

Mechanical and Thermal Properties of Starch-Filled Poly(D,L-lactic acid)/Poly(hydroxy ester ether) Biodegradable Blends

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ABSTRACT: The mechanical, structural, and thermal properties of injection-molded composites of granular cornstarch, poly(D,L-lactic acid) (PDLLA), and poly(hydroxy ester ether) (PHEE) were investigated. These composites had high tensile strengths, ranging from 17 to 66 MPa, at starch loadings of 0–70 wt %. Scanning electron microscopy micrographs of fracture specimens revealed good adhesion between the starch granule and the polymer matrix, as evidenced by broken starch granules. The adhesion of the starch granules to the polymer matrix was the greatest when the matrix PDLLA/PHEE ratios ranged from zero to unity. At a PDLLA/PHEE ratio of less than unity, as the starch content increased in the composites, there was an increase in

the tensile strength and modulus, with a concurrent decrease in elongation. The effects of starch on the mechanical properties of starch/PDLLA composites showed that as the starch content of the composite increased, the tensile strength and elongation to break decreased, whereas Young's modulus increased. In contrast, the tensile strength of starch/PHEE composites increased with increasing starch content. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1775–1786, 2003

Key words: biomaterials; composites; mechanical properties; morphology

INTRODUCTION

Starch has generated considerable research interest as a filler for polymers that reduces their costs and increases their biodegradability. As a filler, it tends to reduce the tensile strength, elongation to break, and toughness of a blend and to increase the blend's modulus.^{1,2} Starch is inexpensive (ca. \$0.10/lb), biodegradable, and available from crops that are produced in abundance, such as corn and wheat. Previously, blends of granular and deconstructed starch with various other polymers have been reported.^{1–5} To impart biodegradability to polymers, starch has been blended with common polymers such as poly(vinyl chloride),⁶ polyethylene,^{7,8} poly(ethylene-co-acrylic acid),^{8,9} and poly(ethylene-co-vinyl alcohol).¹⁰ Moreover, starch has been blended with other biodegradable polymers, such

as aliphatic polyesters, to lower the cost and to enhance the biodegradability of blends. Some examples of polymers with which starch has been blended are polycaprolactone (PCL),¹¹ poly(vinyl alcohol),¹² and poly(hydroxybutyrate-co-3-hydroxyvalerate) (PHBV).^{11,13} Several recent attempts to achieve biodegradability in polymer compositions containing starch were undertaken by Uemura et al.,¹⁴ Wnuk et al.,¹⁵ and Bastioli et al.¹⁶ They blended thermoplastic starch with synthetic polymers such as ethylene/vinyl acetate, PCL, poly(α -hydroxyalkanoate)s, poly(vinyl alcohol), and poly(vinyl pyrrolidone). Other studies involving blends of thermoplastic starch and synthetic polymers were undertaken by Otey and coworkers^{6,17–19} and Fanta and coworkers^{20–22} at the U.S. Department of Agriculture in Peoria, IL. Ramsay et al.¹³ blended granular starch with PHBV. With the starch content increasing from 0 to 50% (w/w), the tensile strength decreased from 18 to 8 MPa, and Young's modulus increased from 1525 to 2498 MPa. The biodegradation rate was faster when starch was present in PHBV and also when the degradation was aerobic rather than anaerobic. Park et al.²³ blended granular cornstarch with poly(lactic acid) (PLA) and also star-shaped PLA. In addition, they incorporated PCL into the blends. Sun and Ke²⁴ blended PLA with granular cornstarch and wheat starch. They found that adhesion between both types of PLA and the starch granules was relatively poor. An increase in the starch content resulted in a reduc-

Names are necessary to report factually on available data. However, the U.S. Department of Agriculture neither guarantees nor warrants the standard of the product, and the use of the name by the U.S. Department of Agriculture implies no approval of the product to the exclusion of others that may also be suitable.

