

PART III

HYDROPHOBIC AND HYDROPHILIC POLYMERIC BLENDS

Starch–Poly(hydroxyalkanoate) Composites and Blends*

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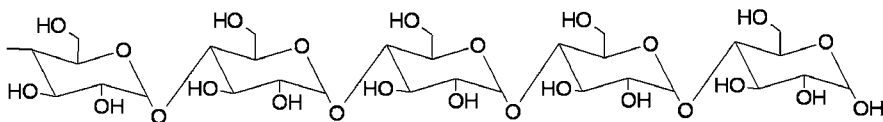
9.1 SUMMARY OF STARCH AND PHA STRUCTURE AND PROPERTIES

9.1.1 Starch

The structure and properties of starch have been described in a number of reviews (Whistler et al., 1984; Parker and Ring, 2001; Tester et al., 2004). Starch is composed

*Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

Amylose



Amylopectin

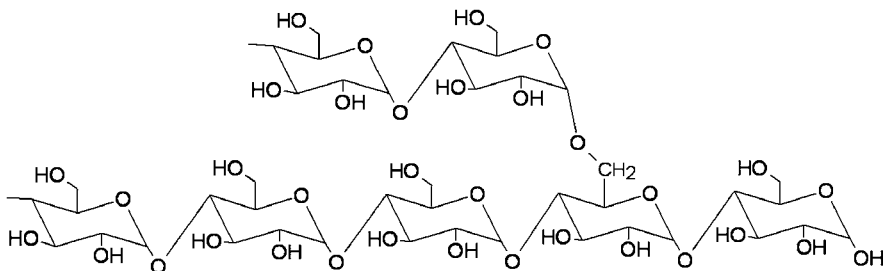


Fig. 9-1 Simplified chemical structures of amylose and amylopectin.

of the polysaccharides amylose and amylopectin (Fig. 9-1) along with small ($<1\%$) amounts of protein and lipid. Amylose is a mostly linear polymer of α -(1,4) linked glucose residues with molecular weights on the order of 10^5 – 10^6 . Amylopectin is highly branched and consists of short, α -(1,4) linked chains of 10–40 glucose residues connected by α -(1,6) bonds. Molecular weights for amylopectin are typically $>10^8$.

Starch is biosynthesized as small granules 1–60 μm in diameter in plants and serves as an energy storage medium. Sources of starch include cereal seeds such as corn, wheat, and rice and tubers such as potato and tapioca. Starch granules are semi-crystalline, with amylopectin forming thin crystalline and amorphous layers. As a result, native granular starch is insoluble in cold water but can absorb water and other small molecules into the granule due to the hydrophilic character of the numerous hydroxyl groups as well as the presence of pores in cereal starches (Huber and Bemiller, 2000). The packing characteristics of starch granules in different fluids have been described (Willet, 2001). Maximum volume fractions of different types of starches are typically in the range 0.58–0.63 and depend on granular shape, size distribution, and degree of interparticulate adhesion.

On heating in water to 60–150°C, starch granules swell, lose their crystallinity (gelatinize) and are dispersed or solubilized in water. At low water contents (10–30%) and moderate temperatures (100–200°C), gelatinized starch possesses rheological properties similar to those of polymer melts (Willet et al., 1995) and can be processed by extrusion, injection molding, compression molding, etc. Other plasticizers such as glycerol, urea, and sorbitol can be substituted in

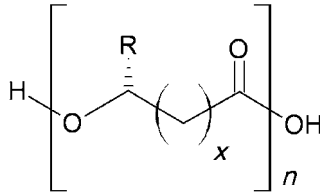


Fig. 9-2 General chemical structure of PHAs. Typically, $x = 1-8$, $n =$ several thousand.

part for water to aid in starch destructureization and to add flexibility to starch (Shogren, 1993).

9.1.2 Poly(hydroxyalkanoate)s

Poly(hydroxyalkanoate)s (PHAs) are aliphatic polyesters biosynthesized by bacteria and function as energy storage reservoirs (Inoue and Yoshi, 1992; Marchessault, 1996; Sudesh et al., 2000). The general structure of PHAs is given in Fig. 9-2. Poly(3-hydroxybutyrate) (PHB) is the most common PHA and is a rather rigid, crystalline polymer having a T_g of 4°C and T_m of 180°C . PHAs can be made with a variety of other hydroxyalkanoate monomers, however. In particular, copolymers of 3-hydroxybutyrate with 3-hydroxyvaleric acid, 3-hydroxyhexanoic acid, and 4-hydroxybutyric acid yield materials that are less crystalline, more flexible, and more easily processable. PHBV, for example, is a copolyester of 3-hydroxybutyrate and 3-hydroxyvalerate. Such copolymers have mechanical properties similar to those of polyethylene and polypropylene and have been commercialized, although production volumes are still fairly low due to high cost.

9.2 WHY BLEND STARCH WITH PHAs?

The main reason for adding starch to PHAs has been to reduce the overall cost, since starch is relatively inexpensive ($\$0.15/\text{lb}$ for corn starch) while PHAs typically cost several dollars per pound. Of course, other cheap fillers such as ground minerals could also be used. The advantage of starch is that, like PHAs, it is completely biodegradable and is already in the form of a fine, white powder. Starch could also potentially serve as a reinforcing filler, increasing the modulus and strength of the blend. Since starch biodegrades very rapidly, it may also have an influence on the overall degradation rate of starch-PHA blends. This could be important to degradation rates of starch-PHA plastics both in the environment and also for in-vivo medical devices.

9.3 PROBLEMS WITH STARCH-PHA BLENDS

The main problems with starch-PHA blends are the poor compatibility of these very different materials as well as the water sensitivity of starch. Since starch is quite

TABLE 9-1 Surface Energy Data for Starch and PHAs

Starch		PHA		Method	Reference
Type	Surface Energy (mN/m)	Type	Surface Energy (mN/m)		
Corn	56	–	–	Drop shape	Shogren and Biresaw (2007)
Corn	35–42	–	–	Dynamic contact angle	Lawton (1995)
–	–	PHBV	41.5	Contact angle	Lawton (1997)
Corn	43	PHBV-12	42.2	Contact angle	Biresaw and Carriere (2001)
Not specified	48–56	–	–		Odidi et al. (1991)

hydrophilic and PHAs are hydrophobic, there is poor adhesion between these two polymers and hence mechanical properties of composites will be poor. Also, since starch readily absorbs water, composite starch-PHA materials will be less water resistant than pure PHA or other commodity plastics. Much of the research on starch-PHA composites has therefore focused on improving adhesion or compatibility between the components.

