases and defects through direct visualization of ultra-thin microtomed layers. In polymer clay nanocomposites, TEM allows one to observe the degree of dispersion, particle size distribution of cellulose nanofibrils (Figure 9.10) (Rodriguez, Thielemans, and Dufresne, 2006), and clay exfoliation, intercalation, or flocculation (Figure 9.11). However, special care must be taken during sample preparation, because a sample must be thin enough to be transparent to the electron beam (Ray and Okamoto, 2003).

Scanning electron microscopy is particularly useful for studying the fracture surface of composites, identifying the various modes of failure, the interfacial region, and therefore identifying filler–matrix interaction. Figure 9.12 shows SEM micrographs of the structure of the nanocomposites of thermoplastic starch (TPS) and cellulose nanofibers. It can be observed

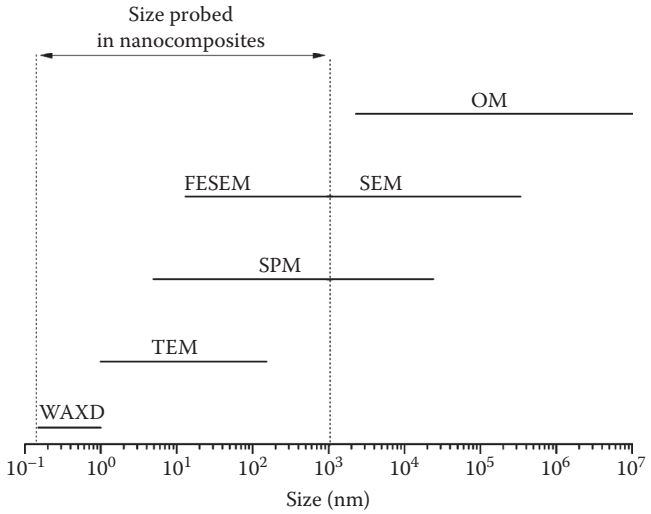

Figure 9.9 Comparison among the size ranges of structures that can be analyzed by TEM, FESEM, SEM, and OM. Field emission scanning electron microscopy (FESEM) is an improved SEM in terms of spatial resolution and minimized sample charging and damage.

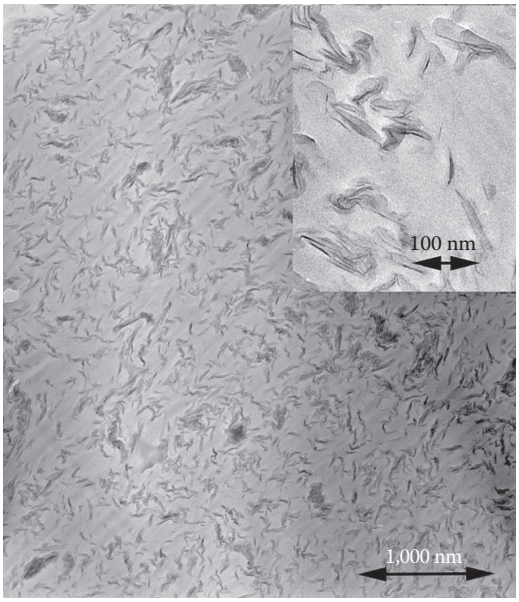

Figure 9.10 TEM micrographs showing (a) particles of montmorillonite dispersed in a starch–poly(vinyl alcohol) matrix at low and high magnification (upper right corner); and (b) cellulose nanofibrils obtained from sisal and a histogram for the distribution of diameters (upper right corner) (Rodriguez, Thielemans, and Dufresne, 2006).

that the nanofibers (white spots) are well dispersed and covered by the matrix with no fiber pull-out or debonding, confirming the improved adhesion between the nanofibers and the polymeric matrix (Chawla, 1998; Medeiros et al., 2005). Scanning probe microscopy (SPM) is also used on surface characterizations such as roughness modification by extraction or surface treatments and nanoindentation tests of the nanofibrils are required (Edgar and Gray, 2003), being particularly useful to investigate self-assembled nanocomposite structures (Decher and Schlenoff, 2002). Conversely, optical microscopy (OM) has little or no practical use in nanocomposites because the dimensions of the reinforcing agents are on the nanoscale, which lies below the resolution limit of optical microscopes.

Measurement of mechanical, physical, dynamic-mechanical, and thermal properties is often used to evaluate the impact of filler on nanocomposites (Orts et al., 2005). For example, addition of stiff cellulose nanofibrils, carbon nanotubes, and clays affect rheological, mechanical (tensile, flexural, and impact), and dynamic mechanical properties of nanocomposites, which can be measured by dynamic mechanical thermal analysis. Inorganic fillers impart high thermal stability, thus measurements of

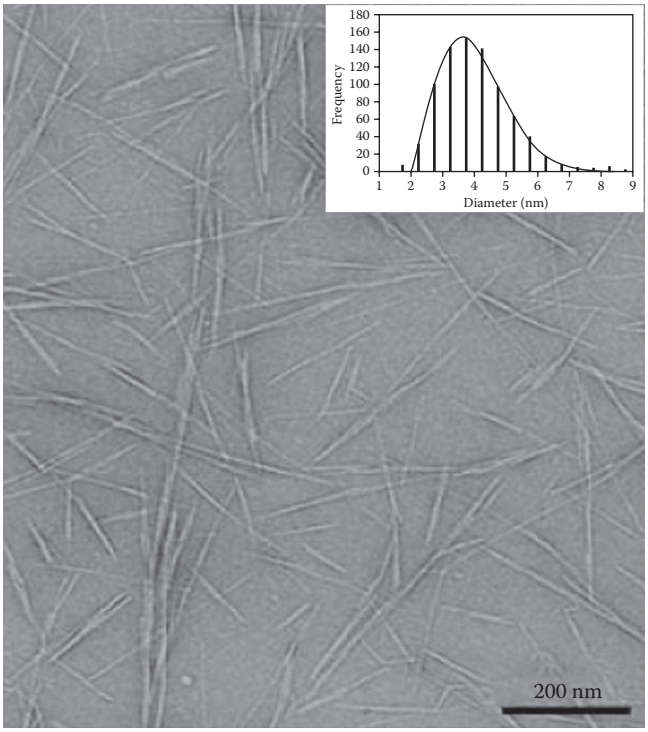

Figure 9.10 (Continued.)

thermal stability (thermal mechanical analysis, TMA, and thermogravimetry, TGA), heat distortion temperature (HDT), and flame retardancy and smoke suppression (flammability tests) are all useful in nanocomposite characterization (Alexandre and Dubois, 2000; Bower, 2002; Ray and Okamoto, 2003; Jansson and Järnström, 2005; Sperling, 2006).

Thermal analysis by differential scanning calorimetry (DSC) has been applied to nancomposites to follow matrix properties after filler addition, allowing us to understand polymer chain mobility and, hence, the nucleating process (Bower, 2002; Sperling, 2006). Knowledge of crystallization kinetics of crystalline matrices is fundamental in setting up processing parameters such as molding temperature and time. Thermal characterization is an important tool considering that retrogradation and crystallization of thermoplastic starch during aging leads to undesired changes in thermomechanical properties, the main drawback for application of starch-based plastics. Increase of the degree of crystallinity of the thermoplastic starch matrix has been reported (Angellier et al., 2006b), implying that crystallization of the matrix occurs at the interface between the filler and the matrix owing to the similar chemical structure of both components.