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tion of the tensile strength and elongation of the blends. They suggested that starch played a role as a nucleating agent for poly(L-lactic acid). In addition, Sun and Ke²⁵ investigated the effects of the starch moisture content, before processing, on the mechanical and thermal properties of starch/PLA blends. Six different moisture contents were investigated, and the moisture content had few effects on the mechanical properties of the blends. Furthermore, the PLA thermal and crystallization properties and the interactions between starch and PLA were relatively unaffected. Other studies involving blends of granular starch and synthetic polymers were undertaken by Griffin,²⁶ who investigated blends containing polyethylene as well as the silanization of the starch granule.

Recently, there has been interest in aliphatic polyesters because of their biodegradability and biocompatibility. One such polymer is PLA on account of its use in biomedical applications and its potential uses in food containers, packaging, fibers, and coatings. PLA is easily hydrolyzed by moisture, and its hydrolysis products are nontoxic to humans.²³ PLA also possesses good mechanical properties and is easily processed. Its brittleness and fairly high cost with respect to many commercial thermoplastics limits its use in many applications.

Another biodegradable polyester, commonly called poly(hydroxy ester ether), (PHEE),²⁷⁻²⁹ is synthesized from the reaction between a diglycidyl ether and a diacid. This polymer is amorphous, possesses good mechanical properties, is biodegradable, and is easily processable.²⁷⁻²⁹ The PHEE used in this study is synthesized by the reaction of adipic acid with a bisphenol A diglycidyl ether.²⁷⁻²⁹ PHEE has been shown to adhere well to starch granules.²⁹ Previous work done at the U.S. Department of Agriculture National Center for Agricultural Utilization Research (NCAUR) involved blending granular starch^{28,30} and thermoplastic starch³¹⁻³³ with PHEE. Laminates, foams, and molded articles containing high levels of starch were developed with acceptable mechanical properties.

St. Lawrence et al.^{34,35} studied the mechanical properties of neat PHEE and starch-filled PHEE composites. They found that there was good adhesion between dried starch granules and PHEE, and as a result, debonding did not occur during mechanical testing. The filled material was more brittle than the neat resin. The brittle nature of the filled composites was shown by low impact strengths and toughness. They found that the moisture content in neat PHEE strongly affected the mechanical properties because of changes in the glass-transition temperature (T_g). As the moisture content increased, there was a reduction in the tensile strength, yield strength, and modulus, but the strain at failure increased. Changes in T_g or the moisture content also altered the mode of failure. As the moisture content increased, PHEE became increas-

ingly ductile. This was evident in the stress-strain curves.

In this study, blends of poly(D,L-lactic acid) (PDLLA), PHEE, and granular cornstarch were prepared to combine the good mechanical properties of PDLLA and PHEE with the low cost of cornstarch. However, until recently, starch and PLA had not been successfully blended without a significant alteration of the mechanical properties because they are incompatible. There is a need for a compatibilizer that can enhance the compatibility of starch and PLA to yield a high-strength biodegradable blend. Wang et al.³⁶ investigated the use of methylenediphenyl diisocyanate (MDI) as a compatibilizer in starch/PLA blends. They found that the addition of low concentrations of MDI (0.25–0.5 wt %) during the hot mixing of approximately equal weights of dry granular starch and PLA dramatically improved the strength and elongation properties of the blend. However, the fate of the methylenediphenyl urethane linkage groups during biodegradation is unknown. In this study, PHEE was investigated as a potential compatibilizer for starch/PDLLA blends. Starch/PDLLA, starch/PHEE, and PDLLA/PHEE blends were compounded and used as control blends. The effects of varying the compositions of the blends with respect to the three aforementioned components on the thermal, mechanical, and structural properties of the blends were investigated.

