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Starch Plastic Packaging and Agriculture Applications

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1 INTRODUCTION

Paper constitutes the most important material in the United States for packaging and containers largely because of its low cost and wide availability (WPO, 2008). It is also perceived as a sustainable material because it is derived from plants and is recycled at a very high percentage (62%) (EPA, 2010). Plastic ranks as the second most used packaging material in the United States. Plastics can provide transparency, greater moisture protection, and various mechanical properties that are superior to paper packaging. Consequently, some types of plastic packaging continue to grow faster than other packaging materials (WPO, 2008). In contrast to paper, only 7% of plastic generated as waste is recycled. This explains why more plastics ultimately end up in landfills than paper or any other packaging material (EPA, 2010). Plastic processors worldwide are becoming increasingly aware that environmentally sustainable packaging has become mainstream. It can no longer be considered only a niche market that can be ignored or given token attention. Informed consumers are demanding sustainable packaging; state and local governments are mandating it; and now, even the largest retailers are building it into the foundation of their marketing strategies (Deligio, 2009; Wood, 2010).

Packaging and containers constitute a nearly \$500 billion global market (WPO, 2008) and make up the largest sector (29.5%) of municipal solid waste (MSW) in the United States (EPA, 2010). Plastic packaging-container

sales alone account for \$130 billion worldwide (WPO, 2008). The development of renewable/sustainable plastics is perceived by the industry as a hedge against the prospect that traditional plastics will be much more costly in the future due to dramatically higher petroleum prices. The sustainability movement is further seen as a positive development for plastic processors since it will drive further innovation and a new generation of materials with properties more comparable to commodity plastics (Wood, 2010).

Until recently, the biopolymers most often discussed in reference to sustainability were starch-based polymers, cellulose, polylactic acid (PLA), and polyhydroxyalkanoate (PHA). The most recent trends have been to broaden the spectrum of sustainability to include materials and practices that move a step closer toward sustainability by simply increasing renewable content or decreasing the overall weight of traditional plastics used. Today's sustainable plastics are not necessarily biodegradable and even include polyolefins made from renewable feedstocks (Dartee, 2010). Broadening the scope of sustainability has helped balance the need for providing affordable packaging today while stimulating investment in research to develop more sustainable alternatives for tomorrow (Dartee, 2010).

Industry announcements regarding new and innovative plastic products occur on an ever more frequent basis. Coca-Cola recently announced they will begin utilizing polyethylene terephthalate (PET) bottles containing 30% renewable content from sugarcane-derived ethylene glycol. They also announced plans to convert all their plastic packaging to the new material by 2020 (Anonymous, 2011c; Whistler & Daniel, 1984). Heinz will use the same material to make 120 million bottles for their ketchup products this year. PepsiCo claims to have developed the world's first totally biobased PET bottle. It is made from biomass including switchgrass, pine bark, and corn husks. Pilot-scale production began in 2012 (Anonymous, 2011g). Other interesting new materials entering the market include a new family of resins (Panacea) containing 10-40% finely ground soy-based protein and an injection mold-grade cellulose-based resin. The cellulose-based resin is being used to make the first biodegradable tubes for toothpaste (Anonymous, 2011a, 2011b, 2011d).

Much of the focus on renewable and sustainable plastics involves the use of starch either as a feedstock or as a component. Although a stable food product, starch is also increasingly used for industrial products. Industrial products in the United States that utilize starch have grown from 13 million metric tons (MMT) in 1975 to over 160 MMT today (USDA, 2010). Starch is inexpensive, widely available, and one of the most abundant biomass products in nature (Schwartz & Whistler, 2009; Whistler, 1984). It is produced in many different plant organs including roots, leaves, seeds, and stems. Commercial starches worldwide are

extracted primarily from cereal grains such as corn (82%) and wheat (8%) and tuber crops such as potato (5%) and cassava (5%) (Le Corre, Bras, & Dufresne, 2010). Millions of metric tons of starch are used annually for making nonfood products including paper sizing, adhesives, gypsum wallboard, and sizing for textiles (USDA, 2010; Whistler, 1984). Much of the recent growth in industrial use of starch can be attributed to the production of ethanol (USDA, 2010).

The hydrophilic nature of starch and its tendency to embrittle with age do not make it very suitable as a replacement for plastics. In spite of its shortcomings, starch continues to remain a viable alternative to petroleum-based plastics primarily because of its low cost and abundance and because it is a renewable material that degrades readily in composting conditions and in many landscape and aquatic environments (Law et al., 2010; Thompson et al., 2004). This chapter discusses starch as a material and addresses some of the global concerns of plastics in the environment, the early development of starch-based plastics, its properties and limitations as a material, and some of the promising technologies entering the marketplace.

2 STARCH PROPERTIES

A considerable volume of literature has been published on the properties and chemistry of starches from various sources (Schwartz & Whistler, 2009; Whistler, Bemiller, & Paschall, 1984). Starch is the principal carbohydrate for energy storage in plants and one of the most abundant plant polymers (Whistler, 1984). In photosynthetic plant organs, a fraction of the carbon fixed in plant chloroplasts is retained as starch and used at night during the respiration process (Zeeman, Kossmann, & Smith, 2010). In nonphotosynthetic organs such as roots, tubers, and seeds, sucrose is converted to starch in specialized plastids known as amyloplasts (Tyson & Ap Rees, 1988; Zeeman et al., 2010). Plant starches synthesized in amyloplasts are formed into cold water-insoluble granules (Figure 15.1) that range from a few micrometers to more than 100 μm depending on the plant source (French, 1984; Tyson & Ap Rees, 1988). Starch can be easily extracted from a variety of starch-rich crops and dried to form a white powder. Its commercial production dates back to the middle ages and has advanced to become the efficient global industry it is today (Schwartz & Whistler, 2009).

Starch is composed of two polymers consisting of D-glucose repeating units, amylose and amylopectin. Amylose is essentially a linear polymer consisting of $\alpha[1 \rightarrow 4]$ -linked glucose moieties, while amylopectin is a much larger, highly branched molecule with $\alpha[1 \rightarrow 6]$ branching linkages. The amylose-amylopectin ratio within a starch granule varies with the

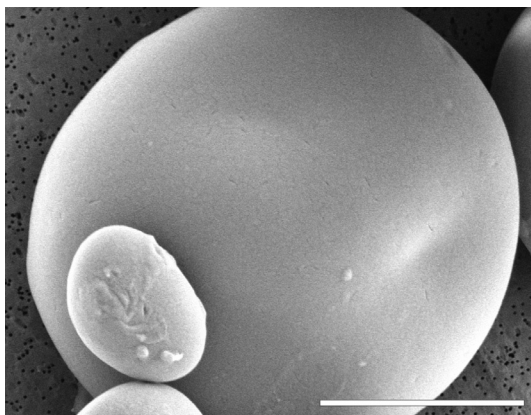


FIGURE 15.1 Scanning electron micrograph of native wheat starch granules. The granules have a bimodal size distribution consisting of small- and medium-size granules (scale bar = 10 μm) (Glenn et al., 2008).

botanical origin of the starch and can vary due to weather and growing conditions (Hoover, 2001; Morrison, Milligan, & Azudin, 1984). Normal wheat starch has 18-30% amylose content with the remainder being amylopectin (Singh, Singh, Kaur, Singh Sodhi, & Singh Gill, 2003). Starch from normal potato genotypes contains 23-31% amylose. There are now waxy genotypes for most of the major starch-rich crops, including potato, wheat, corn, and rice, that are comprised almost entirely of amylopectin (Buleon, Colonna, Planchot, & Ball, 1998; Hermansson & Svegmarm, 1996). There are also genotypes with much higher than normal amylose content (Shi, Capitani, Trzasko, & Jeffcoat, 1998). These genotypes provide starches with properties markedly different from starches of normal genotypes (Shi et al., 1998).