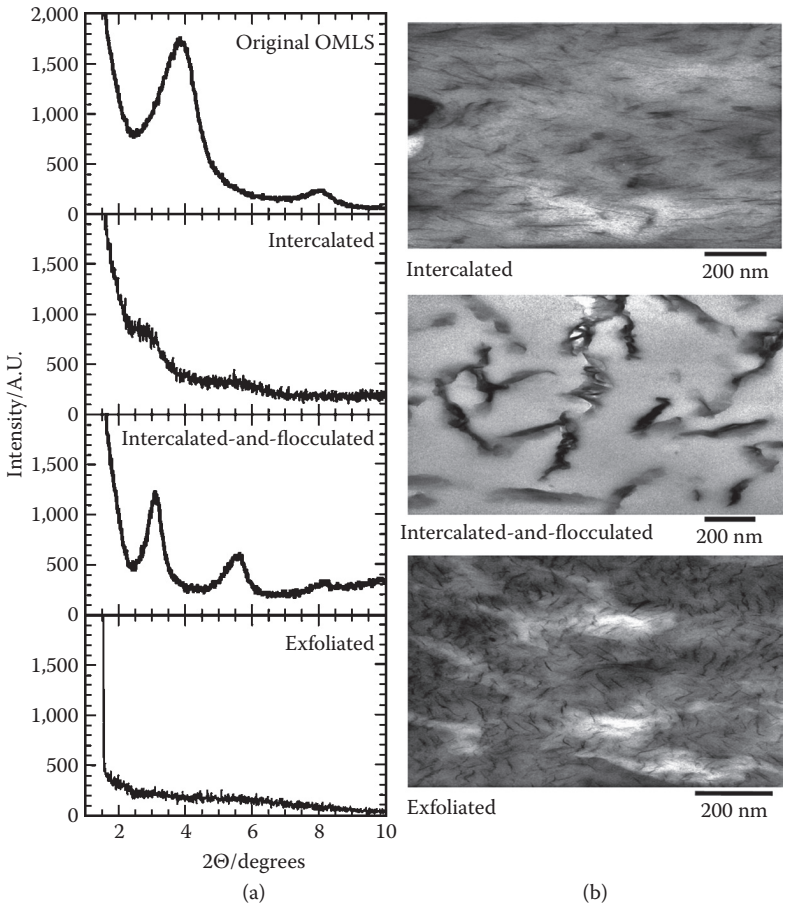

Figure 9.11 Comparison between WADS patterns and TEM images for organically modified layered silicate (OMLS) and nanocomposites displaying three different morphologies (exfoliated, flocculated, and intercalated)(Ray and Okamoto, 2003).

Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) analyses are used to detect functional groups to study the structure of nanocomposites, mainly to evaluate cross-linking, compatibilization, and surface treatment of the fillers. For example, NMR had been used to study nanocomposites based on cross-linked starch and cellulose nanofibrils (Orts et al., 2007). Details about applying NMR to characterize starch and starch gels are discussed in Chapter 4.

Dynamic mechanical thermal analysis (DMTA) measures the response of a material to oscillatory deformation as a function of temperature and decomposes this response in two components: elastic, measured by the

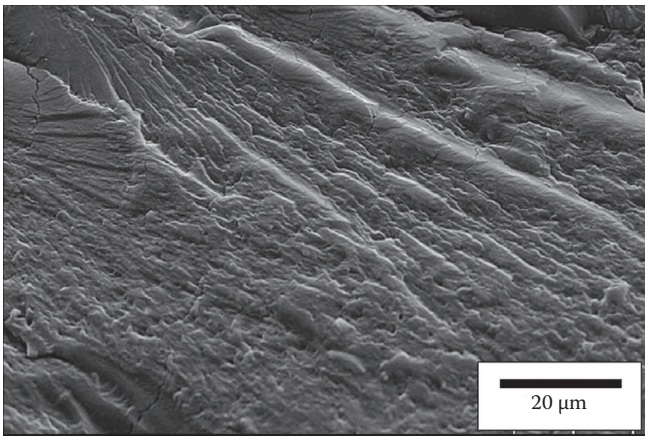

Figure 9.12 SEM images of the cryofractured surface of (a) thermoplastic starch and (b) cellulose nanofibers/starch nanocomposite (Alemdar and Sain, 2008).

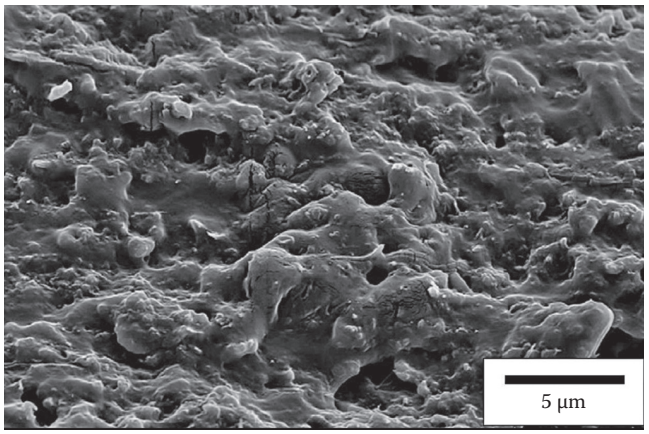

Figure 9.12 (Continued.)

storage modulus (E´), and viscous, measured by the loss modulus (E˝), providing information on changes in molecular mobility with the addition of rigid fillers. It is a very suitable technique to determine mechanical properties of nanocomposites and the influence of filler addition. Moreover, because in many cases there is a need to add a third component in order to improve mechanical properties, glass transition measurements can also be used to evaluate the degree of compatibilization and interaction between multiple components (Bower, 2002; Sperling, 2006).

Gas permeability and changes in barrier properties are another set of important properties of nanocomposites. The migration of gases through

packaging reduces the shelf life of food and beverages, and durability of many other industrialized products (Alexandre and Dubois, 2000; Sanadi et al., 2001; Ray and Okamoto, 2003; Jansson and Järnström, 2005). Some nanocomposites have shown barrier properties because nanofillers, such as exfoliated clays, act as barriers that prevent gas diffusion. Gases need to follow tortuous paths around the nanoparticles, thus making the diffusion path longer as implied in Figure 9.13. As such, measurement of barrier properties can give useful insights on the nature of particle dispersion in nanocomposites.

There is no simple predictable trend in increasing or decreasing a specific nanocomposite property with the addition of nanostructured reinforcements. Several combinations must be tried to offset competing tendencies depending on interactions among the components, filler size, surface properties, shape and aspect ratio, and nature of the polymeric matrix. Table 9.2 summarizes some of the trends in mechanical, physical, and rheological properties of the polymer nanocomposite as a function of the interaction among the components and the crystalline/amorphous nature of the matrix (Jordan et al., 2005).

9.3 Starch-based nanocomposites

As previously mentioned, starch is one of the most studied natural polymers with many potential applications in biodegradable packaging.

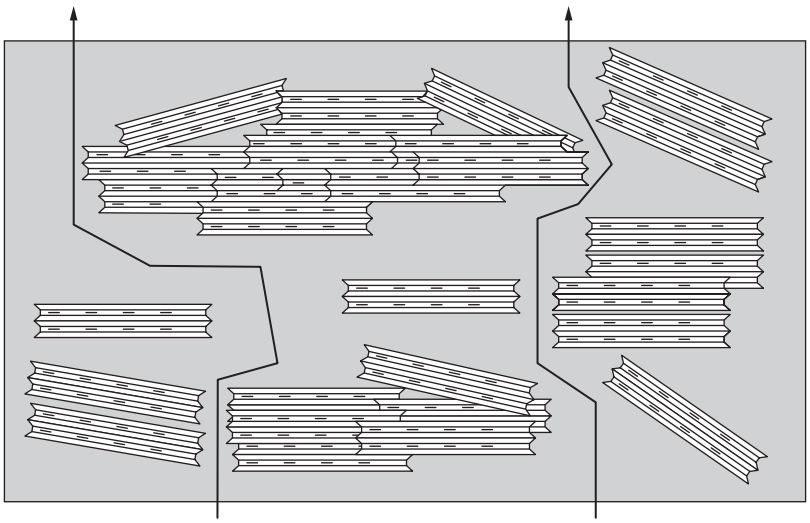

Figure 9.13 Possible diffusion paths of gas molecules in (a) a traditional composite and (b) exfoliated polymerclay nanocomposite. Note the increase in path length which ultimately results in decreased permeability.