Surface energies of starch (Lawton, 1995; Shogren and Biresaw, 2007) and PHBV (Lawton, 1997) as well as work of adhesion (Biresaw and Carriere, 2001) have been estimated. As shown in Table 9-1, there is a rather wide range in experimental estimates for the surface energy of starch. This is likely due to contamination of the surfaces of starch films with hydrophobic compounds (lipids, hydrocarbons, silicon oils, etc.) (Russell et al., 1987; Shogren and Biresaw, 2007), giving lower than expected values. The value of 56 mN/m (Shogren and Biresaw, 2007) may be the most accurate, since a new surface was created during the formation of the pendant drop and the result agrees well with a value of 59 mN/m determined by group contribution theory (Shogren and Biresaw, 2007). These values for the surface energy of starch are significantly higher than for the more hydrophobic PHBV (42 mN/m) and thus give rise to a large interfacial tension.

9.4 GRANULAR STARCH-PHA COMPOSTIES

Ramsay and co-workers first reported on the mechanical properties and biodegradation of starch-PHBV composites (Ramsay et al., 1993). Tensile strength and elongation (Table 9-2) both decreased dramatically with increasing starch loading, reflecting the poor adhesion between phases. Scanning electron micrographs also showed starch granules separating from the PHA matrix. Elastic modulus,

TABLE 9-2 Mechanical Property Data for Selected Starch-PHA Composites

PHA	Starch Type	Starch (wt %)	Additive (wt %)	Tensile Strength (MPa)	Elongation at Break (%)	Modulus (GPa)	Reference
PHBV12	None	0	None	17.7 ± 3.9	25 ± 8	1.5 ± 0.1	Ramsay et al. (1993)
	Wheat	25	None	8.6 ± 2.6	5.1 ± 1.0	2.1 ± 0.1	
	Wheat	50	None	7.7 ± 1.0	1.0 ± 0.2	2.5 ± 0.1	
PHBV12	None	0	Triacetin, 10%	24 ± 1.0	38 ± 2.5	0.18 ± 0.04	Shogren (1995)
	Corn	50	Triacetin, 10%	10 ± 1.0	11 ± 2.5	0.30 ± 0.04	
	PEO-coated corn	50	Triacetin, 10%	19 ± 1.0	21 ± 2.5	0.17 ± 0.04	
PHB	None	0	Triacetin, 30%	11.3 ± 0.7	15.5 ± 1.3	0.19 ± 0.01	Innocentini-Mei et al. (2003)
	Corn	20	Triacetin, 30%	3.0 ± 0.3	2.3 ± 0.2	0.17 ± 0.02	
	Corn-PU	20	Triacetin, 30%	7.5 ± 0.1	6.4 ± 0.2	0.20 ± 0.01	
PHBV8	Corn	25	Acetyltributyl citrate, 5%	17.1	15.6	0.46	Willett et al. (1998)
	Corn-g-PGMA	25	Acetyltributyl citrate, 5%	23.6	13	0.54	
PHBV12	Corn propionate/maleate, DS 1.4	50	Triacetin, 15%	14.0 ± 2.5	6.9 ± 0.6	0.15 ± 0.01	Bloembergen (1995)
PHBV	Corn propionate, DS 2.3	70	None	10.3	0.5	0.90	Rimsa and Tatarka (1994)
PHBV12	Corn	30	None	9.3	3.6	0.93	Swanson, unpublished data (1991)
	Corn	30	0.4% dicumyl peroxide	20.3	3.9	1.1	

however, increased with increasing starch content due to the rigidity of the starch granules. Other authors have reported similar results (Kotnis et al., 1995; Shogren, 1995; Koller and Owen, 1996; Rosa et al., 2003). The effects of added plasticizer and mineral filler have also been studied (Kotnis et al., 1995). Mechanical properties of starch-filled polymers have been related to various theoretical models (Willett, 1994; Owen and Koller, 1996; St. Lawrence et al., 2001). To improve adhesion, investigators have taken two approaches: (1) adding a coupling agent and (2) chemically modifying the starch and/or PHA.

In the first approach, Shogren (1995) showed that coating starch with polyethylene oxide (PEO) greatly increased strength and elongation of starch-PHBV composites (Table 9-1). Values were, however, still less than for pure PHBV. Presumably, PEO has favorable interactions with both starch and PHBV and therefore can serve as a binding or interfacial agent. Other amphiphilic polymers such as hydroxyl functional polyester-ethers (Willett and Doane, 2001), and copolymers such as styrene and maleic anhydride (Krishnan and Narayan, 1996) were claimed to improve the mechanical properties of starch-PHBV blends.

In the second approach, Avella et al. (2002) showed that addition of a free-radical former (2% bis[*tert*-butylperoxyisopropyl]benzene) to PHBV/starch 70/30 caused a two-fold increase in impact resistance to 1.9 kJ/m², similar to 1.8 kJ/m² for pure PHBV. Presumably, some starch-PHBV graft copolymer was formed by free radical combination reactions and acted as an interfacial binding agent. Unpublished work by Swanson from 1991 at USDA/ARS/NCAUR also indicated that addition of a free-radical initiator (0.4% dicumyl peroxide) to a 70/30 PHBV/starch composite gave tensile strengths similar to PHBV-12 alone (20.3 MPa). The same study also indicated that orientation of PHBV and PHBV/starch (<20% starch) blends by drawing resulted in very high elongations (200–400%). Innocentini-Mei et al. (2003) showed that copolymerization of starch with a diisocyanate and propylene glycol resulted in improved tensile strengths and elongations in blends with PHB (Table 9-1), but values were significantly lower than for pure PHB. Composites of starch-*g*-poly(glycidyl methacrylate) (>7% PGMA) and PHBV had significantly higher tensile strengths than unmodified starch-PHBV (Table 9-1) (Willett et al., 1998). Composites of maleic anhydride-grafted starch with PHBV and a CO₂-epoxypropane copolymer were also reported (Li and Liu, 2004). Composites of starch (50%) with acrylic acid-grafted PHB had higher tensile strengths (14 MPa) than unmodified starch-PHB (7 MPa) (Liao and Wu, 2007).