EXPERIMENTAL

Materials

The PDLLA used in this study was supplied by Cargill, Inc. (EcoPLA Division, Savage, MN) with number-average, weight-average, and viscosity-average molecular weights (M_v) of 127,700, 241,200, and 187,500 g/mol, respectively. The number-average and weight-average molecular weights of PDLLA were determined by gel permeation chromatography [Waters model 510 pump (Milford, MA) and model 410 refractive-index detector with a Styragel HR 4 column and tetrahydrofuran (THF) as the solvent]. The sample concentration and injection volume were 0.1% (w/v) and 0.1 mL, respectively. Polystyrene standards with low polydispersity (Polysciences, Inc., Warrington, PA) were used to construct a calibration curve. The Mark-Houwink equation was used to calculate M_v , where $[\eta]$ is intrinsic viscosity. It is as follows in THF at 31.1°C:³⁷

$$[\eta] = 5.50 \times 10^{-4} M_v^{0.639} \quad (1)$$

The PDLLA stereoisomer content was 95% L and 5% D.

The PHEE was supplied by Dow Chemical (Midland, MI) and had a weight average molecular weight of 58,000 g/mol. Dried cornstarch (Buffalo 3401;

roughly 23% amylose and 77% amylopectin) was purchased from CPC International (Englewood Cliffs, NJ). The starch was dried in a convection oven for 4 days at 105°C to less than a 1% moisture content before processing. Wax OP was supplied by Clariant Corp. (Charlotte, NC).

Processing

The PDLA and PHEE were dry-blended in a dry material feeder (AccuRate, Whitewater, WI). These mixtures were then melt-blended in a 12-section, co-rotating twin-screw extruder [ZSK-30, Krupps Werner Pfleiderer, Ramsey, NJ; length/diameter (L/D) = 20]. Starch and wax OP were added to the blend, via a gravimetric feeder (K-Tron, Pitman, NJ) downstream, at section six (L/D = 10), before the final mixing zone of the extruder. All cornstarch formulations contained 1% wax OP as an external lubricant. There were seven heating zones on the extruder, which were set from 52 to 182°C. The die temperature was set at 80°C. Strands were extruded onto an air-cooled conveyor belt, pelletized, sealed in plastic bags, and stored in a freezer at 0°C until needed.

The extruded pellets were injection-molded into tensile bars on a 75-ton Cincinnati Milacron injection molder (model ACT-75-B (Batavia, OH)). The temperatures in the three barrel zones ranged from 121 to 182°C, depending on the composition. For starch contents of less than 60%, the sprue and mold temperatures were set at 182 and 71°C, respectively. For starch contents greater than 60%, the sprue and mold temperatures were set at 193 and 100°C, respectively. The samples were stored at 23°C and 50% relative humidity before tensile testing.

Thermal properties

A dual-cell differential scanning calorimeter (PE DSC 7, PerkinElmer, Norwalk, CT) was used to determine the thermal transitions of the blends. Approximately 20–30 mg of a sample was obtained from an injection-molded tensile bar adjacent to the gate and placed in a stainless steel pan for differential scanning calorimetry (DSC) characterization. Samples were scanned twice, and all scans were carried out from 0 to 180°C at a heating and cooling rate of 10°C/min. The first and second heating curves were recorded in all cases, and liquid nitrogen was used to cool the samples after the first and second heating. All data were obtained from the second heating curve of the DSC thermograms.

Mechanical properties

Tensile testing was carried out with an Instron 4201 tester with Series IX software (Canton, MA) with a 5-kN load cell according to ASTM D 638-99, type I.

The thickness and width of each sample were measured before testing with a micrometer (Testing Machines, Inc., Amityville, NY). The samples were tested after aging for 28 days at 23°C and 50% relative humidity in agreement with ASTM 638-99. The grip distance and gauge length were 101 and 50.6 mm, respectively. The crosshead speed was 50 mm/min. Five specimens on average were tested for each sample.