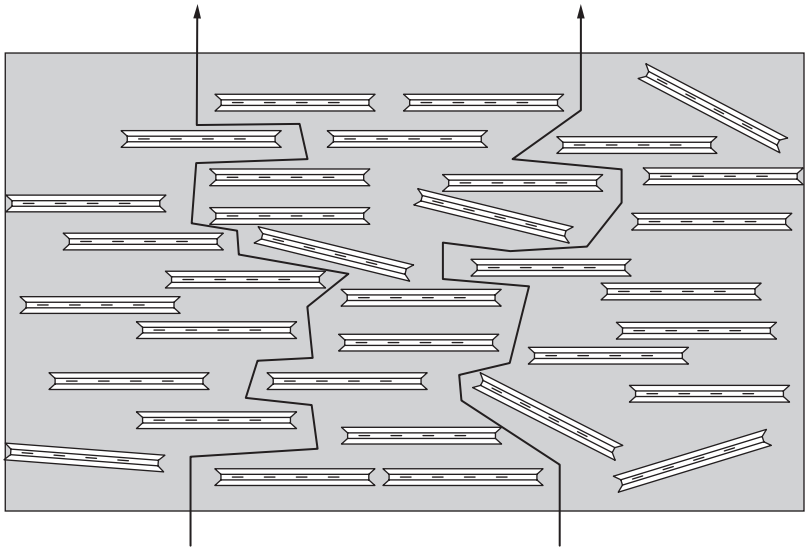

Figure 9.13 (Continued.)

However, due to major drawbacks associated with the use of starch-based materials, such as hydrophilic nature, poor processability, brittleness, and postprocessing crystallization, the number of commercially available starch-based products is still limited.

Several attempts to improve starch-based materials by traditional composite formulation resulted in materials with moderately improved properties, but having limited processability due to high viscosity. Recently, however, starch-based nanocomposites with the addition of low quantities of fillers have given rise to large-scale improvements in physical, mechanical, and barrier properties (Ruiz-Hitzky, Darder, and Aranda, 2005; Rhim and Ng, 2007; Yang, Wang, and Wang, 2007). This section discuss some examples of starch nanocomposites reinforced with inorganic clays or carbon nanotubes and organic (cellulosic) fillers.

9.3.1 Starch nanocomposites with inorganic reinforcements

Inorganic fillers when added to the starch matrix generally lead to composites with better overall properties. Filler surface properties can be modified by several techniques such as organophilization, silanization, alkylation, and surface etching, improving interface properties, processability, and particle dispersion, thereby producing nanocomposites with better properties.

Table 9.2 Summary of Polymer Nanocomposite Trends as a Function of the Nature (Crystalline or Amorphous) of the Matrix and Its Interaction with Nanostructured Fillers

	Polymer matrix		
Property	Crystalline	Amorphous	Interaction
Elastic Modulus	Increases w/volume fraction of filler Increases or no change w decrease in size	Increases w/volume fraction of filler Increases w decrease in size	Good
	Increases w/volume fraction of filler Increases w decrease in particle size Greater increase than for good interaction	Increases w/volume fraction of filler Increases w/decrease in particle size	Poor
Yield Stress/ Strain	Increases w/volume fraction of filler Increases w/decrease in particle size Decreases w/ addition of particles	N/A	Good
	Decreases w/ addition of particles	Decreases w/addition of particles	Poor
Ultimate Stress/Strain	Increases w/decrease in particle size No unified result for change in volume fraction	Nano > micro after 20 wt.%.	Good
	Lower than pure for small volume fraction	Decrease w addition of particles	Poor
Density/ Volume	Increases volume w/ decrease in size NA	Increases volume w/ decrease in size NA	Good Poor
Strain to Failure	Decreases w/ addition of particles	Decreases w/addition of particles Increases w decrease in size	Good
	Decreases w addition of particles	Increases w addition of particles	Poor
Glass Transition Temperature	Decreases w addition of particles	Increases w/addition of particles	Good

Table 9.2 Summary of Polymer Nanocomposite Trends as a Function of the Nature (Crystalline or Amorphous) of the Matrix and Its Interaction with Nanostructured Fillers (Continued)

	Polymer matrix		
Property	Crystalline	Amorphous	Interaction
	Decreases w/ addition of particles	Level until 0.5%, drops off level from 1–10 wt.	Poor
Crystallinity	No major effect	N/A	Good
	No major effect	N/A	Poor
Viscoelasticity	Increases w volume fraction of filler Increases w/decrease in particle size		Good
	N/A	Increases w/addition of particles; drop at 1 wt.% flowed by increase in this property	Poor

Source: Jordan et al. (2005).

Cao et al. (2007) studied the utilization of multiwalled carbon nanotubes (MWCNT) as filler reinforcement to improve the performance of thermoplastic starch. Details about TPS structure and applications are discussed in Chapter 6. Physical properties of TPS/MWCNT nanocomposites improved with an increase in MWCNT content. For 0 to 3.0 wt.%, the composites had an increase in tensile strength by 66% (from 2.85 to 4.73 MPa), Young's modulus by 89% (from 20.74 to 39.18 MPa), and T_g by 53% (from 16.5 to 25.3°C). The incorporation of MWCNT into the TPS matrix also led to a decrease in water uptake of up to 14%. This enhancement was attributed to a hydrogen bond between carbon nanotubes and TPS molecules. In a similar study, Ma, Yu, and Wang (2008) found only a modest increase in Young's modulus and tensile strength and a slight decrease in elongation at break as MWCNT content increased, with interfacial adhesion between the components of the nanocomposite.

Nanocomposites of glycerol-plasticized cornstarch and hydrated kaolin (10, 20, 30, 40, 50, and 60 w/w in parts of kaolin /100 parts of TPS) showed an increase in tensile properties as a consequence of strong bonding between kaolin and the matrix. For instance, nanocomposites filled with 50 wt.% of kaolin showed an increase in the tensile strength and Young's modulus, respectively, from 5 to 7.5 MPa and 120 to 290 MPa, whereas tensile strain at break decreased from 30 to 14 wt.%. Moreover, kaolin led to a reduction in water uptake, although thermal resistance—measured by

the onset of the thermal decomposition curves obtained by thermogravimetry—did not suffer any changes, as would be expected by the addition of much more thermally stable mineral fillers (Carvalho, Curvelo, and Agnelli, 2001).

In a similar study carried out by Chen and Evans (2005), nanocomposites of potato starch reinforced with four different types of clays (natural sodium montmorillonite, natural hectorite, a hectorite modified with 2-methyl, 2-hydrogenated tallow quaternary ammonium chloride, and kaolinite) obtained by melt processing and clay content ranging from 0 to 12 wt.%, showed that treated hectorite and kaolinite formed conventional composites, with little intercalation whereas natural smectic clays, montmorillonite, and hectorite with starch, readily formed intercalated nanocomposites. In all cases, clay increased the elastic modulus of TPS. For nanocomposites, montmorillonite generally provided a slight improvement in the modulus over untreated hectorite.

Characterization of nanocomposites obtained by injection molding of thermoplastic potato starch, natural montmorillonite modified with quaternary ammonium salt (Na^+MMT), and organically modified (MMT) with methyl bis-2-hydroxyethyl ammonium cations located in the silicate gallery and glycerol as plasticizer, showed that composites using unmodified clays had higher tensile strength, thermal stability, and better barrier properties to water vapor than the ones using organophilized MMT. It is likely that the hydrophilic TPS had better affinity to nonorganophilized clays which helped form intercalated nanostructures with the untreated clay (Figure 9.14). This result implied that higher interaction led to better dispersion of the filler in the matrix, resulting in better mechanical, thermal, and barrier properties (Park et al., 2003). Similar results were reported by Chiou et al. (2005), by incorporating montmorillonite clays (both hydrophilic and hydrophobic clays) into wheat, potato, corn, and waxy corn starches. Composites reinforced with hydrophilic MMT had improved mechanical properties due to greater intercalation in the gelatinized starch matrices. Composites from wheat and corn starches showed similar elastic modulus values during gelatinization, whereas both potato and waxy corn starch samples had elastic modulus values that decreased rapidly at higher temperatures. These results could be explained by the high swelling of potato starch, with "softer" granules leading to lower elastic modulus. On the other hand, results from waxy corn could be explained by the low amylose content of this particular starch. The lack of amylose would imply fewer physical cross-links between leached amylose, starch granule, and clay, leading to a lower elastic modulus.