Willett and co-workers also studied the effect of water immersion for 28 days on water absorption and mechanical properties (Willett et al., 1998). Weight gains for PHBV-starch bars containing 25% starch were about 4–5% compared with 0.9% for PHBV alone and 40–50% for starch. After soaking, tensile strengths did not change, elongations increased, and elastic modulus values were reduced to less than half of their dry values. Water vapor permeabilities have not been reported for starch-PHA composites but would be expected to be significantly higher than for pure PHAs. Water vapor permeabilities of PHBVs alone are 20–40 times higher than for polyethylene (Shogren, 1997) and this needs to be considered for certain applications where long-term water resistance is important.

Blends of other chemically modified starches and PHAs have also been considered. Blends of starch acetates with PHB (Zhang et al., 1997) and PHBV (Koenig and Huang, 1995) were found to be incompatible and rather brittle. Blends of starch valerate and PHBV were judged to be compatible for starch valerate contents <20% (Seves, 1998). Starch propionates, maleates and other mixed esters of DS 1.2–1.8 were also found to be partially compatible with PHBV (Bloembergen and Narayan, 1995) and were reasonably strong (Table 9-1). Mechanical properties were rather insensitive to humidity, as expected due to the more hydrophobic nature of the starch esters. Similarly, Rimsa and Tatarka (1994) found that tensile strength and elongation of blends of starch propionate (DS 2.3) changed little with relative humidity. Trimethylsilyl starch acetates were also judged to be partially miscible with PHBV (Choi et al., 1994).

9.5 GELATINIZED STARCH-PHA BLENDS

There have been several studies of blends of PHAs with starch that has been gelatinized or melted in the presence of water and glycerol or other nonvolatile plasticizer (Verhoogt et al., 1995; Thire et al., 2006; Godbole et al., 2003; Lai et al., 2006). These blends are generally incompatible as evidenced by separation of large phase sizes (Verhoogt et al., 1995). The advantage of using plasticized over using granular starch is that plasticized starch has significant flexibility with elongations of typically 10–100% (Shogren et al., 1992). Strength properties of the blends tend to be poor both because of poor interfacial adhesion and because of the rather low strength of the starch-plasticizer phase (1–8 MPa) (Thire et al., 2006; Lai et al., 2006; Shogren, 1993). In addition, the presence of hydrophilic plasticizers such as glycerol increases the water absorption of thermoplastic starch at high humidities (Shogren et al., 1992), so that strength and stiffness would be expected to decline as humidity increased. As with granular starch blends, compatibilizers such as ethylene-vinyl acetate copolymer (Dabi and Kataria, 1994) or poly(vinyl alcohol) (Deng et al., 2002) could be added to improve properties. Properties of blends of plasticized starch with other polyesters have been reviewed (Averous, 2004).

9.6 THERMOPLASTIC STARCH/PHA LAMINATES AND FOAMS

In these types of structures, thermoplastic starch makes up the bulk of the material with the PHA being a small component, typically 5–20% or less. The PHA acts as a water resistant outer coating and/or aids the foam expansion process. Lawton (1997), Shogren and Lawton (1998), and Doane et al. (2000) have described coating starch-based foams and films with PHBV. Solvent-applied PHBV coatings ordinarily have low adhesion to starch (Lawton, 1997), but much improved adhesion was found by first coating starch foam plates with natural resins such as shellac or rosin (Shogren and Lawton, 1998), zein, or hydroxyl-functional polyester (Doane et al., 2000). These materials have both hydrogen bonding

capability and hydrophobic content and thus have good adhesion to both starch and PHAs. Martin et al. (2001) prepared glycerol-plasticized starch films laminated with PHBV by coextrusion. They also found low values of peel strength for PHBV (0.01 N/mm), especially compared with other polyesters such as polyester amide (0.16 N/mm). Wang et al. (2000) found that peel strengths of polyesters on thermoplastic starch could be enhanced by creating a rough interface during the coextrusion process. Adhesion of PHBV to thermoplastic starch using only water as a plasticizer was higher than when glycerol was added. Laminates of thermoplastic starch with PHAs have also been claimed in the patent literature (Buehler, 1994; Wnuk, 1995; Bastioli et al., 1996; Bond and Noda, 2003), but little information on the properties of the materials were provided.

Water vapor permeabilities of PHBVs (for 25 μm thick film) ranged from 1.8–3.5 $\text{g}/\text{m}^2/\text{day}$ at 6°C, 13–26 $\text{g}/\text{m}^2/\text{day}$ at 25°C, and 124–245 $\text{g}/\text{m}^2/\text{day}$ at 50°C (Shogren, 1997). Therefore, a coating of PHBV/shellac on an 8-in. (20 cm) diameter starch foam plate for instance would transmit <0.8 g water per day at room temperature. Such a small amount of water would not be expected to significantly change the mechanical properties of a starch plate weighing 10–20 g (Shogren and Lawton, 1998). Martin et al. (2001) also found that thermoplastic starch films extrusion laminated with polyesters did not swell significantly after soaking in water for a few days. Thus, thermoplastic starch foams and films laminated with a

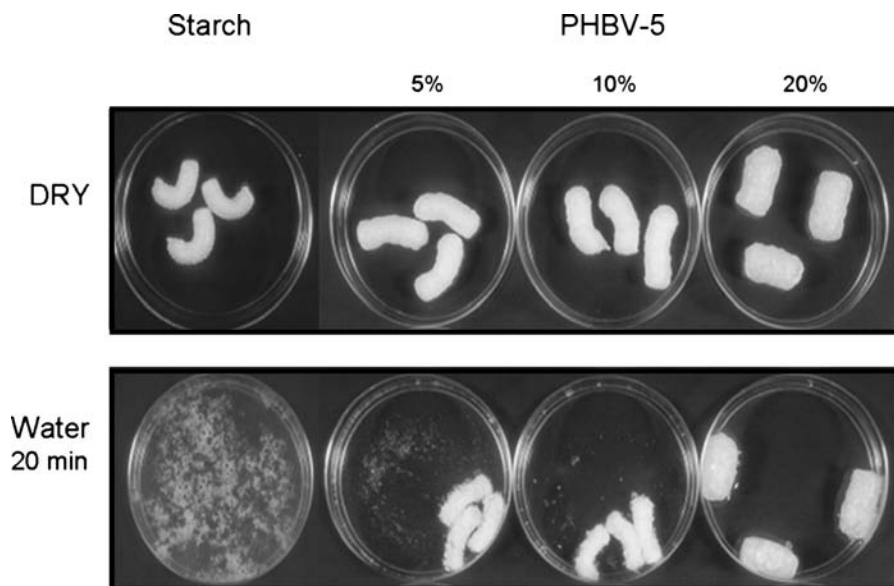


Fig. 9-3 Photographs of extruded foam peanuts containing corn starch and starch/PHBV-5 (5–20% PHBV) before and after soaking in water for 20 min. Peanuts were prepared as described in Willett and Shogren (2002).

thin layer of PHA appear to be suitable for applications requiring short-term exposure to water.