Structural analysis

Scanning electron microscopy (SEM) was performed with a scanning microscope (JSM-6400V, JEOL, Peabody, MA). The fracture surface of a tensile bar was mounted on an aluminum mount with double-sided adhesive tape. The fracture surface was then sputter-coated with gold before analysis. Magnifications were approximately 1000. Low accelerating voltages (2–5 kV) were required to avoid damage to the specimens during examination.

Transmission electron microscopy (TEM) was performed at Dow Chemical (Midland, MI) with a Philips electron microscope (FEI Co., Hillsboro, OR) operating at 120 keV. Before the analysis, the blends were sectioned cryogenically with a Reichert E cryoultramicrotome (Leica Instruments, Deerfield, IL). The sections were collected on a 300-mesh copper grid, removed from the cryochamber, and poststained in ruthenium tetroxide (RuO_4) vapors for 2 min, before examination, to stain the PHEE domains. The RuO_4 was a stabilized 0.5% solution (Polysciences). Because the starch granules tended to pick up moisture (condensate) after removal from the cryochamber, the starch swelled slightly and delaminated from the PDLA/PHEE blend. Six different starch/PDLA/PHEE formulations were examined.

RESULTS AND DISCUSSION

Thermal analysis

The T_g values for injection-molded samples of PHEE [Fig. 1(a)] and PDLA [Fig. 1(b)] were 28.9 ± 0.3 and $55 \pm 1^\circ\text{C}$, respectively. PHEE had a moisture content of $2.0 \pm 0.1\%$. Three replicates were used to obtain the standard deviations. Walia et al.³³ showed that PHEE with a moisture content of 2% had a T_g value of about 30°C. Jamshidi et al.³⁸ reported a T_g value for PLA of 55–60°C that depended on its molecular weight. The aforementioned T_g value was within but on the lower end of what Jamshidi et al. reported. The crystallization exotherm and the melting endotherm were very small for the PDLA reheating thermogram [Fig. 1(b)]. This is indicative of the slow rate of crystallization for PDLA. Finally, the crystallization and melting temperatures for PDLA were 121.5 ± 6 and $150.4 \pm 0.5^\circ\text{C}$, respectively.