Amylose is primarily a linear polymer composed of 500-20,000 (1 \rightarrow 4) linked α -D-glucopyranosyl units (Shannon & Garwood, 1984; Whistler & Daniel, 1984). Amylose forms into a helical structure with a hydrophobic core due to the arrangement of hydrogen groups exposed in the interior of the helix (Almeida et al., 2010; Buleon et al., 1998). Amylose is able to form complexes with fatty acids, iodine, and alcohols (Almeida et al., 2010). In the case of fatty acids, the aliphatic part of the molecule is believed to reside inside, while the polar group lies outside of the helical structure (Buleon et al., 1998). There is some evidence that within the starch granule, amylose is localized in the amorphous regions (Shamekh, Forssell, Suortti, Autio, & Poutanen, 1999). However, others have found it difficult to assign a specific location for amylose and suggest that it may be randomly dispersed in the granule matrix (Atkin, Abeysekera, Cheng, & Robards, 1998; Oates, 1997). Amylose is a mobile molecule that leaches out of the granule when hydrated (Fannon & Bemiller, 1993).

Amylopectin is one of the largest known natural polymers ($\sim 10^7$ - 10^9 Da) (Buleon et al., 1998; Singh et al., 2003) made up of α -(1 \rightarrow 4) D-glucopyranose chains with α -(1 \rightarrow 6) branches (Shannon & Garwood, 1984; Whistler & Daniel, 1984). About 5% of the glycosidic linkages are α -(1 \rightarrow 6) branches. X-ray diffractometry has been used to study the crystallinity of starch granules (Hoover, 2001). Diffraction patterns that are characteristic of different plant types have been defined. Cereal starches have an A-type X-ray pattern, tuber starches generally have a B-type pattern, and legumes have mixed pattern defined as C type (Hoover, 2001; Sarko & Wu, 1978; Singh et al., 2003). Starch granules contain between 15% and 45% of crystallite material (Blanshard, 1987). Amylopectin provides the bulk of the matrix for the starch granule and it contains the crystalline fraction of the granule (Oates, 1997). The branches of the amylopectin form double helices and are arranged in crystalline domains (Sarko & Wu, 1978). The crystalline regions are believed to be hard and brittle but may be interspersed with amorphous regions of amylopectin that are assumed to have greater mobility and behave more like a rubbery polymer (Morgan, Furneaux, & Larsen, 1995). Some large starch granules have onion-like layers, suggesting that they grow by the deposition of layer upon layer (Martin & Smith, 1995) of carbohydrate. However, this structure has not been observed in small starch granules from rice or barley (Oates, 1997).

Starch granules have a relatively smooth surface (Figure 15.1) that is impervious to large molecules due to the tight packing of amylopectin molecules (French, 1984). However, the granules are hydrophilic and begin to hydrate and swell when heated in water (Fannon & Bemiller, 1993; Hermansson & Svegmarm, 1996; Richardson, Kidman, Langton, & Hermansson, 2004). The behavior of starch when heated in water reveals the complex nature of the granule structure. During heating, the starch chains within the granule become more mobile as hydrogen bonding between adjacent glucose units is disrupted and water penetrates the matrix (Rodriguez-Gonzalez, Ramsay, & Favis, 2003). The increase in chain mobility allows the granule to become more elastic and to swell. At the same time, amylose and small amounts of amylopectin begin to leach from the granule matrix into the aqueous medium (Fannon & Bemiller, 1993; Ghiasi, Hosenev, & Varriano-Marston, 1982; Oates, 1997; Shamekh et al., 1999). Granule hydration may be further accelerated by the presence of small pores that reportedly span from the granule surface to the core region (Baldwin, Adler, Davies, & Melia, 1994; Huber & Bemiller, 2000; Kim & Huber, 2008).

Micrographs of starch granules from heated aqueous slurries reveal that starch granules do not simply dissolve in an "outside to inside" fashion as might be expected. Instead, they appear to dissolve from the "inside out" (Atkin et al., 1998; Glenn et al., 2008; Li, Vasanthan, Hoover, & Rossnagel, 2004) (Figure 15.2a). This pattern of starch dissolution

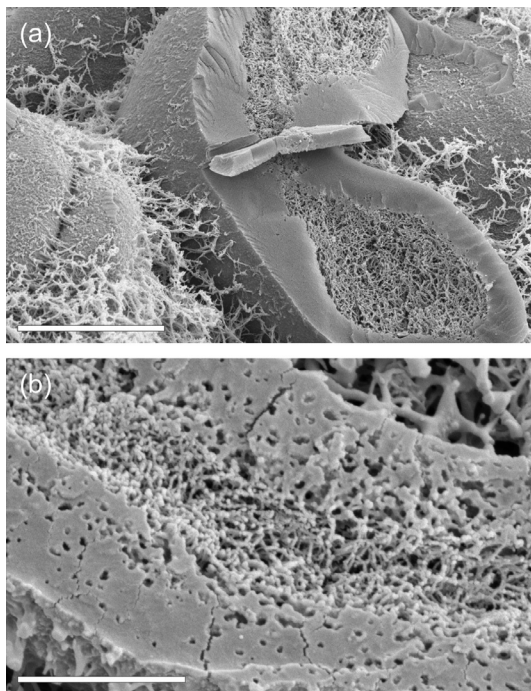


FIGURE 15.2 Scanning electron micrographs of wheat starch granules after heating to 95 °C for (a) 1 min and (b) 60 min. Note the starch granule appears to dissolve from the inside out (a). The granule remnant or envelope remains insoluble after extensive heating although it does become more porous (b) (scale bars = 5 and 2 μm , respectively) (Glenn et al., 2008).

may be due more to the insolubility of the granule surface and underlying material that has been termed collectively as the starch granule remnant or envelope. The starch granule envelope is believed to be comprised mostly of amylopectin. Water may penetrate the interior of the granule through pores or by simply penetrating the hydrated granule surface by diffusion. Swelling of the granule as it hydrates expands the volume of the granule interior that becomes filled with water-solubilized starch material (Figure 15.2a).

Aqueous slurries of starch form a viscous paste when heated. The viscosity of starch pastes increases as granules swell and hydrate. The hydration and solubilization of the granule interior creates an internal pressure that can eventually cause the envelope to rupture and release its contents into the continuous phase. Starch pastes typically increase to a peak viscosity and then drop in viscosity, presumably due to the rupture of the granule envelope (Glenn et al., 2008; Hoseney & Atwell, 1977). The granule envelopes that remain after the granules have ruptured are called

“ghosts.” The ghosts remain difficult to solubilize with only mild shear conditions, even after extensive cooking (Glenn et al., 2008; Hosoney & Atwell, 1977). The ghosts become more porous after extensive cooking due to extraction of the soluble fraction from the matrix (Figure 15.2b).