Willett and Shogren (2002) have described properties of extruded starch/PHBV foams containing 5–20% PHBV. Addition of PHBV enhanced foam expansion considerably, giving foam densities of 25 kg/m³ with 20% PHBV-5 compared with 61 kg/m³ for starch alone. Addition of other linear polymers also gave higher foam expansions, suggesting that perhaps the viscoelastic properties of the added polymer are important for expansion. Most of the PHBV existed as separate elongated inclusions about 1–5 µm in length within the starch matrix. Foam surfaces were, however, enriched with PHBV, probably due to the lower surface energy of PHBV than starch. As a result, the starch/PHBV foams had much greater water resistance than starch foams and fragmentation on impact (friability) was reduced. Photographs of starch foam peanuts prepared with 0–20% PHBV-5 are shown in Fig. 9-3. After soaking in water for 20 min., the pure starch peanuts have largely dispersed in water, whereas the peanuts containing 20% PHBV-5 have similar size and shape as the dry ones.

9.7 BIODEGRADABILITY, RECYCLING, AND SUSTAINABILITY

There have been several studies of the biodegradation of starch–PHA blends in different environments (Yasin et al., 1989; Tanna et al., 1992; Lauzier, 1993; Ramsay et al., 1993; Yasin and Tighe, 1993; Imam et al., 1995; Willett and O'Brien, 1997; Imam et al., 1998; Imam et al., 1999; Gordon et al., 2000; Avella et al., 2002; Rosa et al., 2003) as well as studies of the individual components (Allen et al., 1994; Vikman et al., 1995). Selected data from these studies are summarized in Table 9-3.

TABLE 9-3 Biodegradation of Starch–PHA Composites

Starch (%)	PHA	Thickness (mm)	Environment	Time (day)	Weight loss (%)	Reference
0	PHBV19	0.8	Activated sludge	30	30	Ramsay et al. (1993)
25		0.8	Activated sludge	30	85	
50		0.8	Activated sludge	30	100	
0	PHBV7	0.5	Compost	20	60	Tanna et al. (1992)
30		0.5	Compost	20	100	
0	PHBV12	3.2	Soil	125	7	Imam et al. (1998)
30		3.2	Soil	125	25	
50		3.2	Soil	125	49	
0	PHBV12	0.5	Marine	150	10–20	Imam et al. (1999)
30		0.5	Marine	150	50–90	
50		0.5	Marine	150	90–100	
30	PHBV5	Not given	Compost	20	100	Avella et al. (2002)

In all cases starch-PHA blends were found to be biodegradable over a period of weeks to months in all environments tested including soil, compost, activated sludge under aerobic and anaerobic conditions, and marine environments. This was expected since both starch and PHAs are natural products that are hydrolyzed by amylases and esterases. A number of factors influence biodegradation rates including sample thickness, moisture content, temperature, microbial activity, presence of starch/PHA degraders, presence of plasticizer, and molecular weight and crystallinity of the polymers. Rates of biodegradation tended to be high in compost and activated sludge, probably due to the high numbers of PHA depolymerase-producing microorganisms as well as the high temperatures used in composting. In the marine environment, microbial counts can vary significantly depending on location (near shore vs. deep water) (Imam et al., 1999). Imam and co-workers also found that starch-degrading microorganisms were about 10 times more abundant than PHA degraders. As a result, biodegradation and removal of starch from the composite samples largely preceded biodegradation of PHBV. In most of the studies, rates of biodegradation increased with starch content, probably because more surface area for microbial/enzyme attack was created as the more rapidly degraded starch was removed. Rates of degradation also increased with addition of CaCO_3 filler (Willett and O'Brien, 1997). These aspects allow the tailoring of biodegradation rates of starch-PHA composites to suit a particular application.

Slow but significant rates of hydrolysis of starch/PHBV and PHBV occur on exposure to aqueous environments (Yasin et al., 1989; Yasin and Tighe, 1993). This may be an important factor if PHA blends are to be considered for very long-term applications such as consumer durables.

Much of the initial interest in biodegradable plastics was the result of the perceived shortage of landfill space, hazards of nondegradable plastics to wildlife, and the MARPOL treaty, which forbids disposal of plastics from ships at sea. The costs of landfilling, which are particularly high in some areas of coastal U.S.A., Europe and Asia, continue to provide impetus for the development and use of biodegradable plastics. For many applications such as agricultural mulch film, planting pots, and military meals-ready-to-eat packaging, it is difficult or expensive to collect and dispose of these plastic articles after use. Nondegradable plastics in the marine environment including old netting, fishing line, and garbage washed into the sea from coastal areas continue to threaten marine life.

More recently, with growing worldwide concern about global warming and shortages of oil, there is interest in PHBV, starch and other polymers made from renewable resources such as agricultural commodities. Although biodegradation is still an option for disposal of starch-PHBV materials, more consideration is being given to recycling back into the monomeric hydroxyacids (Kaihara et al., 2005; Reddy et al., 2003). This can easily be accomplished by enzymatic depolymerization. Presumably, new PHAs could then be biosynthesized from the hydroxyacids and glucose from depolymerized starch. As the prices of agricultural commodities of all kinds grow rapidly due to increases in global population, economic growth, and increased biofuel production, this may become a more attractive option than mineralization back to CO_2 and water. Recycling of polyesters such as PHAs by the

depolymerization/repolymerization route should be much easier than for petrochemical addition polymers like polyethylene and this bodes well for the future of PHA–starch composites.

The sustainability of PHAs and starch blends has been reviewed recently by Patel and Narayan (2005). They conclude that energy use and CO₂ emissions for the production of PHAs are currently similar to or higher than those for petrochemical polymers. This is likely to change in the future, however, as production becomes more efficient. They did note, however, that a Japanese study found CO₂ emissions to be much lower for PHB production than for commodity synthetic polymers. They also summarized findings that energy use and CO₂ emissions are significantly lower for starch, thermoplastic starch, and starch blends than for polyethylene or polystyrene.