Effects of plasticizers on nanocomposites have been widely studied (Pandey and Singh 2005; Qiao, Jiang, and Sun, 2005; Chiou et al., 2007). Nanocomposites with organically modified montmorillonite (OMMT) and acetylated starch (TPAS) plasticized with glycerol showed a better

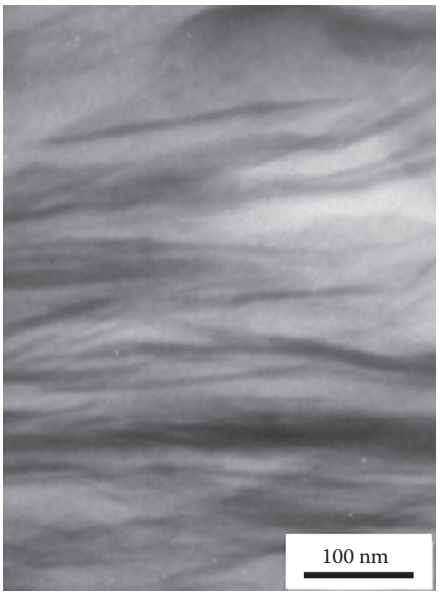

Figure 9.14 TEM micrographs of nanocomposites of montmorillonite and thermoplastic starch (MMT/TPS) with (a) 5% untreated MMT, (b) 10% untreated MMT, (c) 5% organophilized MMT, and (d) 10% organophilized MMT (Park et al., 2003). Note the differences between dispersions of natural (hydrophilic) and organophilized (hydrophobic) clays.

reinforcement than composites with montmorillonite (MMT), resulting in a decrease in the hydrophilic nature of acetylated starch. This improved the dispersion of OMMT in TPAS when compared with unmodified MMT (Qiao, Jiang, and Sun, 2005). These results corroborated those obtained by Park (2003), where better interaction is observed in unmodified MMT with unmodified starch because of their similar hydrophilic nature.

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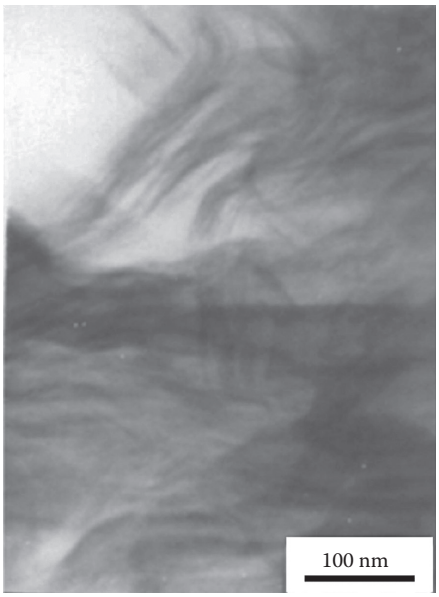
Studies of nanocomposites based on native corn starch (75 wt.%) with sodium montmorillonite with different addition sequences of glycerol (20 wt.%) as plasticizer and clay (5 wt.%) showed that the sequence of component-addition had a significant effect on the nature of composites formed and, accordingly, the final properties. In these experiments, solution dispersion was obtained by (i) gelatinization of starch followed by plasticization and addition of clay dispersion and boiling for 30 min; (ii) mixture of clay dispersion with starch in water and boiling for 30 min with constant vigorous stirring, followed by the addition of plasticizer; (iii) starch, clay dispersion, and glycerol mixed together and boiled for 30 min; and (iv) glycerol mixed with clay dispersion and stirred for 5 h at room temperature followed by addition of starch and heating for 30 min (Pandey and



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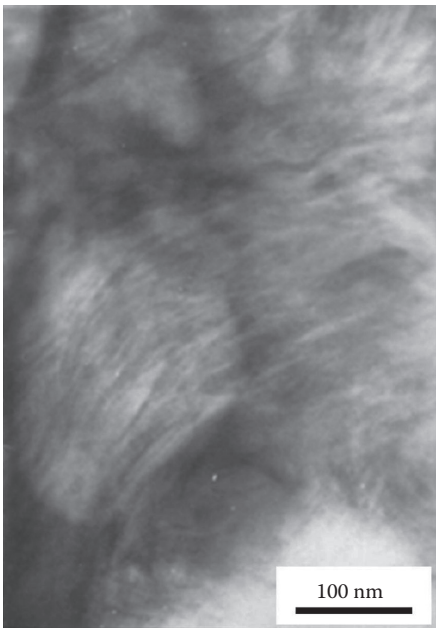

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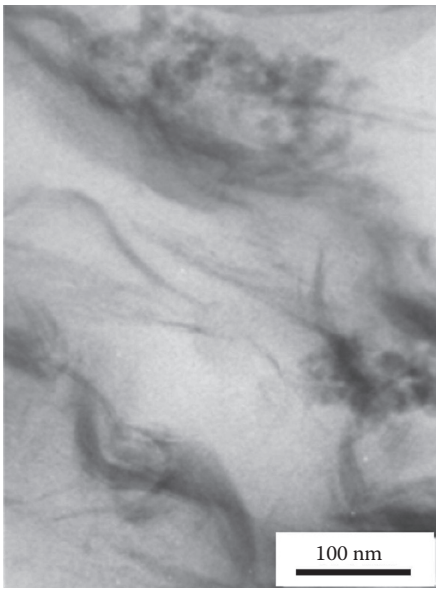


Figure 9.14 (Continued.)

Singh, 2005). The best mechanical properties can be obtained if plasticizer is added after mixing clay in the starch matrix.

Nanocomposite foams obtained by melt processing of TPS with urea as plasticizer and ammonium-treated montmorillonite (NH_4MMT) showed enhanced dispersion due to the NH_4MMT in the TPS, producing exfoliated TPS–clay nanocomposites (Chen, Chen, and Evans, 2005). Synergistic effects of the urea as plasticizer with ammonium enhanced clay dispersion and foaming. Nanocomposites of glycerol-plasticized starch reinforced with montmorillonite exhibited a significant enhancement in mechanical properties, showing significant improvement in Young's modulus with the addition of 5 wt.% of clay (Cyras et al., 2008).

9.3.2 Nanocomposites based on starch and organic reinforcements

Cellulose nanofibrils have been the most studied organic reinforcement in starch-based nanocomposites because of their remarkable mechanical properties. The affinity between starch and cellulose due to their structural similarity can be exploited, not only to enhance the mechanical properties of composites, but also to produce biodegradable materials (Avérous, 2004; Zhao, Torley, and Halley, 2008).

There are three significant differences between clay-reinforced and cellulose nanofibril-reinforced nanocomposites: (i) typical cellulosic

nanofibrils are long crystalline ''needles'' ranging in size from 10–20 nm in width and an average aspect ratio of 20–100, providing contrast to the lamellar structure of most clays; (ii) cellulose surfaces provide a greater potential for surface modification using well-established carbohydrate chemistry; and (iii) sources of cellulose microfibrils, including wood, straw, bagasse, bacteria, and sea animals (tunicates), are widely diverse, providing a wide range of potential nanoparticle properties (Orts et al., 2005). Moreover, cellulose nanofibrils are known to align in the magnetic and electrical fields (Sugiyama, Chanzy, and Maret, 1992; Yoshiharu et al., 1997), opening up the possibility to control the degree of orientation during processing. One example is the extrusion blow-molding of packaging films and electric or magnetic devices with orientation in film processing.