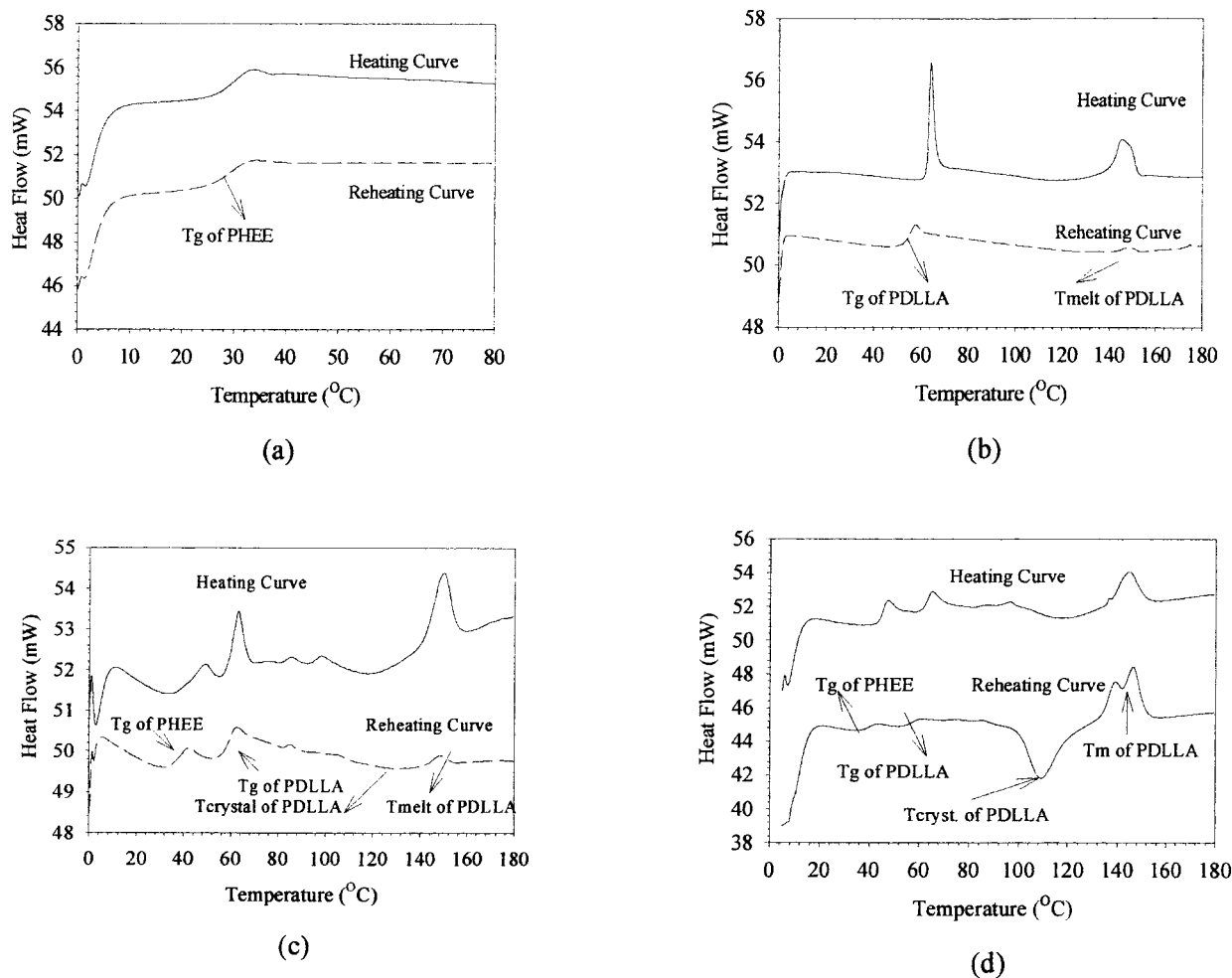


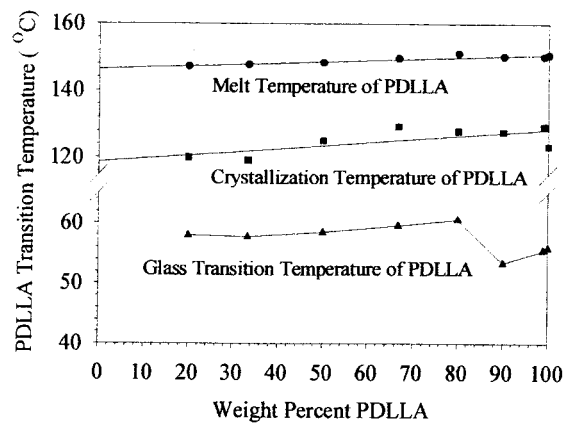
Figure 1 DSC thermograms of (a) adipic PHEE, (b) PDLLA, (c) a 50/50 PDLLA/PHEE blend, and (d) a 59/20/20/1 starch/PDLLA/PHEE/wax OP composite.

Two T_g 's were observed for all the blend and composite compositions containing PDLLA and PHEE, indicating that PDLLA and PHEE are immiscible [Fig. 1(c,d)]. The values of the T_g values in the starch-filled composites ranged from 39 to 46°C and from 52 to 61°C for PHEE and PDLLA, respectively. The crystallization and melt temperatures for PDLLA in the composites ranged from 104 to 129°C and from 140 to 151°C, respectively. A large recrystallization exotherm can be seen in Figure 1(d) but not in Figure 1(b,c); this indicates that starch may accelerate the crystallization of PDLLA in starch/PDLLA/PHEE composites. This theory was proposed by Park et al.²³ in their studies of starch/PLA blends. They found that the maximum crystallization and melt temperatures occurred at a 5% starch content. In addition, they found that the PDLLA crystallite size increased with an increase in the starch content.