Gelatinization is the general term used to describe the breakdown and dissolution of the starch granule in aqueous media. The crystallinity of the granule is progressively destroyed as hydrogen bonding between adjacent glucose units is disrupted (Rodriguez-Gonzalez et al., 2003). Starch is considered fully gelatinized when the starch granules have been dissolved to the point that only starch ghosts remain in the solution (Atkin et al., 1998; Rockland, Jones, & Hahn, 1977). When a hot gelatinous starch melt is cooled, the dispersed amylose molecules reassociate in a process known as retrogradation and form elastic gels (Blaszczak, Fornal, Valverde, & Garrido, 2005; Fannon & Bemiller, 1993; Richardson et al., 2004). Starch gels consist of a three-dimensional matrix of a continuous phase of amylose molecules containing uniformly dispersed ghosts that act as filler (Figure 15.3a and b) (Morris, 1990). The heterogeneous nature of starch pastes may not be a concern in many food and industrial applications and can, in fact, even be beneficial. However, other applications may require a more homogenous melt that can be achieved only by a more complete destructuring of the starch granule using more severe processing conditions (Wittwer & Tomka, 1987). For instance, complete dissolution of the starch granule structure has been achieved in high-amylose cornstarch by processing at elevated temperatures and pressure using a batch reactor (Glenn et al., 2008). Such a destructurized starch matrix would appear as that in Figure 15.3c.

3 PLASTICS AND THE ENVIRONMENT

Much of the concern over the use of plastics today is centered around its impact on the environment. These concerns include sustainability. Nearly 6% of the world's crude oil production is used for making approximately 245 MMT of plastics globally on an annual basis (Johansson, 2009) (Table 15.1). Since plastics are mostly derived from fossil fuel feedstocks, all of the concern over the heavy dependence of the world on nonrenewable resources and the environmental impact of extracting fossil fuels applies to plastics. But while the concern with burning fossil fuels is primarily due to air pollution and the increasing concentration of greenhouse gases in the atmosphere, the challenge with plastics is the sheer volume of solid waste produced and the persistence of plastic pollution in the landscape and marine environment.

Dumping waste into oceans was common before measures were taken to curtail the practice. Still, worldwide, a significant amount of plastic

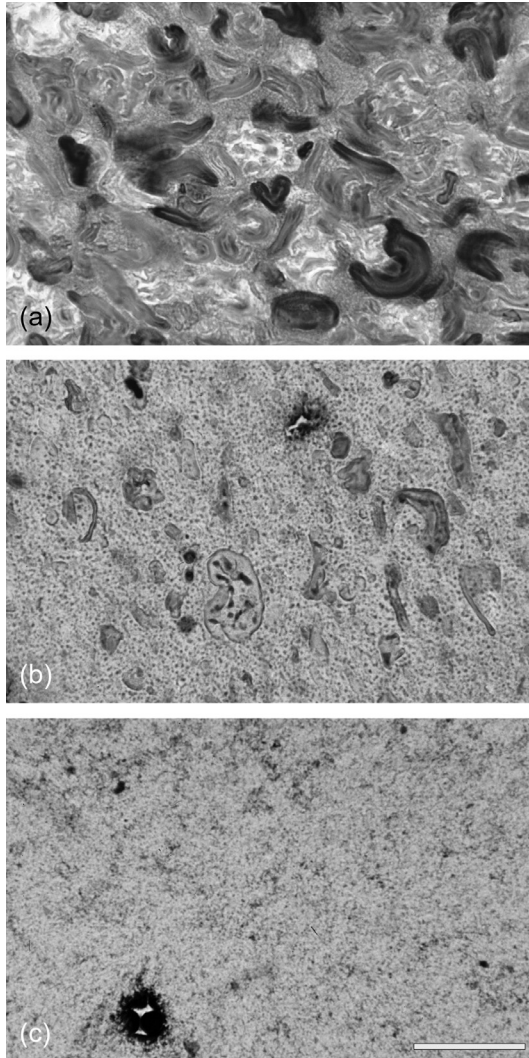


FIGURE 15.3 Light micrograph sections of starch gels stained with iodine potassium iodide. The blue is amylose and pink is amylopectin. Wheat (a), normal amylose corn (b), and high-amylose corn (c) starches (scale bar = 50 μm).

waste is believed to wash out to sea from storm drains, rivers, and waste water (Walker, Reid, Arnould, & Croxall, 1997). China, one of the world's largest plastic producers, noted that the largest source of its marine pollution was from discharging wastewater to sea. Nearly half of China's wastewater is currently dumped at sea (Zou, 2009). This practice worldwide continues to be a concern as a major source of marine pollution.

TABLE 15.1 Plastic Production in the World and United States and Municipal Solid Plastic Waste Generated in the United States in 2010 (Values in Million Metric Tons, MMT)

| | |
|--|-------------------|
| Global production of plastics (2009) | 245 ^a |
| U.S. production of plastics (2010) | 46.7 ^b |
| U.S. plastic waste generated—total | 29.8 ^c |
| U.S. plastic package waste generated | 12.5 ^c |
| U.S. nondurable plastic waste (plates, cups, etc.) | 6.65 ^c |
| U.S. durable plastic waste generated | 10.7 ^c |

^a Johansson (2009).

^b ACC (2011).

^c ACC (2011), EPA (2010).

Marine pollution can also be traced to ships and other marine businesses (Zou, 2009). Unlike many other pollutants, plastics have low density and tend to float at or near the water surface where they persist for many years (Boerger, Lattin, Moore, & Moore, 2010). The “Great Pacific Garbage Patch” also known as the North Pacific Central Gyre (NPCG) is an area about the size of the state of Texas where ocean currents gather floating waste (Boerger et al., 2010; Kaiser, 2010). The NPCG is described as the world’s largest garbage dump consisting of roughly 80% plastic (Kaiser, 2010; Walker et al., 1997). Since its discovery in 1972, other gyres have been discovered in other oceans that also have a higher than normal content of plastic debris (Kaiser, 2010).

The long-term impact of plastic debris in the marine environment is of concern since birds, mammals, and fish may become entangled in plastic debris or ingest plastic particles (Boerger et al., 2010). There is now evidence that exposure from ultraviolet radiation and mechanical agitation from the movement of waves help slowly disintegrate plastics over time into microscopic debris that floats near the water surface (Kaiser, 2010). Microscopic debris can absorb chemical toxins from seawater, thus presenting an even greater threat to marine life that ingest the plastic debris (Kaiser, 2010). Recent studies have found microscopic plastic debris in plankton, thus raising fears of the accumulation of toxins and plastic debris in sea life that ultimately thrive on plankton (Kaiser, 2010; Zhang, Zhang, Feng, & Yang, 2010). The source of plastics includes both user-generated plastics as MSW and industrial waste that includes nurdles or plastic pellets used as a feedstock for plastic processing (Provencher, Gaston, Mallory, O’hara, & Gilchrist, 2010). It is believed most plastic pellets come from spills on land that are washed into waterways and eventually released into the ocean (Weiss, 2006). Because seabirds confuse the pellets for food, seabird populations are particularly

susceptible to industrial plastics (Provencher et al., 2010; Weiss, 2006). The long-term impact of marine pollution from plastics is uncertain, but the issue is garnering more attention and is changing the way waste is being handled (Kaiser, 2010; Zhang et al., 2010).

4 PLASTIC USES

4.1 Agricultural Uses

4.1.1 Films

In Europe alone, an estimated 2-3 million tons of plastics is used each year in agricultural applications (Kyrikou & Briassoulis, 2007). Polyethylene films are used extensively to increase yields, extend growing seasons, reduce the usage of pesticides and herbicides, and help conserve water. About half of the agricultural plastic is film used for agricultural mulches, greenhouses, silage covers, tunnels over rows of crops, and hotboxes (Kyrikou & Briassoulis, 2007). Ideally, these films could be made of renewable polymers. Films made of starch blends were some of the first films containing renewable content tested as agricultural mulch (Otey, Mark, Mehlretter, & Russell, 1974). More recently, PLA, a polymer derived from starch fermentation, was blended with fiber to make composite films for mulch applications (Finkenstadt & Tisserat, 2010). In spite of the research efforts, petroleum-based polyolefin films continue to be the dominant material used for agricultural applications. The environmental impact of plastic films used for agricultural mulches should account for the beneficial impact of mulches including a reduction in the use of pesticides, herbicides, water, and energy. The films may be serviceable during a single growing season or for multiple years depending on the crop and the cultural practices employed (Finkenstadt & Tisserat, 2010).