In plasticized materials, the mechanical properties are strongly related to moisture content and humidity conditions, and the addition of nanofibrils on nanocomposites can reduce water uptake. The distribution of compounds in the matrices also changes the mechanical properties. Anglès and Dufresne (2000, 2001), observing nanocomposites from glycerol-plasticized waxy maize starch and cellulose whiskers extracted from tunicates by casting and evaporation under vacuum, concluded that glycerol and water redistributed themselves within the matrix, diffusing toward the cellulose/amylopectin interface, and changing properties in a short time period. Mechanical properties of these nanocomposites are more dependent on plasticizer and moisture content than on the addition of whiskers. In this example, accumulation of plasticizer at the interface increased the ability of amylopectin chains to crystallize, leading to the formation of a transcrystalline zone around the whiskers. Such crystalline zones accounted for the lower water uptake of the nanocomposites with increasing filler content. A very low reinforcing effect was observed upon the addition of tunicin whiskers as a consequence of this plasticizer accumulation at the interfacial zone.

Nanocomposites from cellulose microfibrils gelatinized with potato starch (Dufresne and Vignon, 1998) reduce water sensitivity, increasing thermomechanical stability. Mechanical properties of nanocomposites based on glycerol-plasticized waxy maize starch and cellulose whiskers (Anglès and Dufresne, 2000, 2001; Dufresne, Dupeyre, and Vignon, 2000) show a relationship between plasticizer content and relative humidity conditions during storage. The reinforcing effect is more significant in plasticized starch due to the decrease in glass transition temperature of the matrix down to temperatures lower than room temperature.

Consequently, the reinforcing effect of cellulose nanofibrils in plasticized starch matrices plays a fundamental role in moisture, the amount and type of plasticizer, and the specific reinforcement (Mathew and Dufresne, 2002). Glycerol-plasticized nanocomposites are hampered by

accumulation of glycerol on the cellulose whisker surface giving rise to antiplasticization effects (Anglès and Dufresne, 2000; Dufresne, Dupeyre, and Vignon, 2000), and thus poor mechanical properties.

Nanocomposites from waxy maize starch plasticized with sorbitol and tunicin whiskers exhibited a single glass transition without any evidence of preferential migration of plasticizers toward the cellulose nor transcrystallization of amylopectin on the cellulose surface. Fractured surfaces of the composites showed uniform distribution of whiskers in the matrix for all the compositions (Figure 9.15). Glass transition temperature

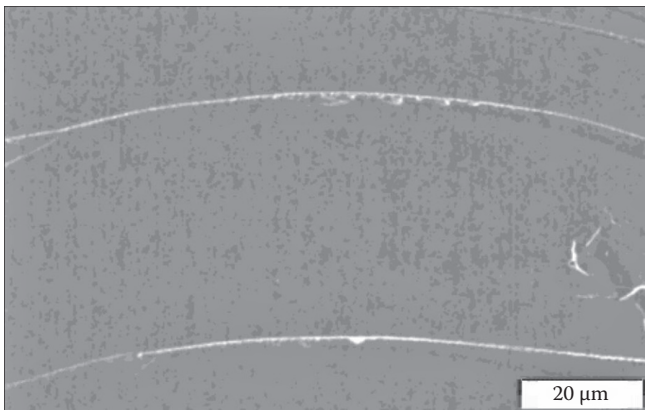
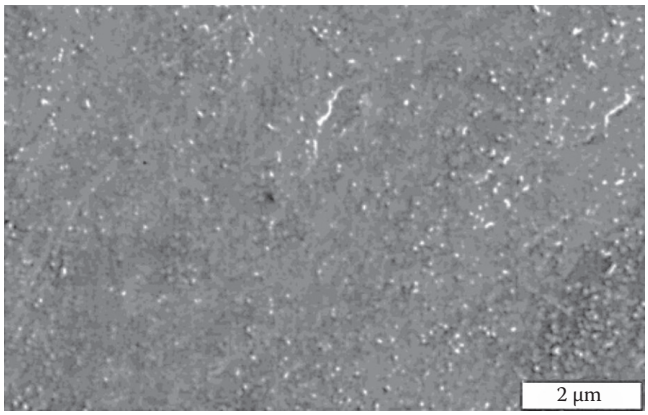


Figure 9.15 SEM micrographs of the fractured surfaces of (a) unfilled sorbitol plasticized starch matrix and related composites filled with (b) 5, (c) 15, and (d) 25 wt.% tunicin whiskers (white dots) (Mathew and Dufresne, 2002).



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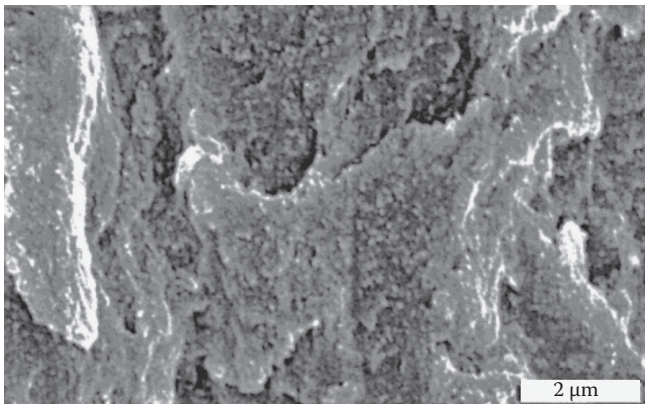

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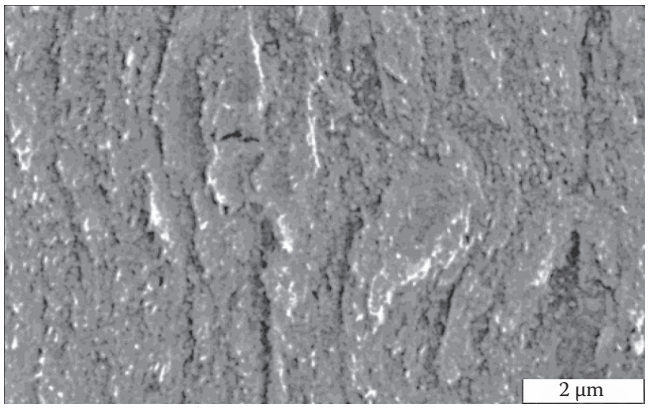

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of the plasticized amylopectin matrix increased up to a whisker content of ~10–15 wt.%, and a significant increase in crystallinity was also observed in the composites by increasing either moisture content or whiskers content, whereas water uptake of the composites remained roughly constant upon whisker addition (Mathew and Dufresne, 2002).

Addition of cellulose microfibrils extracted from cotton, softwood, or bacterial cellulose at low concentrations to wheat or potato starch blended with pectin has a significant effect on their mechanical properties (Orts et al., 2005). Young's modulus of wheat starch nanocomposites reinforced with cotton nanofibrils increased by 5 times with the addition of only 2.1 wt.% of nanofibrils (Table 9.3). In this example, the source of cellulose nanofibrils influences the mechanical properties of the composites;

Table 9.3 Young's Modulus (E) and Elongation at Maximum Load (ε_m) of Composites of Wheat Starch and Cellulose Nanofibrils Extracted from Cotton as a Function of Fiber Content

Nanofibrils (%)	E (Gpa, %)	ε_m (%)
0	1.39 (0)*	2.7 (0)
2.1	5.09 (266)	3.9 (44)
5	9.34 (572)	8.4 (210)
10.3	12.45 (796)	8.8 (226)

Source: Orts et al. (2005).

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composites reinforced with cotton and wood-derived microfibrils are indistinguishable, whereas composites reinforced with bacterial cellulose exhibit Young's modulus and elongation at maximum load significantly lower. On the other hand, the addition of 5 wt.% of cellulose nanofibrils to a 50–50 wt.% starch–pectin blend results in a decrease in mechanical properties. These results corroborate previous works on starch-based nanocomposites (Anglès and Dufresne, 2000, 2001; Dufresne, Dupeyre, and Vignon, 2000), where the addition of a third component can give rise to complex interactions between the components, often resulting in poorer mechanical properties.