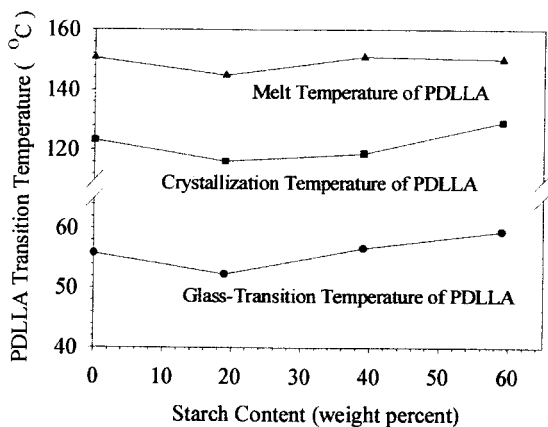
The DSC transition temperatures of PLA were plotted as a function of the PDLLA content and starch content for PDLLA/PHEE blends and starch/PDLLA composites, respectively [Fig. 2(a,b)]. As the PDLLA content increased in PDLLA/PHEE blends, T_g re-

mained fairly constant from 0 to 80% and decreased slightly from 80 to 100% PDLLA. There also were gradual linear increases in both the crystallization and melt temperatures for PDLLA as the PDLLA content of the blend increased [Fig. 2(a)]. The decrease in T_g at PDLLA levels greater than 80% cannot be explained. The small decreases in the crystallization and melting temperatures of PDLLA with an increase in the PHEE content could possibly be explained by an inhibition of PDLLA crystallization by PHEE. Smaller PDLLA crystallites would have lower values of crystallization and melt temperatures, although this was not confirmed by microscopy. For starch-filled PDLLA, there were no changes in the PDLLA T_g and crystallization temperature with changes in the starch content, within experimental error.

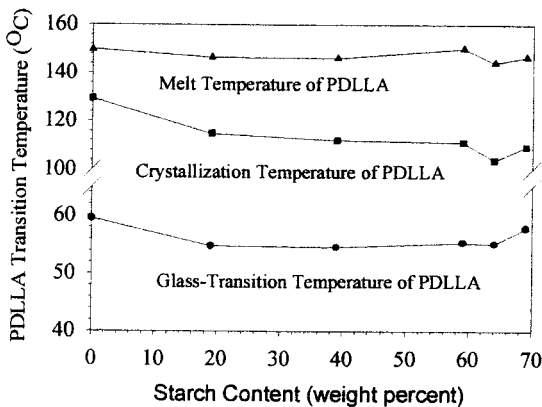
For the starch-filled PDLLA/PHEE composites, most of the thermal transition temperature data did not show any distinct trends with respect to the PDLLA/PHEE ratios. The transition temperatures of PDLLA remained relatively constant with an increase in the starch content [Fig. 2(c)]. With respect to T_g , there were generally insignificant changes in T_g with



(a)



(b)



(c)

Figure 2 Plots of (a) the PDLLA transition temperature versus the percentage of PLA for a PDLLA/PHEE blend, (b) the PDLLA transition temperature versus the percentage of starch for starch-filled PDLLA, and (c) the PDLLA transition temperature versus the percentage of starch for a starch-filled 2/1 PDLLA/PHEE composite.

an increase in the starch content. PDLLA crystallization temperatures decreased with the addition of starch to the unfilled blends. This suggests that the

rate of PDLLA crystallization possibly increased with the addition of starch to the unfilled blend and that the starch acted as a nucleating agent for PDLLA in the starch-filled PDLLA/PHEE composites.

All starch/PDLLA/PHEE/wax OP composites exhibited a double melting endotherm for PDLLA during the second heating [Fig. 1(d)]. The double melting endotherm could be attributed to the presence of morphologically different crystal structures, such as folded-chain crystals and crystals containing partially extended chains.^{23,39} Another theory proposes recrystallization during melting and, consequently, the formation of higher melting crystals.^{23,40} The double melting endotherm was only observed in injection-molded samples. It is unclear why this phenomena was observed.