4.1.2 Specialized Uses

Plastics have found uses in various niche applications in agriculture. These applications range from binders for feeds to soil amendments. One interesting application for plastics is in making controlled-release devices. Many different types of controlled-release systems have been developed for agricultural applications including hollow fiber membranes, capillaries, and polymer devices that swell and absorb the active agent (Funes, Zerba, & González Audino, 2009; Teixeira, Miller, Epstein, & GUT, 2010). These devices tend to be nonbiodegradable and may require that the spent devices be recovered, thus incurring additional labor expense.

Starch-based controlled-release devices have been made for controlling parasitic mites in honeybee colonies (Glenn et al., 2006). Reservoir-type

devices were made by using a solvent displacement process to form starch gels containing an active ingredient, 2-heptanone (Erickson, Degrandi-Hoffman, Becker, Whitson, & Deeby, 2005). A heat-sealable food-grade vapor barrier film was used to envelope the starch gel and control the vapor transmission rate. The controlled-release devices were made of degradable food-grade materials that obviated the need to remove spent devices from honeybee colonies.

Starch-based microspheres ($<10\ \mu\text{m}$) were also developed for mite control in honeybee colonies for delivery of less volatile natural control agents. The microspheres were loaded with 25% active ingredient yet remained a free-flowing powder. The microspheres were designed to deliver active ingredients to individual honeybees by adhering to the hairs on their thoraxes in a manner similar to pollen grains (Glenn et al., 2010).

4.2 Consumer and Industrial Products

Many of the plastic products that enter the marketplace eventually find their way to an MSW facility. The U.S. Environmental Protection Agency has kept MSW data for several decades on materials recycled or disposed of as MSW. Plastic waste began to appear in the MSW in 1970 and has grown steadily to total approximately 30 MMT (Figure 15.4). Disposal

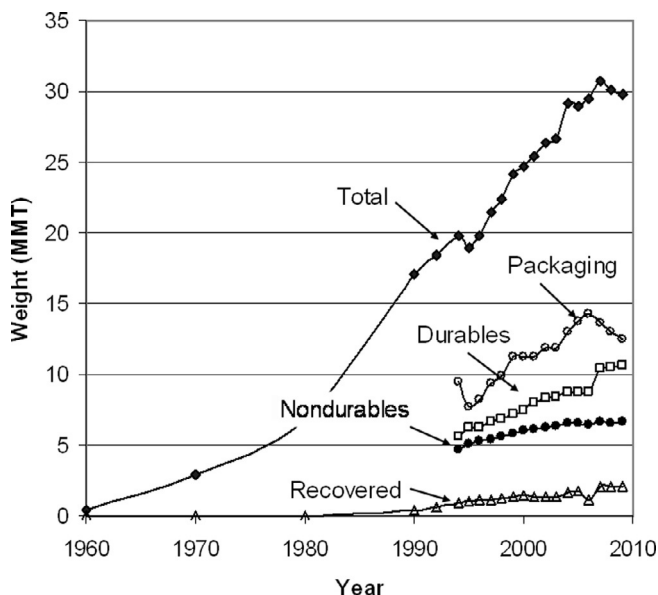


FIGURE 15.4 Plastic waste generated in the United States over the last 50 years. The data include plastic packaging waste, plastic from durable and nondurable products, and amount of recycled plastics (EPA, 2010).

of plastic waste in U.S. landfills has been a concern due, in part, to the sheer volume and the diminishing landfill capacity near urban centers (EPA, 2010). Plastic discards are categorized by the EPA as durable goods, packaging and containers, and nondurable goods (EPA, 2010) (Table 15.1).

4.2.1 Durable Goods

Plastic durable goods make up about 35% of the plastics deposited in landfills (Figure 15.4). Durable plastic products take advantage of the excellent chemical and moisture resistance, low density, superior mechanical properties, and low cost of plastic materials. While the public perception may be that all plastics need to be more degradable, that is not the case with this large sector of plastic products. Durability of plastics is essential in an ever-increasing number of products such as plastic auto parts, household appliances, and construction materials, including pipes for residential and industrial water and sewer lines. Some of these durable plastic goods have a service life of several decades or longer.

Assessing the environmental impact of durable plastic products can be complex since the environmental costs and benefits of such products need to be carefully examined as well (Cellura, Ardente, & Longo, 2012; Wikström & Williams, 2010; Williams, Wikstrom, & Lofgren, 2008). For instance, the environmental cost of the plastic used in manufacturing cars should be weighed against the benefit of lower gas consumption due to reduced vehicle weight. The environmental impact assessment should also consider the recycling rate, which is very low (3.8%) for plastic durable goods (EPA, 2010).

4.2.2 Packaging and Containers

Packaging and containers make up the largest sector (29.5%) of plastic waste in MSW (EPA, 2010) (Figure 15.4). Plastic packaging has become an integral part of the global marketplace (WPO, 2008). From Internet shopping to retail stores, packaging fills a critical role in not only protecting products during transport but also displaying products and providing consumer appeal. Changes in package design can significantly stimulate or depress product sales (Lee, Gao, & Brown, 2010). Still, packaging design has begun integrating sustainability as never before, in part, because sustainability itself has become a marketing angle. Retailers are now realizing that customers respond positively to products marketed in more sustainable or green packaging. Retailers have taken measures to require manufacturers and suppliers to implement sustainable packaging goals such as reducing the amount of primary and secondary packaging and downgauging the thickness of their plastic film to reduce the amount of plastic used to package each item (ACC, 2011; Deligio, 2009; Wood, 2010).

While efforts to minimize packaging and reduce its environmental impact must continue to be a priority, it is also important to recognize

and acknowledge that packaging serves an essential role in society. Perhaps, no other packaging segment better illustrates this than the food industry. Food packaging is the largest sector of the packaging industry serving one of the largest industries in the world (WPO, 2008). The movement of much of the world's population from an agrarian to an urban society has been possible only by the development of efficient food production and distribution practices. Food packaging has served and continues to serve a critical function in facilitating food transport, preservation, sanitation, storage, and distribution from the farm to the masses throughout the world.

It can be argued that the impact of food packaging in minimizing food waste more than compensates for the resources used in the packaging itself. Estimates claim that 25-50% of the food produced globally is wasted (Mena, Adenso-Diaz, & Yurt, 2011). It may be no coincidence that the amount of food wasted based on per capita food consumption and food waste data (EPA, 2010; USDA, 2002) is much lower (12.5%) in the United States where food packaging is heavily used. Packaging that preserves foods and minimizes waste also conserves all the resources invested in bringing that product to market (Cellura et al., 2012; Wikström & Williams, 2010; Williams et al., 2008). Wasted food consumes the energy and resources used for cultivation, harvest, and transportation to market and requires additional energy for transportation to landfills. The contribution of food waste to methane production, an important greenhouse gas, also has environmental implications (Mena et al., 2011). Other tangible benefits of food packaging are improved food safety and hygiene (Chawengkijwanich & Hayata, 2008; EPA, 2010; Gemili, Yemencioğlu, & Altinkayaa, 2009; WPO, 2008).