9.8 APPLICATIONS AND PRODUCTION

Applications for PHA/starch blends can be diverse since properties of PHAs run the gamut from highly flexible, mimicking polyethylene, to rigid, similar to polypropylene or poly(ethylene terephthalate). These can include film and sheet for packaging, disposable items, and agriculture; injection molded articles for food serving, housewares, electronics, and automotive uses; foams for cushioning and insulation; and fibers for textiles, wipes, filtration and hygiene, and coatings/adhesives. The degree of market penetration for starch/PHA blends will depend on the price of PHA and the amount of PHA needed in the blend. Initially, blends that require PHAs to be only a small fraction of the material such as PHA-laminated starch films and foams may be preferred. Applications such as biodegradable garbage bags and mulch films (Halley et al., 2001) are attractive targets since they are single-use items. The starch component of the films can serve as a good barrier against permeation of oxygen or various organic molecules (Rankin, 1958), a property lacked by PHAs or other hydrophobic polymers such as polyethylene. Currently, microbial PHAs are produced on a small scale by Metabolix/ADM but a 110 million pound per year plant is set to start in late 2008. Later, production of PHAs in plants is expected at prices comparable to or lower than petrochemical polymers.

9.9 FUTURE RESEARCH NEEDS AND DIRECTIONS

From previous studies, it appears that compatibilization of granular starch/PHA blends by free radical generation works well. This work needs to be confirmed, studied in greater depth and extended to gelatinized starch blends. In addition, other methods such as grafting onto starch, that have proved valuable for blends of starch with other polyesters (Mani and Bhattacharya, 2001; Dubois and Narayan, 2003; Kalambur and Rizvi, 2006) could be investigated. Starch–PHA graft copolymers could have some additional interesting applications as surfactants and as self-assembled nanostructures. Starch-based nanocomposites have been prepared with

other polyesters and nanoclays and these show improved mechanical properties (Dufresne, 1998; Kalambur and Rizvi, 2004). The compatibility of moderately and highly derivatized starches with PHAs is a guessing game at present and would benefit from molecular modeling approaches. PHAs biosynthesized with functional or reactive side-chains are another avenue for improving compatibility that can be pursued. The effects of starch modification or reactive compatibilization on the biodegradation rates have not been characterized extensively. Starch has the potential to form inclusion complexes with ionic polymers (Shogren et al., 1991), so similar complexes might form between starch and a carboxy-modified PHA, for instance. Few studies have addressed the problem of increased water sensitivity of starch-PHA composites. Competition of starch/PHA blends with natural fiber-PHA composites is apparent (Hodzic, 2005) and the advantages and disadvantages of both need to be compared and analyzed. Finally, natural PHA latex and blends with starch have potential as adhesives (Lauzier et al., 1993) and further investigation in this area seems warranted.

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Biodegradable Blends Based on Microbial Poly(3-hydroxybutyrate) and Natural Chitosan

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10.1 INTRODUCTION

Biodegradable blends have been attracting increasing interest because of their potential applications, which range from environmentally degradable resins through biomedical implants to absorbable surgical sutures. Among the various biodegradable materials, microbial poly(3-hydroxybutyrate) (PHB) and chitosan (CS) have been a new focus of research as important candidates for biomaterials because they are renewable polymers from sustainable natural resources. PHB is a natural occurring crystalline polyester, which is accumulated as intracellular energy reserves (Doi 1990; Reddy et al., 2003). CS is a natural polysaccharide produced by the

deacetylation of chitin, which is the second most abundant biopolymer in nature after cellulose. Although both PHB and CS are biocompatible and biodegradable *in vivo* and *in vitro*, they are difficult to apply individually because of some inherent drawbacks (Avella et al., 2000; Chen et al., 2002).

The blending of PHB and CS is a convenient and effective approach to improve their physicochemical properties and to develop low-cost and high-performance biodegradable composites. Because there are many functional groups on its molecular chains, CS is very useful in the development of composite materials such as blends or alloys with other polymers (Society, 1988; Muzzarelli, 1977). Blending of PHB with CS offers the possibility of new materials for medical applications due to their low cost and excellent biocompatibility and biodegradability, especially in tissue engineering. NIH 3T3 fibroblasts can be cultured on scaffolds made from the PHB/CS blends (Cao et al., 2005). The presence of PHB enhances cell attachment to the scaffolds and the cells spread and grow well on PHB/CS scaffolds. In addition, the PHB and CS conjugates may form strong and elastic films (Yalpani et al., 1991) and copolymers of PHB grafting CS also show high antibacterial activity, which can be used for wound dressings (Hu et al., 2003). By incorporating PHB with CS, the functional groups on the CS chains can be available for further modification such as conjugation of biomolecules, which will widen the application of the blend system. Nanofiber technology represents an important direction for material research studies, and material performance of chitosan nanofibers in the medical field is very promising (Ohkawa et al., 2006). An elegant method for nanofiber production is now well known as “spinning,” which allows fabrication of a fine and dense meshwork of polymer fibers directly from solution in the presence of an electric field (Doshi and Reneker, 1995). Application of the pure chitosan nanofibers in medical technology has been reported as a guided bone regeneration material (Shin et al., 2005) and as a scaffold for regenerating nerve tissue. Poly(L-lactide) (PLLA)/CS fabrics are produced by the blend spinning technique. The compatibility between PLLA/CS fabrics and osteoblasts under *in vitro* degradation has been investigated for the potential application of PLLA/CS fabrics as supporting materials for chest walls and bones. Excellent adhesion between osteoblasts and PLLA/CHS fabrics is observed, indicating good biocompatibility of the fabrics with osteoblasts (Zhang et al., 2007). PLLA/CS fabrics may thus be an ideal osteoblast carrier for the repair of damaged chest wall and bones over a large area, since the pore size and porosity of the PLLA/CS braid can be adjusted according to the cell characteristics. Given that PHB is usually hydrolyzed by extracellular depolymerases but is hardly degraded by intracellular depolymerases, fabrics based on PHB and CS are likely to have wider application as biomedical materials than PLLA/CS fabrics because PHB shows longer biodegradation times *in vivo* than does PLLA (Sang, 1996).