In studies with glycerol-plasticized starch nanocomposites reinforced with cellulose nanofibrils from wheat straw, Alemdar and Sain (2008) found that the addition of 10 wt.% of cellulose nanofibrils improved the tensile strength and Young's modulus of the composites. Nanocomposites based on wheat starch plasticized with glycerol and reinforced with cellulose nanofibrils extracted from ramie fibers by acid hydrolysis (Lu, Weng, and Cao, 2006) showed improvement in water resistance, good dispersion, good adhesion between components, an increase in Young's modulus (from 56 to 480 MPa), and improvement in tensile strength (from 2.8 to 6.9 MPa) with increasing filler content from 0 to 40 wt.% (Figure 9.16).

Mechanical, dynamic mechanical, and thermal properties of nanocomposites of potato starch reinforced with either cellulose nanofibrils (CNF) or layered silicate (LS) plasticized with water and sorbitol with 5 wt.% of either CNF or synthetic hectorite, showed well-distributed reinforcements in the starch matrix (Kvien et al., 2007) with a significant improvement in tensile properties compared to the pure matrix (Table 9.4). Significant improvement of the storage modulus at elevated temperatures, on layered silicate nanocomposite, was observed, which could be expected taking into account the high thermal resistance and surface area of layered silicates.

Although these results provide interesting insights into composites reinforced with organic (CNF) and inorganic (LS) reinforcements, more work is required to understand the nature of starch-based nanocomposites,

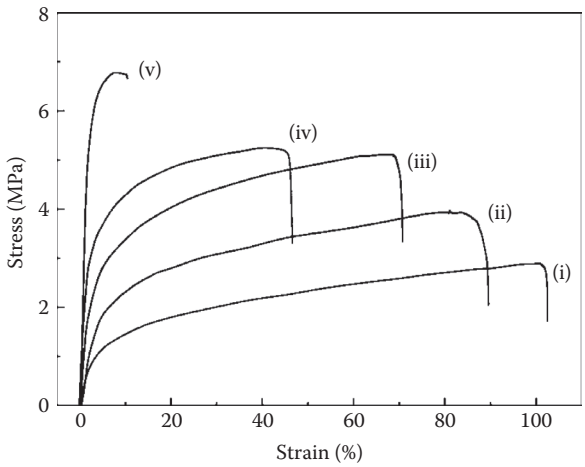


Figure 9.16 Stress versus strain curves for nanocomposites of starch reinforced with ramie nanofibrils: (i) glycerol-plasticized starch, and composites with (ii) 5, (iii) 10, (iv) 25, and (v) 40 wt.% of ramie nanofibrils (Lu, Weng, and Cao, 2006).

especially the fundamental surface interactions between matrix and filler. This is especially true given the differences between the various types of clays and nanofibers, because there is a wide range of clay materials and cellulose nanofibers. Moreover, nanocomposite properties are strongly dependent on the interfacial region/adhesion which also depends on particle size, superficial energy, surface modification, and so on.

Considering that there is no commercial process for large-scale isolation of cellulose nanofibrils, the applicability of highly loaded cellulose-based nanocomposites is presently limited. The production of plasticized-starch-based nanocomposites with improved properties can be feasible, implying that large-scale commercial isolation may be worth considering. Moreover, the average deformation of plasticized-starch nanocomposites is higher than for nonplasticized ones, thereby opening

Table 9.4 Tensile and Dynamic Mechanical Properties of Starch and Starch Nanocomposites Reinforced with Cellulose Nanofibrils (S-CNF) and Layered Silicate (S-LS)

Materials	E(MPa)[a]	σ_y(MPa)	ε_{max} (%)	E′ at 25°C (MPa)	E′ at 60°C (MPa)
Starch	370 ± 35	11.3 ± 1.0	25 ± 11	370 ± 97	69 ± 7
S-CNF	460 ± 10	13.7 ± 1.3	32 ± 10	502 ± 10	182 ± 20
S-LS	460 ± 45	12.5 ±1.3	31 ± 12	1,020 ± 20	286 ± 40

[a] E =Young's modulus; σ_y =yield strength; ε_{max} =elongation at break; E′=storage modulus.
Source: Kvien et al., 2007.

up the possibility of developing less brittle starch-based composites with potential applications in packaging materials.

9.3.3 Starch-based nanocomposite blends: Nanocomposites of starch in combination with other polymers

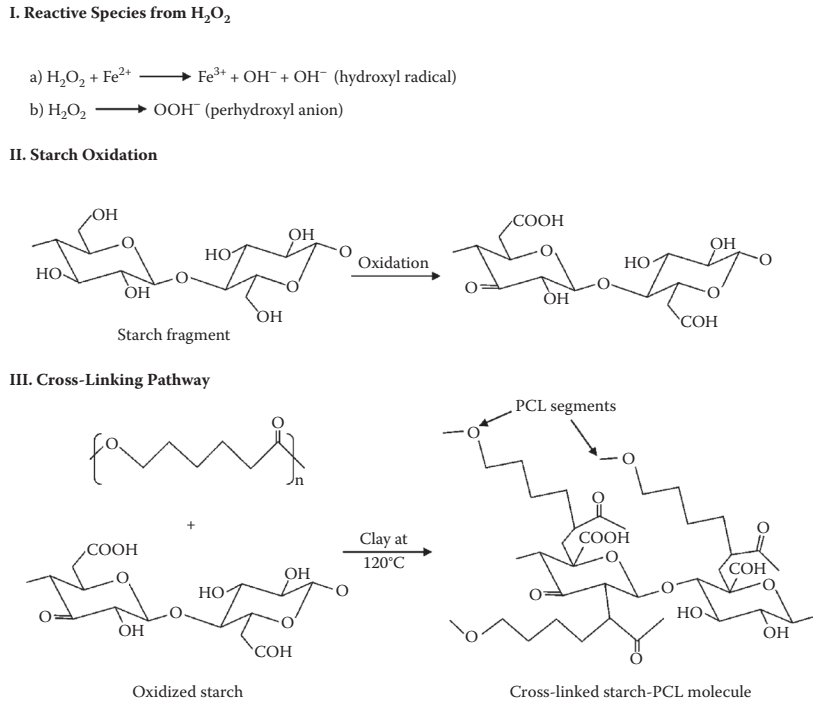
Blends of starch with natural and synthetic polymers have been extensively studied in order to overcome aging effects (i.e., recrystallization after processing), to impart better mechanical properties, and to reduce the hydrophilicity of starch (Chandra and Rustgi, 1998, Ray and Okamoto, 2003; Okamoto, 2005). The addition of natural biodegradable polymers, nevertheless, has gained more attention with the intent of producing fully biodegradable blends (Corradini et al., 2006).

Although this chapter is concerned mainly with starch nanocomposites as a matrix component where the addition of organic or inorganic nanoparticles improves mechanical or physical properties, it must be considered that starch blends with other polymers and nanostructure reinforcements—polymer–nanocomposite blends—can provide another viable approach toward improving even more starch-based nanocomposites.

Examples of nanocomposite blends with enhanced properties are increasingly available in the literature. For example, improved blends were obtained by polyethylene–octene elastomer, starch and montmorillonite (Liao and Wu, 2005); commercial starch/PCL blend and montmorillonite (Pérez et al., 2007); starch, poly(vinyl alcohol), and montmorillonite (Dean et al., 2008); and starch, poly(lactic acid), and montmorillonite (Lee, Chen, and Hanna, 2008).