4.2.3 Nondurable Plastic Waste

Nondurable plastic goods consist of trash bags and single-use food service items including plates, bowls, and cups (EPA, 2010). Polystyrene (PS) is the plastic resin used mostly in plastic food service items (79%) and virtually no significant recycling is reported (EPA, 2010). The use of PS for single-use food service items is of particular concern because PS is especially persistent and difficult to degrade in the environment (Gorden, 2006). Furthermore, PS foam products are very lightweight and easily dispersed in the landscape by wind or carried into waterways by storm drains (Gorden, 2006). Much of the research aimed at using biopolymers to replace petroleum-based plastics has focused on developing bags and food service containers. Food service items comprise 3% of the plastic discarded as MSW and total about 0.9 MMT on an annual basis (EPA, 2010). Of all the plastic goods produced, plastic food service items are often considered the best candidate for replacement by renewable biopolymers. This is because materials used in food service items are typically single-use

disposable items. Oftentimes, the functional service of a plate or cup amounts to less time than it takes for a hot food or beverage product to become cold. Technology developed to use starch in these products could be further developed to expand to other packaging products.

5 STARCH-BASED PLASTICS

The interest in utilizing starch as a replacement for plastics started in the 1970s and intensified in the 1980s right along with the dramatic growth in the use of plastics worldwide and the concerns about the effects of plastics on the environment (Figure 15.4). By itself, starch is a poor substitute for petroleum plastics due to its moisture sensitivity and inferior mechanical properties. However, numerous strategies have been tested resulting in commercialized technologies for incorporating starch in plastics. A survey of the more common approaches has been included in this section.

5.1 Granular Starch

The early studies on the use of starch in plastics were focused primarily on its beneficial effect as a plastic additive rather than as an ingredient for improving biodegradation or renewable content. The benefits of adding starch to polyurethane foam formulations were investigated more than 50 years ago (Dosmann & Steel, 1961). Starch was included in a mixture of an organic diisocyanate and a polyol resulting in flexible foam products with improved mechanical properties (Dosmann & Steel, 1961). A rigid urethane foam containing starch was also reported (Bennett, Otey, & Mehlretter, 1967; Otey, Westhoff, Kwolek, Mehlretter, & Rist, 1969). In these materials, starch was believed to react with -NCO groups formed by an excess of isocyanate in the reaction mixture (Otey et al., 1969).

Using starch in plastic film was reported first in 1964 (Shulman & Howarth, 1964). Starch powder was dispersed in plastic film that was intended for use in making raincoats. The starch granules increased the water vapor permeability of the film, which allowed it to “breathe” and be more comfortable. Other studies investigated the use of a modified granular starch (starch xanthates) in a rubber latex matrix (Buchanan, Weislogel, Russell, & Rist, 1968). The starch xanthate was evaluated as a modifier of latex coagulation, as a reinforcing agent, and as an accelerator of vulcanization (Buchanan et al., 1968).

As concerns arose from the growing use of plastics, research exploring the use of starch to improve biodegradability began. Griffin was the first to report using starch as a filler in plastic films with the intention of improving the biodegradability of plastics (Griffin, 1973, 1974). In a later patent, Griffin claimed that adding starch to various polyolefins made

them biodegradable meaning that they would ultimately break down due to the action of living organisms (Griffin, 1977). This claim was later refuted when it was shown that although the starch component could biodegrade, starch did not affect the biodegradation of the polyolefin matrix (Koenig & Huang, 1995). The Griffin process involved drying the starch (moisture content <1%) and chemically treating the granule surface to improve compatibility with the polymer matrix. Degradation of the polymer was facilitated by adding a prooxidant to the resin. Evidence for microbial degradation was based on fungal growth found in composted film samples.

Griffin was successful in extrusion-blowing film of low-density polyethylene (LDPE) containing up to 30% starch and reported acceptable thermal stability and melt-flow properties needed for processing various commodity resins. Adding starch as a filler to plastics generally increased moisture sensitivity, reduced the tensile strength, and increased the thickness of films (Griffin, 1977; Lim, Jane, Rajagopalan, & Seib, 1992). Starch granules with smaller diameters have less of a negative effect on the mechanical properties of starch-filled plastics probably due to the benefit of greater exposed surface area in smaller granules (Lim et al., 1992). Even greater exposed surface area can be obtained by forming starch nanoparticles (Le Corre et al., 2010). The nanostarch can be added in higher amounts (25-40%) compared to native starch granules yet still result in thin films with good strength and clarity (Schut, 2008).

Starch xanthates and native starch powders were evaluated as fillers in poly(vinyl chloride) (PVC) near the time of Griffin's work (Westhoff, Otey, Mehlretter, & Russell, 1974). The goal was to make the PVC more biodegradable by interspersing starch throughout the polymer matrix. The starch performed well as a filler and promoted the growth of fungi in composting studies (Westhoff et al., 1974). As mentioned earlier, however, only the starch component was biodegradable (Koenig & Huang, 1995). In contrast, using starch as a filler in a degradable synthetic polymer such as polycaprolactone provided fully biodegradable plastic composites (Koenig & Huang, 1995). Starch-filled plastic technology is still used today to incorporate starch into polyethylene and other polyolefins. Since whole starch granules are used, the amount used commercially is typically only 6-20% weight (Otey, Westhoff, & Russell, 1977; Röper & Koch, 1990). These composite materials would not fully biodegrade but would be considered more sustainable due to the renewable content provided by the starch.

5.2 Thermoplastic Starch

Native starch is not a thermoplastic material and will thermally degrade before its glass transition temperature (T_g) is reached (Dufresne, Dupeyre, & Vignon, 2000). The T_g of dry starch and its melting temperature

(230-240 °C) are both higher than the degradation temperature of starch (220 °C) (Orford, Parker, Ring, & Smith, 1989; Russell, 1987; Shogren, 1992). However, as noted in the previous section, when starch is heated in the presence of plasticizers such as water or polyols, the semicrystalline structure of the starch granule is disrupted. When this occurs, the glass transition temperature falls well below the thermal degradation temperature and the starch indeed behaves as a thermoplastic.

During the time that Griffin was investigating starch as a filler in plastics, Otey was investigating the use of starch films as a replacement for plastics (Otey et al., 1974). Using starch as a matrix material afforded the opportunity to use a much higher amount of starch in the product. Starch had long been known to gelatinize when heated in water forming a thermoplastic of sorts with a continuous matrix having good film-forming properties (Lloyd & Kirst, 1963). Interest in using starch as a nonsupported film in food and agricultural applications was deemed attractive because of its low cost, wide availability, and biodegradability. Unfortunately, the cast starch films tended to embrittle and were sensitive to moisture (Lloyd & Kirst, 1963; Otey et al., 1974). Plasticizing the starch films with glycerol or ethylene glycol improved the flexibility of the films but they had very little wet strength (Lloyd & Kirst, 1963). Cast starch-based films with improved strength could be made by blending starch with other polymers (Maxwell, 1970). Films of starch/ethylene copolymer-poly(vinyl alcohol) (EVA) blends were used to coat paper to improve strength and physical properties (Maxwell, 1970, 1971). Films made from blends of starch, glycerol, poly(vinyl alcohol) (PVA), and a cross-linking agent were then coated with a thin layer of PVC or other plastic to make cast films with good functional properties for agricultural mulch (Otey et al., 1974).

The development of thermoplastic processing technology has played an important role in achieving mass production of inexpensive plastic products. Any plastic substitute that can be processed as a “drop-in” replacement using existing plastic processing equipment has a built-in advantage of seamless integration into existing processing capacity. Otherwise, specialized equipment must be designed, manufactured, and purchased by processors, all of which can deter commercial interest.