So far there have been few studies on the blending of PHB and CS because they are difficult to mix due to their natural properties. Generally, PHB and CS are blended by solution blending rather than melt blending because CS hardly melts and its glass transition temperature (T_g) is very close to the thermal decomposition temperature of PHB (Sakurai et al., 2000). The properties of melt-blended CS with aliphatic polyesters such as poly(lactic acid) (PLA) show that the CS and polyesters form

phase-separated systems (Correlo et al., 2005). The general properties of the blends are usually strongly relevant to the preparation methods, and preparation with different methods will exhibit major differences in terms of properties, particularly in the PHB/CS blend system. Three major methods for preparing PHB/CS blends are presented below, together with the corresponding properties of the blends.

10.2 PREPARATION AND PROPERTIES

10.2.1 Solution-Casting Method (Ikejima et al., 1999)

10.2.1.1 Preparation of PHB/CS and PHB/Chitin Blends 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was used as a common solvent. PHB, CS, and chitin were dissolved in HFIP and cast on a poly(tetrafluoroethylene) (PTFE) dish. After drying, PHB/CS and PHB/chitin films with different compositions were obtained. Although this method is very simple, the common solvent HFIP is very expensive, which limits its application.

10.2.2 Characterization and Properties

10.2.2.1 Miscibility In general, differential scanning calorimetry (DSC) is not a good method to accurately measure the T_g values of CS and its blends. The molecular structure of CS consists of rigid β -1,4-linked D-glucosamine units, so changes in heat capacity corresponding to changes in specific volume (or molecular mobility) at T_g are correspondingly small. This gives rise to a very small observed baseline step change in the DSC curves (Sakurai et al., 2000), which will introduce a large error in the DSC measurement of the T_g of CS. Because the conventional method of T_g measurement using DSC could not be applied in the PHB/CS blend system, dynamic mechanical thermal analysis (DMTA) was used to detect the miscibility of the PHB/CS blends (Ikejima and Inoue, 2000). However, the temperatures of the $\tan \delta$ transition detected in the PHB/CS blends were not greatly different from that detected in pure PHB (around 15°C, which corresponded to the T_g of the PHB amorphous region).

There was an exception, in that a single T_g was found in the PHB/CS blend system where the T_g of CS was found to be 103°C (Cheung et al., 2002), implying that the PHB/CS blends were miscible. For all different compositions, the T_g values were higher than those of the calculated weight-averaged values. This was attributed to the strong intermolecular hydrogen bonding between the PHB and CS components. The phenomenon is completely different from the common miscible blends with specific interactions in which the T_g values of the blends are intermediate to those of two components (Zhang et al., 1997), whose values can be described by several equations such as the Fox, Gordon–Taylor, and Couchman equations. In order to further investigate the phase structure of the PHB/CS blends, ^1H CRAMPS (combined rotation and multiple pulse spectroscopy) was used. ^1H T_1 was measured with a modified BR24 sequence that yielded an intensity decay to zero mode

rather than the traditional inversion recovery mode (Cheung et al., 2002). Single exponential T_1 decay was observed for the PHB/CS blends and their T_1 values were either faster than or intermediate to those of the plain polymers. The $T_{1\rho}$ decay of β -hydrogen belonging to PHB was biexponential. The slow $T_{1\rho}$ decay component was explained as a result of the crystalline phase of PHB. The fast $T_{1\rho}$ of β -hydrogen and the $T_{1\rho}$ of CS in the blends either followed the same trend as or were faster than the weight-averaged values based on the $T_{1\rho}$ of the plain polymers. Together with the result that single T_g was detected by DSC, evidence from solid-state ^{13}C NMR strongly suggested that CS was miscible with PHB at all compositions.

10.2.2.2 Thermal and Crystallization Behavior In the PHB/CS blend system investigated by Ikejima (Ikejima et al., 1999), the melting curves of the blends exhibited two melting peaks in the range of PHB melting. The peak appearing at a lower temperature was attributed to the melting of the crystalline film as cast. The other melting peak at a higher temperature was attributed to the melting of the recrystallized component. Although the PHB/CS blends were prepared and investigated under the same conditions, a single melting peak was found in the same blend system (Cheung et al., 2002); in particular, the peak at a lower temperature appeared in a different temperature region. This is possibly due to the differences in the materials used.

DSC also revealed that the crystallization of the PHB component in the blends was suppressed with increasing CS content. Taking advantage of the FTIR crystalline-sensitive peak of the PHB carbonyl stretching band, the crystallinity of the PHB component was determined quantitatively, and the results was in agreement with that obtained from the DSC measurement. Compared with α -chitin, CS exhibited a stronger ability to suppress the crystallization of PHB, due to the presence of the amino groups (Ikejima et al., 1999). From the solid-state ^{13}C NMR results, PHB in the blends was found to be trapped in the "glass" environment of CS. The corresponding X-ray diffraction (XRD) data also confirmed the results (Ikejima and Inoue, 2000). Because the CS resonances in the solid-state ^{13}C NMR spectra were significantly broadened after blending with PHB, it was suggested that there were intermolecular hydrogen bonds between the carbonyl groups of PHB and the amino groups of CS. The specific interaction between PHB and the highly rigid CS molecules surrounding the PHB molecules would make the PHB molecules in the blends inflexible, and would induce insufficient crystallization relative to pure PHB. Hence, the lamellar thickness of the PHB crystalline component became thinner, which was large enough to show detectable XRD peaks but was too small to show an observable melting endotherm in the DSC thermogram and the crystalline band absorption in the FTIR spectrum (Ikejima et al., 1999; Ikejima and Inoue, 2000).

10.2.2.3 Environmental biodegradation Environmental biodegradation of PHB/CS blends was investigated using the biochemical oxygen demand (BOD), whose values were determined by the amount of oxygen consumption (Ikejima and Inoue, 2000). Compared with the low biodegradability of pure CS and chitin,

the biodegradability was clearly improved by blending with PHB, especially for CS. This was attributed to the low crystallinity of the PHB component.

10.2.3 Precipitation Blending Method (Chen et al., 2005)

10.2.3.1 Preparation of PHB/CS and Maleated PHB/CS Blends PHB and maleated PHB (PHB-*g*-MA) dissolved in dimethyl sulfoxide (DMSO) were mixed with the CS solution in acetic acid–DMSO. After being well homogenized, mixtures with different compositions were precipitated in excess acetone, and the precipitates were filtered off and dried to obtain the PHB/CS blends and the PHB-*g*-MA/CS blends.