Small amounts of MMT are also used to obtain biodegradable blends of starch and polyester with significantly improved tensile properties. Nanocomposite blends, with different starch–polyester ratios and organophilized with montmorillonite at 1.5 and 5 wt.%, prepared by twin screw extrusion showed that the addition of MMT improved both the processing and tensile properties when compared to original starch blends. The type of nanocomposite produced (intercalated or exfoliated) depended on the amount of clay added and the ratio of starch to polyester, which also influenced mechanical and thermal properties (McGlashan and Halley, 2003).

Nanocomposite blends are easier to process than the base blends using a film-blowing tower (McGlashan and Halley, 2003; Kalambur and Rizvi, 2005, 2006). Reactive extrusion to develop biodegradable starch–polycaprolactone (PCL) nanocomposite blends (using Fenton's reagent to oxidize starch and initiate cross-linking between oxidized starch and PCL) showed enhanced properties and improved interfacial adhesion between starch and PCL (Scheme 9.1). These biodegradable nanocomposite blends contained up to 40% starch, resulting in tough materials with



Scheme 9.1 Oxidation and cross-linking steps used during reactive extrusion to produce starch/polyester/montmorillonite nanocomposite blends with improved properties (Kalambur and Rizvi, 2005).

elongational properties comparable to that of 100% polyester (Kalambur and Rizvi, 2005, 2006)..

Less known is the ability to use starch nanocrystals as reinforcement in polymer matrices. Starch nanocrystals with dimensions of a few nanometers are formed from acid hydrolysis of starch granules. These starch crystals are mainly formed of crystalline amylose, because acid hydrolysis removes the amorphous domains comprised mostly of amylopectin (Dufresne, Cavaillé, and Helbert, 1996; Dufresne and Cavaillé, 1998).

Such starch nanocrystal-reinforced nanocomposites have been prepared with poly(β-hydroxyoctanoate) (Dubief, Cavaillé, and Helbert, 1999), natural rubber (Angellier et al., 2005; Angellier, Molina-Boisseau, and Dufresne, 2005b,2006), poly(styrene-co-butyl acrylate) (Angellier et al., 2005c), waxy maize starch (Angellier et al., 2006b), sorbitol-plasticized pullulan (Kristo and Biliaderis, 2007), and poly(vinyl alcohol) (Chen et al., 2008). Moreover, the possibility of surface modification by grafting can lead to reinforcements compatible with hydrophilic and hydrophobic matrices (Thielemans, Belgacem, and Dufresne, 2006; Labet, Thielemans,

and Dufresne, 2007). Considering a glycerol plasticized starch matrix, the increase of relaxation temperature can be associated with the glass–rubber transition of amylopectin-rich domains as increasing the starch nanocrystal content (Angellier et al., 2006b). The reduction in the molecular mobility of matrix amylopectin chains for filled materials is explained by the establishment of hydrogen bonding between both components. This increase of T_g led to a considerable slowing down of the retrogradation of the matrix, perhaps corresponding to a reduction in chain mobility (Chapter 5).

Oxygen and water permeability of natural rubber reinforced with waxy maize starch nanocrystals decreases continuously upon addition of starch nanoparticles (Angellier et al., 2005). It shows that the hydrophilic nature of starch nanocrystals does not increase the permeability of natural rubber to water vapor. Starch nanocrystals exhibit reduced oxygen diffusion when adding the filler and accounting for oxygen permeability. This phenomenon could be mainly due to the structural modification of the film and not to the decrease of the solubility of oxygen. Both observations were ascribed to the nanoscale platelet-like morphology of starch nanocrystals, which increases difficulty of the diffusion path in matrices. Conversely, no significant differences in water vapor permeability were observed in samples with sorbitol and pullulan plasticized starch for reinforced unfilled films compared to those containing up to 20 wt.% of nanocrystals (Kristo and Biliaderis, 2007). Moreover, the possibility of surface modification by grafting can lead to reinforcements compatible with hydrophilic and hydrophobic matrices (Angellier et al., 2005d). Alkenyl succinic anhydride (ASA), used for acylating the surface of starch nanocrystals, has been widely employed as a sizing agent in papermaking on pulp fibers in aqueous systems. The surface chemical modification of waxy maize starch nanocrystals with ASA is done by a toluene–(dimethylammo)pyridine system. Isocyanates, such as phenyl isocyanate (PI), can also be used to chemically modify the surface of starch nanocrystals (Angellier et al., 2005d). The lower polarity of the modified nanocrystals is demonstrated by their migration to the methylene chloride phase from the aqueous phase as can be seen in Figure 9.17.

A promising way of processing new nanocomposites consists of transforming starch nanocrystals into a co-continuous material through long-chain surface chemical modification. Nanoparticles are surface modified by grafting agents bearing a reactive endgroup and a long hydrophobic tail. The general objective of this surface chemical modification is to increase the apolar character of the nanoparticle. From this procedure, biocomposite materials based on fully renewable resources can then be processed by classical methods such as hot-pressing, extrusion, injection

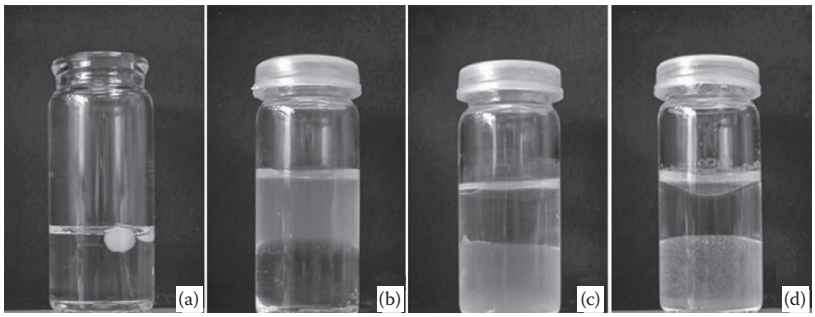


Figure 9.17 Wettability tests: (a) a drop of an aqueous suspension of waxy maize starch nanocrystals in dichloromethane, (b) migration of unmodified starch nanocrystals in distilled water, and migration of (c) alkenyl succinic anhydride(ASA)-modified and (d) Phenyl isocyanate(PI)-modified starch nanocrystals modified with (c) ASA and (d) PI in dichloromethane (Angellier et al., 2005d).

molding, or thermoforming from these. Very few reports in the literature have applied this very promising methodology.

Surface modifications on nanocrystals from chemical-modified starch with poly(ethylene glycol) methyl ether (PEGME) and stearic acid chloride obtained by grafting methods provide unique properties to the nanocrystals, especially their ability to avoid aggregation due to reduced hydrogen bonding and polar interactions between individual particles (Thielemans, Belgacem, and Dufresne, 2006).

Starch nanoparticles grafted with polytetrahydrofuran, polycaprolactone, and poly(ethylene glycol) monobutyl ether chains using toluene 2,4-diisocyanate as linking agent resulted in individualization of nanoparticles or the formation of a film and, as expected, the grafting efficiency decreased with the length of the polymeric chains (Labet, Thielemans, and Dufresne, 2007).

Long-chain surface modifications can yield some extraordinary possibilities. The surface modifications can act as binding sites for active agents in drug delivery systems or for leaching out toxins in purifying and treatment systems. These surface modifications may also be able to interdiffuse, upon heating, to form the polymer matrix phase. However, the covalent linkage between reinforcement and matrix will result in near-perfect stress transfer at the interface with exceptional mechanical properties of the composite as a result. The large surface area, inherent in nanoparticles, guarantees a large surface activity and a high grafting per unit mass of particles. Their small size also reduces the required chain length for interdiffusion to assure sufficient matrix phase cohesion.

9.3.4 Methods of improving filler/matrix interaction in starch-based nanocomposites

Carbohydrate chemistry is a well-established field with proven techniques to modify starch and cellulose functionality. Nanocomposites of formamide–ethanolamine-plasticized thermoplastic starch (FETPS) as the matrix and ethanolamine activated montmorillonite (EMMT) as the reinforcing phase can be obtained in two steps: (i) mixture of starch with formamide and ethanolamine followed by extrusion in a single screw extruder and pelletization; and (ii) mixture of formamide FETPS with 0–10 wt.% of added MMT previously activated with ethanolamine followed by extrusion. Intercalated FETPS and EMMT layers can improve interaction through modification, resulting in suitable mechanical properties (Figure 9.18), thermal stability, and water resistance (Huang et al., 2005).