Extrusion technology is one of the fundamental processes used in processing thermoplastics and has been used for decades to process starch-rich foods. Early concepts for extrusion technology date back to the 1700s where a piston was used to force lead through a die to make lead pipe. The process was subsequently used for extruding clay pipe, soap, and pasta. Both single- and twin-screw extruders were developed around 1870 for use in processing rubber and for making sausage (Riaz, 2000). In the mid-1930s, food companies began using extrusion to make breakfast cereals and snack foods from starch-rich cereals. During this period of

time, the first extruder for thermoplastics was built by Paul Troester in Germany (Rauwendaal, 2001). In the late 1930s, Roberto Colombo and Carlo Pasquetti from Italy designed a twin-screw extruder for processing cellulose acetate (Riaz, 2000).

Initially, the extruders were heated with steam but, subsequently, were designed with electrically heated barrels and screws with longer length/diameter ratios for starch-based foods (Rauwendaal, 2001). Scientific studies and modeling work on plastic extrusion commenced during the 1950s. By 1965, the basic theories for extrusion had been developed as well as extrusion systems complete with feeders and dies (Rauwendaal, 2001). Some early studies on starch-rich foods were actually performed using extruders designed for plastics (Anderson, Conway, & Peplinski, 1970; Riaz, 2000). Studies on the effect of various extruder variables on the properties of cornstarch took place as early as 1972 (Lawton, Henderson, & Derlatka, 1972). One of the early studies on processing parameters of starch was performed using twin-screw extrusion (Mercier & Feillet, 1975). These studies were some of the first aimed at modeling starch extrusion. Subsequent work on extrusion processing of starches from a food perspective continued to provide the foundation for starch extrusion (Colonna, Doublier, Melcion, Monredon, & Mercier, 1984; Mercier, 1977; Mercier & Feillet, 1975; Wiedmann, 1987).

Today, it is widely recognized that extrusion processing can be used to completely destructure starch and form a homogenous melt. In the food industry, extrusion is referred to as a "high-temperature (150-170 °C), short-time (20-200s)" (HTST) bioreactor that is able to gelatinize, melt, and destructure starch granules (Colonna et al., 1984; Kokini, 1993; Lai & Kokini, 1991). Plasticized starch does indeed behave as a thermoplastic and is referred to as thermoplastic starch (TPS) (Dufresne et al., 2000). Extrusion processing melts TPS at a much lower moisture content (10-20%) than that used for conventional cooking methods (Kokini, 1993; Wiedmann, 1987).

Extrusion processing is used to compound plasticized starch and form a pelletized extrudate of TPS that can be further processed using extrusion plastic processing equipment such as injection molding or film blowing (Otey, Westhoff, & Doane, 1980; Wiedmann & Strobel, 1991). Although TPS can be processed like traditional plastics, it is not suitable for most applications because of its moisture sensitivity. For that reason, starch blends with moisture-resistant polymers were explored. Blends of starch and poly(ethylene-co-acrylic acid) were processed into films using plastic film blowing equipment (Otey et al., 1980; Otey, Westhoff, & Doane, 1987). The film was biodegradable and intended for use as an agricultural mulch or as a packaging material. Blends of starch and synthetic polymers such as EVA and PVA that had shown promise as films for paper or agricultural mulch (Maxwell, 1970, 1971; Otey et al., 1974) were found

particularly useful when compounded by extrusion to make blends (Bastioli, 1998).

Subsequent research on blends of TPS and moisture-resistant polyesters has resulted in starch blends with adequate moisture resistance and mechanical properties (Bastioli, 1998). Other promising TPS/polymer blends are with synthetic biodegradable resins that are aliphatic polyesters and aliphatic-aromatic copolyesters. These polyesters fall within two groups, amorphous and semicrystalline. The amorphous polyesters are flexible and are comparable to LDPE. The semicrystalline polyesters are more rigid and are more comparable to PET, PS, or polypropylene (PP) (Leaversuch, 2002). The aliphatic-aromatic copolyesters are typically based on butanediol, adipic acid, and terephthalic acid. The aliphatic polyesters are a polybutylene succinate (Leaversuch, 2002). These polymers are made in modified PET facilities from petrochemical feedstocks and typically biodegrade in about 3 months. The market for these biodegradable polyesters has grown at a robust annual rate of about 30% (Leaversuch, 2002).

Another approach to improving the properties of TPS has been to form starch composite materials. Polymer composites with improved barrier, mechanical, and heat resistance properties have been reported using clay nanoparticles (Alexandre & Dubois, 2000; Park, Lee, Park, Cho, & Ha, 2003). The most commonly used nanoclays include montmorillonite, a 2:1 phyllosilicate that has a stacked platelet structure with each platelet having a thickness of approximately 1 nm and lateral dimensions on the order of micrometers. The hydrophilic interlayer between each platelet structure can be rendered more hydrophobic through a cation-exchange process with alkylammonium ions. Water vapor transmission rates of potato starch have been reduced by nearly 50% by incorporating only 5 wt% of such clays (Park et al., 2003). In addition, the dynamic elastic moduli and tensile strength were increased. The improved properties of the starch-clay composite materials are due to uniform dispersion of the clay platelets in the starch matrix (Figure 15.5). The platelets create a tortuous pathway through the starch matrix that significantly lowers the water vapor transmission rates (Chiou, Yee, Glenn, & Orts, 2005). In addition, the dispersed platelets provide more surface area for starch-nanoclay interactions that, in turn, improve the mechanical properties of the starch composites.

Cellulose microfibrils provide another nanosized material for making starch composites (Medeiros et al., 2008). In 1995, researchers in Grenoble published a notable paper where they created nanocomposites derived from cellulose whiskers dispersed in a copolymer acrylate latex film (Favier, Chanzy, & Cavaille, 1995). They showed that the dynamic storage modulus was improved more than threefold at 3-6% cellulose loadings (Favier et al., 1995). Typical cellulosic microfibrils are long crystalline

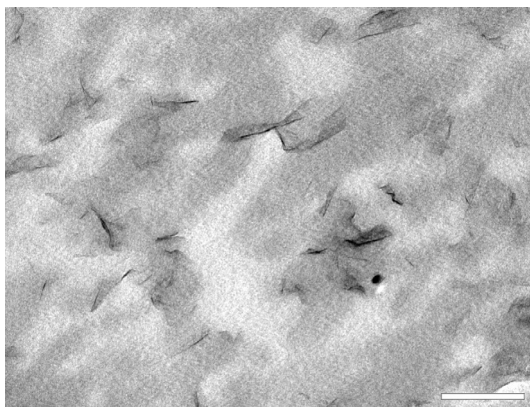


FIGURE 15.5 Transmission electron micrograph of starch-clay composite. The clay particles appear as dark lines dispersed throughout the starch matrix (scale bar = 200 nm).

“needles” ranging in size from 10 to 20 nm in width, with an average aspect ratio of 20-100 (Azizi Samir, Alloin, & Dufresne, 2005). Several groups (Dubief, Samain, & Dufresne, 1999; Favier et al., 1995) have continued work on the hypothesis that natural cellulose microfibrils can act in a fashion similar to the clay nanocomposites in reinforcing polymers. Part of the promise lies in the fact that the axial Young’s modulus of the basic cellulose crystalline microfibril has been measured to be 137 GPa (Leitner, Hinterstoisser, Wastyn, Keckes, & Gindl, 2007; Wu, Henriksson, Liu, & Berglund, 2007), which is similar to Kevlar and “stronger than steel.” Incorporating nanofibers in TPS increases tensile strength and modulus (Alemdar & Sain, 2008) and decreases moisture sensitivity of starch composites (Svagan, Hedenqvist, & Berglund, 2009). While research in starch nanocomposites continues to show promise, cost considerations have deterred commercialization.