Because few common solvents are known for PHB and CS, precipitation blending allows on to obtain PHB/CS blends more easily and cheaply than the common solution-casting. The method may also be extended to similar blend systems consisting of hydrophilic CS and hydrophobic aliphatic polyesters (Chen et al., 2005).

10.2.4 Characterization and Properties

10.2.4.1 Intermolecular Hydrogen Bonds In the PHB/CS blend system, the detection of intermolecular hydrogen bonds depends on the preparation methods of the samples and the related measurements. When the PHB/CS blends were prepared with the solution-casting method, intermolecular hydrogen bonds between the two components could be detected by ^{13}C solid-state NMR, while no detectable changes were found in the FTIR spectra. However, obvious changes were seen in the FTIR spectra of PHB/CS blends that were prepared by the precipitation blending method. It was interesting that in the precipitation blending method the intermolecular hydrogen bonds between PHB and CS components depended on the compositions in the blends. In the FTIR spectra of the PHB/CS blends with compositions of 20/80 and 40/60, the CS amino band at 1596 cm^{-1} disappeared, and the PHB amorphous carbonyl vibration at 1740 cm^{-1} became very clear, which indicated that the intermolecular hydrogen bonds were caused by the PHB carbonyls and the CS amino groups in the amorphous phase. Compared with the PHB/CS blends, the blends containing PHB-*g*-MA and CS showed intermolecular hydrogen bonds up to a higher composition of PHB-*g*-MA/CS = 60/40, indicating that the MA groups grafted onto PHB chains could further form hydrogen bonds with amino groups on the CS chains and then intensify the interaction between two components (Chen et al., 2005). When the PHB content amounted to 60% or above and the PHB-*g*-MA content was 80%, the intermolecular interaction between both components disappeared. X-ray photoelectron spectroscopy (XPS) provides a very sensitive way to detect changes in the molecular interactions in the blends. In PHB/CS blends, it was found that the N1s binding energy (BE) of CS in the blends with the compositions of 20/80 and 40/60 was increased, and the C1s BE values of the PHB carbonyl bonds in the blends with the same compositions decreased. These BE shifts were exhibited more obviously in the PHB-*g*-MA/CS blends, besides the changes of the PHB C1s peak shapes. This was because the

chemical environments of carbon or nitrogen atoms in the blends were perturbed by specific intermolecular hydrogen bonds.

10.2.4.2 Thermal Behavior of PHB/CS and PHB-g-MA/CS Blends

PHB/CS blends prepared by the solution-casting method can gradually crystallize as the solvent slowly evaporates, whereas crystallization is difficult during the precipitation process. Hence, PHB/CS blends prepared by the precipitation blending method exhibited a single melting peak in the heating process, which resulted mainly from the melting of the crystals formed during both the thermal treatment and heating process. As the PHB content in the blends decreased, the melting temperatures, the melting enthalpies, and the crystallinity of the PHB/CS blends gradually decreased, which suggests that the introduction of CS into PHB could effectively hinder its crystallization. The MA groups grafted onto the PHB chains might further suppress the crystallization of the PHB component.

10.2.4.3 Crystallization of PHB/CS and PHB-g-MA/CS Blends When PHB was blended with CS, the crystallization of the PHB component was clearly suppressed. Moreover, the CS diffraction peaks disappeared in all compositions (Fig. 10-1a), indicating that the crystallization of CS was obviously changed. The suppression was more remarkably in the PHB-g-MA/CS blends. It should be noted that the crystallite growth of the PHB and PHB-g-MA components was different in different directions. Relative to that of the (020) diffraction, the intensity of the (110) diffraction in the PHB and PHB-g-MA components was always suppressed in the blends with compositions for which there were specific interactions (Fig. 10-1b), indicating that the hydrogen bonds in the blends not only affected the crystallinity of the blends but also disturbed the original crystal structures of the two components.

10.2.5 Emulsification Casting Method (Cao et al., 2005)

10.2.5.1 Preparation of PHB/CS Films CS dissolved in acetic acid was mixed with PHB solution in chloroform. After being cast into films, the mixtures were neutralized in 0.5 M NaOH aqueous solution, washed thoroughly with deionized water, and then dried at room temperature. It is noted in the method that the viscosity of the CS solution should be high enough to keep the stability of the PHB droplets dispersed in the CS solution. It is very difficult to form homogeneous solutions with water and chloroform, and serious phase separation will take place in the PHB/CS blend as the solvents fully evaporate. Because of this solubility limitation, the method can only prepare blend films with a low PHB content (the highest PHB content in the blends is 30%) (Cao et al., 2005).

In order to improve the emulsification effect, the emulsifying agent poly(vinyl alcohol) (PVA) was used (Shih et al., 2007). PHB solution in methylene chloride was mixed with CS solutions in acetic acid in the presence of 1% (g/ml) PVA. The emulsified microspheres (shown in Fig. 10-2) were finally collected by a freeze-drying method.

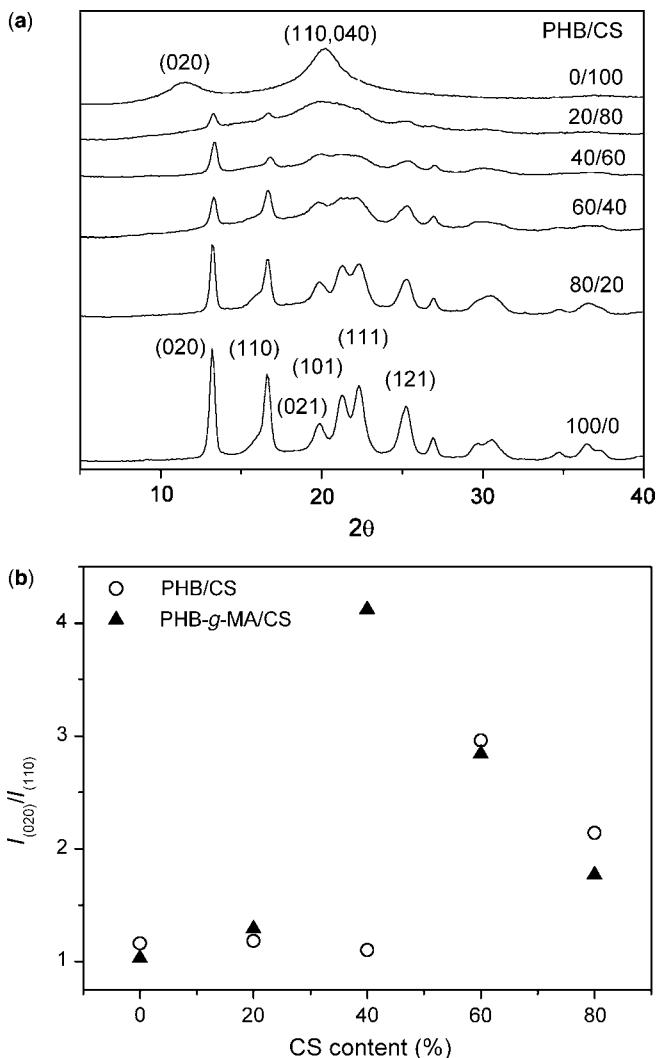


Fig. 10-1 (a) WAXD profiles of PHB, CS, and the PHB/CS blends with different compositions prepared by the precipitation blending method. (b) The relationship of the values of $I_{(020)}/I_{(110)}$ with CS content in the blends.