Improvements in mechanical properties of biodegradable nanocomposites from thermoplastic cornstarch (TPCS) plasticized with urea and formamide and citric acid-activated montmorillonite can also be obtained by melt-intercalation (Huang, Yu, and Ma, 2006). Addition of chitosan nanoparticles into cassava starch–montmorillonite nanocomposites can increase surface hydrophobicity of films (Kampeerapappun et al., 2007). For example, at 5 wt.% montmorillonite, the contact angles of composite films increased from 62° to 72, 75, 78, and 83° with an increase in chitosan content from 0, 5, 10, 15, and 20 wt.%, respectively. Decrease in hydrophilicity of the nanocomposite films displayed a lower transmission rate of water vapor as can be seen in Figure 9.19.

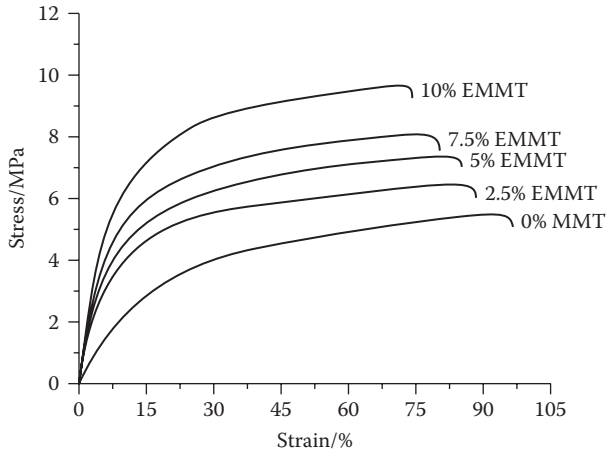


Figure 9.18 Effect of the addition of ethanolamine-activated montmorillonite (EMMT) on stress–strain curves of nanocomposites with thermoplastic starch plasticized with formamide and ethanolamine (FETPS) (Huang et al., 2005).

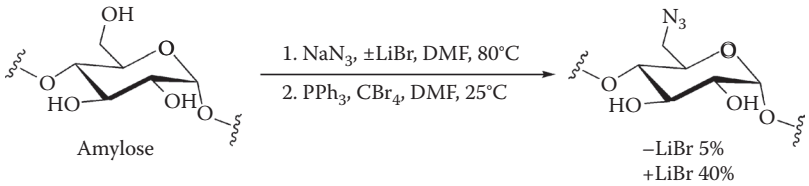
Figure 9.19 Starch/MMT/chitosan nanocomposite film with improved hydrophobic nature (Kampeerapappun et al., 2007).

Nanocomposites of starch and cellulose nanofibrils modifed by azide cross-linking (Orts et al. 2007) improved the compatibility between both the polymer matrix or the cellulose nanofibrils. Azide derivatives of different starches were synthesized as depicted in Scheme 9.2. ^{13}C NMR and FT-IR spectra confirmed the azide derivative can be selectively cross-linked with heat or application of UV light. Nanofibrils derived from sulfuric acid hydrolysis of cotton cellulose added to extruded wheat starch gels at concentrations of 2–10 wt.% had a significant effect on mechanical properties of the nanocomposites, mainly on Young's modulus and elongation at maximum load increased (Figure 9.20).

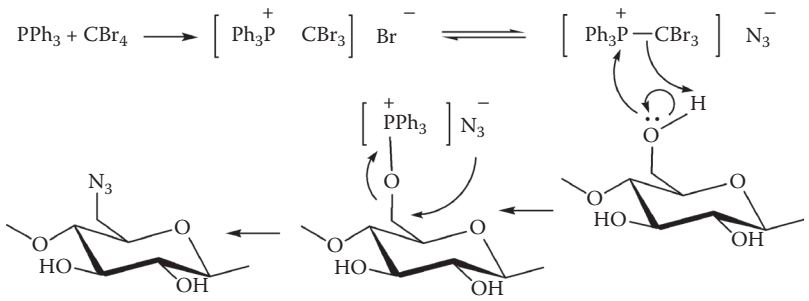
9.4 Final remarks

Efforts to develop new materials from environmentally friendly, biodegradable, and renewable resources have grown in recent years. Among these new materials, starch is one of the most studied and promising raw materials for the production of biodegradable plastics because it is a widely abundant and relatively low-cost natural polysaccharide obtained from a great variety of crops. Moreover, its use in the plastics industry has been considered a viable approach to reduce surplus agricultural products and develop biodegradable materials with a more favorable carbon footprint than petroleum-derived feedstocks.

The advent of new techniques for fabrication and characterization of materials on the nanoscale has made possible the production of starch-based nanocomposites with enhanced mechanical and physical properties,



Scheme 9.2 Proposed azidation reactions for (a) starch: synthesis of 6-azido-6-deoxyamylose; and (b) cellulose: synthesis of 6-azido-6-deoxycellulose (Orts et al., 2007).



Scheme 9.2 (Continued.)

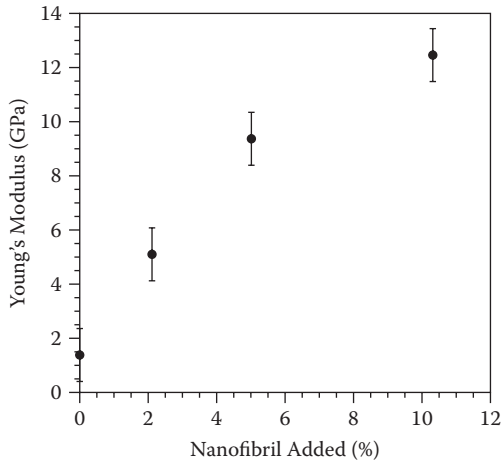


Figure 9.20 Effect of nanofibril concentration on (a) Young's modulus (GPa) and (b) maximum elongation to break (%) of wheat starch thermoplastic strings reinforced with cotton-derived nanofibrils (Orts et al., 2007).

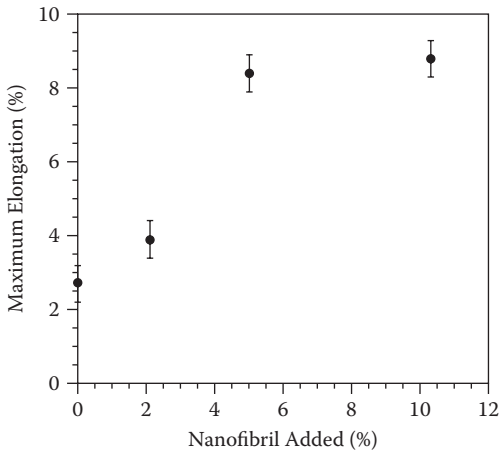


Figure 9.20 (Continued.)

and greatly improved their optical transparency when compared to traditional composites. These properties can be relatively easily tailored to a particular application by addition of nanostructured fillers or reinforcements such as clays, cellulose nanofibrils, and carbon nanotubes.

Much has been done in order to improve composite properties by understanding the nature of individual components, their mechanisms of interaction, reinforcement dispersibility, processability, hydrophilicity, costs, and other economical and environmental aspects. However, despite all efforts toward better starch-based nanocomposites, effectiveness of interactions at the interfacial region between reinforcements and starch matrix durability in outdoor applications and moisture sensitivity continue to be a challenge that still limits the large-scale production, use, and commercialization of biodegradable nanocomposites based on starch.

In summary, the technology reviewed here shows a growing effort to produce starch-based nanocomposites with improved properties and to scale up nanocomposite production and applications in many sectors of the plastics industry. It shows how biodegradable materials can be exploited to produce composites with tailored properties by the correct choice of components, their relative proportions, and methods of modification.

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