5.3 Companies Marketing TPS-Based Products

The list of companies using extrusion technology to make TPS-based commercial products is ever-changing. Notwithstanding, the following list includes many of the companies currently marketing TPS-based products.

5.3.1 Novamont

One of the early innovators in developing TPS blends for commercial production is the Italian company, Novamont. Founded in 1989, Novamont has developed four different classes of materials all based on blends of TPS and synthetic polymers (Bastioli, 1998). The film-grade product is based on blends of TPS and polycaprolactone (Bastioli, Cerutti, Guanella,

Romano, & Tosin, 1995). This grade degrades in a composting environment in about 20-35 days (Bastioli, 1998). The injection molding grade is a blend of TPS and cellulose derivatives. It degrades in about 4 months and is a rigid material that may replace PS. A foaming grade is also available that contains more than 85% TPS. The foam product is used as a replacement for PS foam for loose-fill packaging (Bastioli, 1998). The final class of materials is a blend of TPS and polyethylene vinyl alcohol (EVA) (Bastioli, Bellotti, Del Giudice, & Gilli, 1993). This grade is noncompostable and degrades in about 2 years in a liquid environment (Bastioli, 1998). The current production at Novamont has exceeded 60,000 MT.

Novamont continues to develop their technology. In 1997, Novamont purchased the Warner-Lambert patents for TPS/polymer blends. They later acquired (2004) the technology from Eastman Chemical to produce the polyester (Estar Bio). This polyester is now being produced using oil from a nonfood crop and is being blended with TPS (Schut, 2008). The biobased polyester has enabled Novamont to increase the renewable polymer content of their resins to about 50% (Anonymous, 2010). They also intend to commercialize "nanostarch" particles for use in film grades of Mater-Bi. The nanostarch allows for higher renewable content in films while maintaining good strength and clarity (Schut, 2008).

5.3.2 *Cereplast*

Cereplast is located in El Segundo, CA. It was founded in 1996 and began marketing the Novamont product in North America. In 2000, Cereplast began developing their own TPS technology and started marketing Cereplast products in 2001. Cereplast recently opened a 36,000 MT facility in Indiana (Cereplast, 2011). The Cereplast products include single-use food service items including cups, bags, and cutlery (Cereplast, 2011).

5.3.3 *Ecobras*

BASF, the world's leading chemical company, has entered the starch blend market. BASF produces the biodegradable polyester, Ecoflex (polybutyrate adipate terephthalate, PBAT). In 2007, BASF aligned itself with Corn Products International and began selling a starch/PBAT blend for the Latin American market. The blend contains about 50% cornstarch and is designed for making films although it can be injection molded as well.

5.3.4 *Biotec*

Biotec GmbH in Germany has about 11,000 MT capacity (Schut, 2008). Its products include pure TPS and various blends of starch and copolyesters. It has six commercial formulations for injection molding, rigid and flexible extrusion, and foams. Many of the finished products include

biodegradable carrier bags, bin liners, and refuse bags. Most sales are in Europe (Schut, 2008).

5.3.5 Plantic

Plantic Technologies was incorporated in Victoria, Australia, but is located today in Melbourne, Australia. Plantic acquired technology in 2001 for making high-amylose cornstarch TPS plastic sheets and trays. They found that TPS sheets could be thermoformed into trays and used to package fatty foods or products with a water activity of 35-70%. The business started making trays for a candy company. Plantic entered the global market in 2004 and recently developed multilayered polymer films with a starch film core that has improved moisture resistance, gas barrier properties, and physical properties. Plantic has announced joint ventures with several companies in recent years including DuPont for making cosmetic and food packaging and Bemis Co., Inc., Neenah, WI, to develop blown film for dry-goods packaging (Schut, 2008).

5.3.6 Biolice

Biolice was developed by Limagrain, a leader in the European agricultural sector. Biolice is a TPS made from cereal flour that is blended with biodegradable polyesters. Biolice is a rigid packaging material that can be thermoformed into single-use items like drink trays and cups. Films can also be made from the resin for agricultural mulch and carrier bags. The product is being marketed in France and is completely biodegradable.

5.3.7 KTM Industries

KTM Industries is a company located in Lansing, MI. The company uses an extrusion process similar to that used to make PS foam sheets. The process involves extruding TPS through an annular die to form a foam tube. The tube is sliced and opened flat to form sheets of starch foam that can then be used for packaging operations. The foam sheets can be cut and glued to form padding for specific packaging applications. The company also makes colored loose-fill products for children craft projects. Other companies using TPS for making starch-based loose-fill products include StarchTech, Inc., and National Starch with its Eco-Foam product.

5.4 TPS-Polyolefin Blends

5.4.1 Cerestech

Cerestech, Inc. was incorporated in 2001 in Montreal, Canada. The company produces blends of TPS and commodity thermoplastics in a one-step extrusion process. The process involves preparing starch/glycerol/water blends of approximately 48%, 32%, and 20%, respectively

(Rodriguez-Gonzalez et al., 2003). The starch preparation is fed into a twin-screw extruder to form a TPS melt. A second single-screw extruder is attached to the twin-screw extruder in a perpendicular position to allow a thermoplastic polyolefin such as high-density polyethylene to be melted and injected directly into the TPS melt. The melt blend is compounded further using high shear to form a blend of the two incompatible resins. Although the polyolefin and TPS form an incompatible blend, the domains of the respective polymers range from several micrometers to less than one micrometer (Rodriguez-Gonzalez et al., 2003). Blends containing up to 50% starch have been produced with excellent mechanical properties and moisture resistance (Rodriguez-Gonzalez et al., 2003).

The carbon footprint of these blends is significantly reduced compared to the neat polymer due to the starch content. A family of blends (Cereloy) based on starch and various polyolefin resins is being developed. Cerestech has granted a worldwide license to Teknor Apex to produce the blends. The blends are being sold at a similar or lower price than the neat polymer. Teknor Apex is also marketing blends of starch and recycled PP and PE to further improve the environmental profile of its products (Anonymous, 2011e).

5.5 Starch Baking Technology

A baking technology that was first developed for the food industry has been adapted for making starch-based foam food service products (Hass, Hass, & Tiefenbacher, 1996; Tiefenbacher, 1993). The starch baking process is analogous to the process used in making waffles and wafer cookies. A starch dough is first made containing gelatinized or pregelatinized starch, native starch, water, fiber, fillers, and other additives and then kneaded in a mixer for about 10 min. A predetermined amount of aqueous starch dough is placed into a preheated (150-200 °C) mold cavity that is then clamped closed. The dough quickly heats and the starch component is gelatinized forming a melt that fills the entire mold cavity. A skin forms on the upper and lower surfaces where the molten dough contacts the mold. Steam that forms during the process acts as a blowing agent and creates a foam structure in the core region of the product. Steam is allowed to vent from the mold, and within about 45-60 s, the product dries and solidifies into the desired shape. The starch-based product appears very similar to PS foam. The procedure is described in detail elsewhere (Glenn, Orts, & Nobes, 2001; Shey, Imam, Glenn, & Orts, 2006).