Mechanical properties of the PDLLA/PHEE blends

The ultimate tensile strength for PDLLA/PHEE blends aged for 28 days decreased as the PHEE content was increased (Fig. 3). There was a pronounced decrease in the ultimate tensile strength of the blend at 50 wt % PHEE. The distinct decrease in the tensile strength was attributed to the phase inversion of the two components. At levels of 0–46% PHEE, the continuous phase was thought to be PDLLA with PHEE dispersed in PDLLA. When the levels of PHEE exceeded 50% in the blend, PHEE became the continuous phase with PDLLA dispersed in it. TEM micrographs [Fig. 4(a,b)] of starch/PDLLA/PHEE composites show that at 8% PHEE, PHEE was dispersed in the PDLLA matrix. When the PHEE level was 27% (54% PDLLA), there was a lamellar array of PDLLA and PHEE, which suggested that a phase inversion was taking place. The elongation of the blends (%) showed the same trend [Fig. 5(a)]. There was essentially no change in the elongation up to 46% PHEE, and then there was a large increase in the elongation above 50% PHEE. The same trend holds true for Young’s modulus, but it is not statistically significant [Fig. 5(b)].

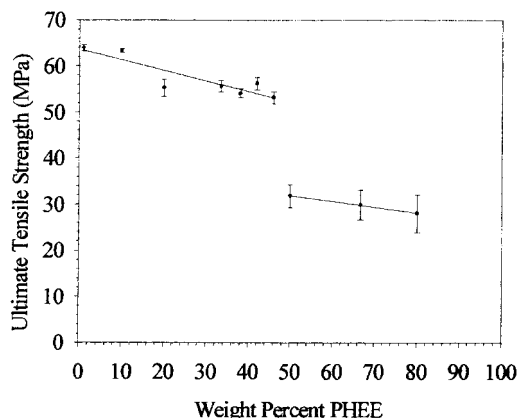
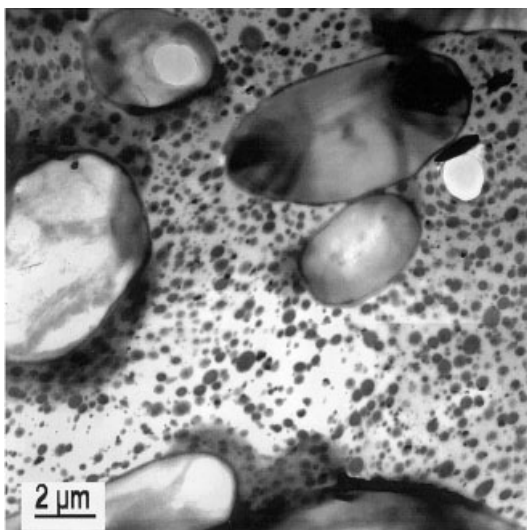
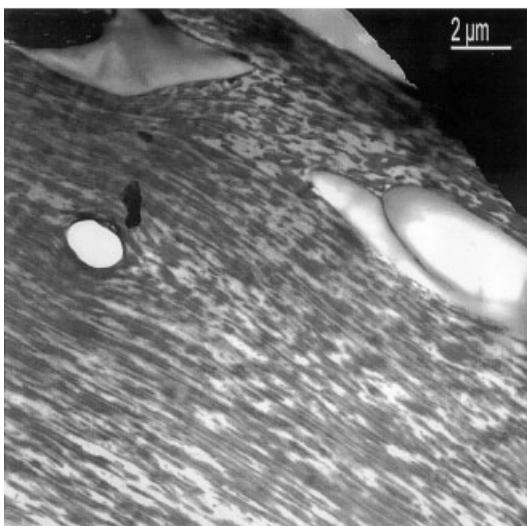


Figure 3 Ultimate tensile strength versus the percentage of adipic PHEE in a PDLLA/adipic PHEE blend.