10.2.6 Characterization and Properties

10.2.6.1 Physical Properties of PHB/CS Films In the PHB/CS films prepared with the emulsification casting method, PHB remained as microspheres in the blend films. There was no interfacial adhesion between the PHB microspheres and the CS matrices due to a lack of intermolecular interaction. After blending PHB with CS, the PHB/CS films exhibited a higher tensile strength than the pure CS film. With

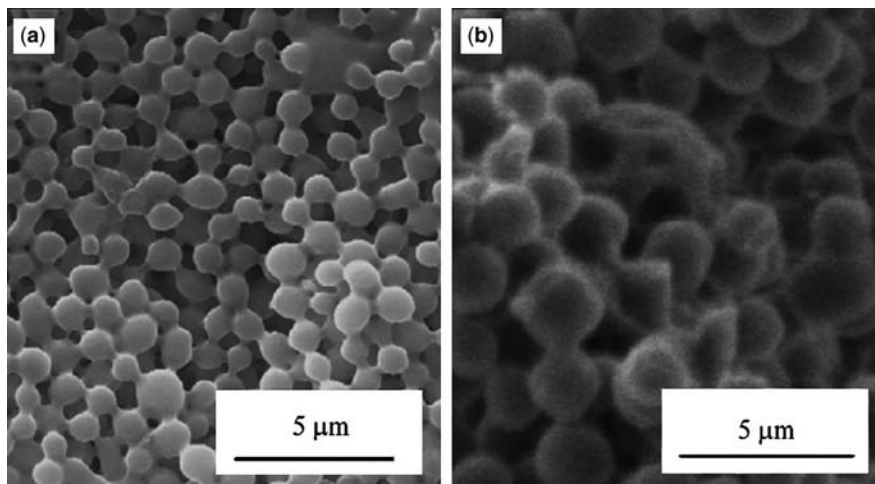


Fig. 10-2 SEM images of PHB/CTS microspheres at different PHB/CTS ratios: (a) 1 : 1; (b) 5 : 1.

increase in the PHB content, the elastic modulus of the PHB/CS films decreased and the elongation-at-break increased, which was attributed to the toughening effect of the PHB microspheres by a crack-pinning mechanism. In addition, the swelling capability of the PHB/CS films was lowered because of the introduction of hydrophobic PHB. The same method was used to prepare the PLA/CS blends. The incorporation of PLA into CS improved the water barrier properties and decreased

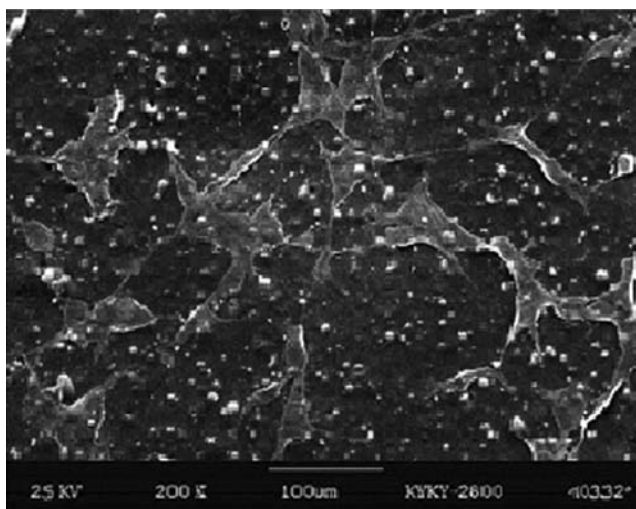


Fig. 10-3 SEM image of NIH 3T3 cells on PHB/CS films after 24 h in culture.

the water sensitivity of CS. However, the tensile strength and elastic modulus of CS clearly decreased with the addition of PLA (Suyatma et al., 2004).

10.2.6.2 Cytocompatibility of PHB/CS Films NIH 3T3 fibroblasts were used to examine the cytocompatibility of PHB/CS films. The fibroblasts were attached to the blend films, and exhibited normal flat morphology even if the cell were grown on PHB microspheres (shown in Fig. 10-3). These results indicated that the PHB/CS films could support the attachment and growth of fibroblasts. The experiments on cell adhesion and cell proliferation further showed that the PHB/CS films had better cytocompatibility than the CS film, probably due to the better biocompatibility of PHB and the rough surface of the blend films.

10.3 CONCLUSIONS

New kinds of biomaterials based on PHB and CS can be produced using different effective blending methods. PHB/CS blends are expected to possess excellent biocompatibility and biodegradability and are especially suitable for application as biomedical materials. When prepared by the solution-casting method, the PHB/CS blends are miscible at all compositions, which means that the blends should synergistically possess the properties of both components. The introduction of CS hinders the crystallization of PHB because of the rigid CS surrounding environment and intermolecular hydrogen bonds between the components. The precipitation blending method offers an easy and convenient approach to prepare the blends or composites including hydrophilic CS and hydrophobic polyesters. The ductility of CS can be improved by decreasing self-hydrogen bonds among CS chains and lowering its crystallinity (Alexeev et al., 2000; Kolhe and Kannan, 2003). Thus, by manipulating the formulation conditions, the composition, and the thermal treatment, one may use the precipitation blending method as an effective way to improve the ductility of CS. The emulsification casting method differs from these two methods. By taking advantage of suitable solvents and emulsifying agents, polymeric blends with complete different solubility can be achieved. By adjusting the types of solvents and emulsifying agents, and changing the evaporation rate of the solvents, the phase morphology and size of the blends may be effectively controlled to satisfy the end-use demand.

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