The properties of the baked starch foams are dependent upon various factors, including moisture content and starch type (Andersen & Hodson, 1996, 2000; Lawton, Shogren, & Tiefenbacher, 2004; Shogren, Lawton, Doane, & Tiefenbacher, 1998). Immediately following the baking process,

the baked starch foams are brittle and lack flexibility but appear very similar to expanded polystyrene foam. Under dry storage conditions, starch blends and composites lose water quickly and become brittle, yielding a matrix of low modulus. Under high-moisture conditions, starch can absorb moisture, yielding a loose and flexible matrix. Thus, to obtain starch food packaging materials with acceptable properties, other substances such as fillers, compatible additives, plasticizers, and a moisture resistance film coating are generally required.

Incorporating cellulose fibers in formulations improved both the flexibility and the strength of baked starch foams (Andersen & Hodson, 1997; Glenn, Orts, & Nobes, 2001). For example, addition of softwood pulp fiber (Figure 15.6) improved flexural properties and lowered the foam density (Glenn, Orts, & Nobes, 2001; Glenn, Orts, Nobes, & Gray, 2001). Foam properties were further improved by utilizing chemically modified starches and additives such as aspen fiber, PVA, and monostearyl citrate (Lawton et al., 2004; Shogren, Lawton, Tiefenbacher, & Chen, 1998). Modified starches improved flexibility, and aspen fiber improved the strength, whereas monostearyl citrate improved water resistance. Interestingly, not all fibers help improve foam properties. Addition of corn fiber in formulations had a rather negative impact on starch foam packaging trays, as corn fiber tended to decrease the mechanical strength and increase baking time and batter volume (Cinelli, Chiellini, Lawton, & IMAM, 2006). Trays produced with a high fiber ratio in conjunction with PVA, however, showed improved water resistance.

Baked foam products with improved moisture resistance were made by incorporating PVA in the starch-based composition (Shogren, Lawton, Tiefenbacher, et al., 1998). Alternatively, protective food-grade, hydrophobic, thermostable, and degradable polyester films have been effective

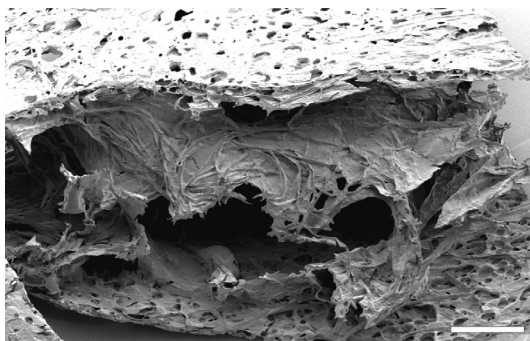


FIGURE 15.6 Scanning electron micrograph of cross section from starch/fiber baked foam composite material. A fairly dense skin was formed on the surface of the foam. The interior of the foam was porous with walls formed from the starch/fiber composite (scale bar = 0.5 mm) (Glenn, Orts, Nobes, & Gray, 2001b).

in improving moisture resistance when applied directly onto the baked product (Glenn, Orts, Nobes and Gray, 2001). More recently, natural rubber latex has been used as a moisture-resistant additive for the baked starch foams (Shey et al., 2006). Moisture resistance in starch foams improved when a small amount of latex was added in the formulation in the presence of nonionic additives. Latex also improved the flexibility of the foam product. Such approaches to improve moisture resistance, however, add to the overall cost of the product.

An Austrian company, Biopack, was the first to commercially produce starch-based baked foam trays for food packaging. Apack (Germany) also began producing starch-based food packaging made by a similar baking process. The name Apack has since changed to IBEK Verpackungshandel GmbH. This company produces over 150 million pieces a year with production facilities in China, Thailand, and Canada. Another of the early leaders in the development of baked starch containers was EarthShell Corporation located in the United States. EarthShell was granted over 130 patents in the field and was able to successfully produce commercial single-use disposable baked trays, dinner plates, and soup bowls for the fast-food industry. These products are currently being sold in the U.S. markets. More recently, EarthShell has licensed its technology to Renewable Products, Inc., located in Lebanon, MO, for manufacturing and distributing EarthShell packaging plates and bowls in the United States.

The baking technology is also being used by Biosphere Industries, LLC in Carpinteria, CA, and Durango, CO. Biosphere has a patented technology for making products to compete with cardboard and plastic foams and for baking trays and food service ware (Biosphere, 2011). They use primarily starches from cassava and potato and natural fibers in their engineered products.

5.6 Starch Fermentation Products

The use of starch in fermentation products has grown to be the largest industrial use of starch. Nearly 40% of the entire U.S. corn crop production was used for ethanol production in 2010 (USDA, 2010). Braskem, the largest petrochemical company in Latin America, has constructed a 0.2 MMT plant for making “green polyethylene” from sugarcane-based ethanol and is considering plans to build another (Murphy, 2010). Corn-based ethanol is not currently being considered as a feedstock for green polyethylene since sugarcane ethanol conversion is much more energy-efficient. However, the development and optimization of this technology could lead to future consideration (Defosse, 2009; Johansson, 2009).

Cargill Dow LLC, owner of NatureWorks, is the world’s largest bioplastic manufacturer. The NatureWorks production facility is located in

Nebraska. Their Ingeo-brand PLA products are produced from the fermentation of cornstarch. At full capacity, the NatureWorks facility can produce 136,000 MT utilizing 340,000 MT of corn (BIOPOL, 2010). NatureWorks projects are at full capacity in 2-3 years and are currently enjoying a 25-30% annual growth in the market. A new plant in Thailand was recently announced that will have a production capacity similar to that of the Nebraska plant. The Thailand plant will use cassava starch and sugar from sugarcane as feedstock (Anonymous, 2011f).

PHAs are linear polyesters produced by bacteria through a sugar or lipid fermentation process using unbalanced growth conditions (Chen & Wu, 2005). More than 150 different monomers have been identified that produce polymers with a wide range in mechanical properties (Chen & Wu, 2005). The PHA is produced as an energy storage molecule in bacteria much like starch in plants. PHAs represent a family of polymers that have a considerable potential as fully degradable plastic polymers. To date, the most commercial production is from Tianan Biologic Material Co. in Ningbo, China. It has increased its capacity to more than 900 MT/year (Schut, 2008). Tianan's commercial PHA contains about 5% valerate, though developmental grades have up to 15% valerate, and even higher valerate content is being tested. Valerate adds flexibility to the polymer. Other companies producing PHAs include Metabolix (Cambridge, MA).

6 FUTURE PROSPECTS

With an ever-increasing world population, the question is not whether the global environment will be impacted by our presence but how and to what degree. The implementation of sustainable practices will help minimize our impact on the environment and conserve resources for future generations. To that end, there is a need to perpetuate the culture of environmental stewardship and sustainability that has grown stronger in recent years. Consumers and municipalities must continue to demand more sustainable packaging materials and practices. Retailers must continue to provide suppliers incentives for greater sustainability in their packaging choices. Although some of the starch-based materials and other biopolymers may not currently be cost-competitive with petroleum plastics, this may change as petroleum prices increase.

Starch is poised to establish an even stronger role in the manufacture of sustainable plastics and other bioproducts largely because it is abundant, renewable, and inexpensive. The cost and availability of starch may improve even further in the future if lignocellulose supplants cornstarch as the preferred feedstock for ethanol production in the United States. Strategies for improving the properties of starch-based plastics such as blending starch with other polymers, using starch in composite materials,

and using starch as a fermentation feedstock to make other biopolymers have been successful in developing viable replacements for petroleum-based plastics. The prospects for starch in the packaging sector continue to become brighter as the market for sustainable plastics drives further innovation and development.

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