(a)



(b)

Figure 4 TEM micrographs of starch/PDLLA/PHEE/wax OP blends: (a) 59 wt % starch incorporated into a blend consisting of 4/1 (w/w) PDLLA/PHEE and (b) 19 wt % starch incorporated into a blend consisting of 2/1 (w/w) PDLLA/PHEE. The dark areas are the PHEE resin. The light areas (matrix) are the PDLLA resin. The starch granules were roughly 6–10 μm in size.

Overall, there was a decrease in Young's modulus as PHEE increased in the blends. However, there was a large decrease in Young's modulus at 50% PHEE. Because of scatter in the Young's modulus data, the trends are more ambiguous than those for the tensile strength and elongation data. The stress–strain behavior can be attributed to the fact that the PDLLA/PHEE blend was immiscible. As the blend became richer in one component, the tensile properties tended to approach that of the single component, as observed.

The tensile strength data are consistent with some degree of PDLLA/PHEE adhesion. This is consistent with the data of Cao et al.,⁴¹ who investigated the

interactions between PDLLA and PHEE. They studied the association between PDLLA carbonyl groups and PHEE hydroxyl groups and between PHEE carbonyl groups and PDLLA hydroxyl groups with FTIR spectroscopy and DSC. FTIR spectroscopy suggested that there was no association between PDLLA and PHEE in these blends at PDLLA/PHEE weight ratios between 0 and unity. The intra-association of PHEE increased as the PDLLA/PHEE weight ratio increased from 0 to unity. As the PDLLA/PHEE weight ratios increased from 60/40 to 90/10, there was an increase in the degree of association between the PDLLA carbonyl groups and the PHEE hydroxyl groups. DSC showed PHEE to have a T_g value of roughly 39°C up to a PDLLA/PHEE ratio of unity. For a PDLLA/PHEE weight ratio between 60/40 and 90/10, T_g of PHEE was roughly 44°C, and this suggested interassociation between PDLLA and PHEE.

Mechanical properties of the cornstarch/PHEE composites

The ultimate tensile strength of the starch/PHEE composites increased as the starch content increased (Table I). A maximum tensile strength was reached when the starch content was 30%. There was a decrease in the ultimate tensile strength at a 50% starch content, but the value was still greater than that of neat PHEE. The increase in the tensile strength with the starch content was contrary to what we expected to be observed. This was most likely due to the starch granules, which, behaving as rigid fillers, had a higher tensile strength than PHEE. The strong affinity of the starch granules for PHEE might also have contributed to the increase in the tensile strength with the starch content. This strong affinity can be seen in an SEM micrograph of a starch/PHEE composite (Fig. 6). As a result of this strong affinity, the fracture path propagated through the matrix as well as the starch granules, as evidenced by fractured starch granules. As expected with any filled system, there was a decrease in elongation and an increase in Young's modulus of the starch/PHEE composite with an increase in the starch content (Table I). The moisture contents of the blends with starch/PHEE weight ratios of 0/100, 10/90, 30/70, and 50/50 were 2.1, 2.5, 3.3, and 3.3%, respectively.

St. Lawrence et al.³⁵ investigated the mechanical properties of PHEE as a function of the strain rates and degree of undercooling. The degree of undercooling is defined as $T_i - T_g$, where T_i is the testing temperature. In this study, the degree of undercooling was -6°C . The Instron crosshead speed (50 mm/min) corresponded to a strain rate of $1.65 \times 10^{-2} \text{ s}^{-1}$. The value of the tensile strength (Table I) agreed, within experimental error, to what St. Lawrence et al. predicted at a strain rate of $3.3 \times 10^{-2} \text{ s}^{-1}$, but the elongation was much lower and Young's modulus (Table I) was

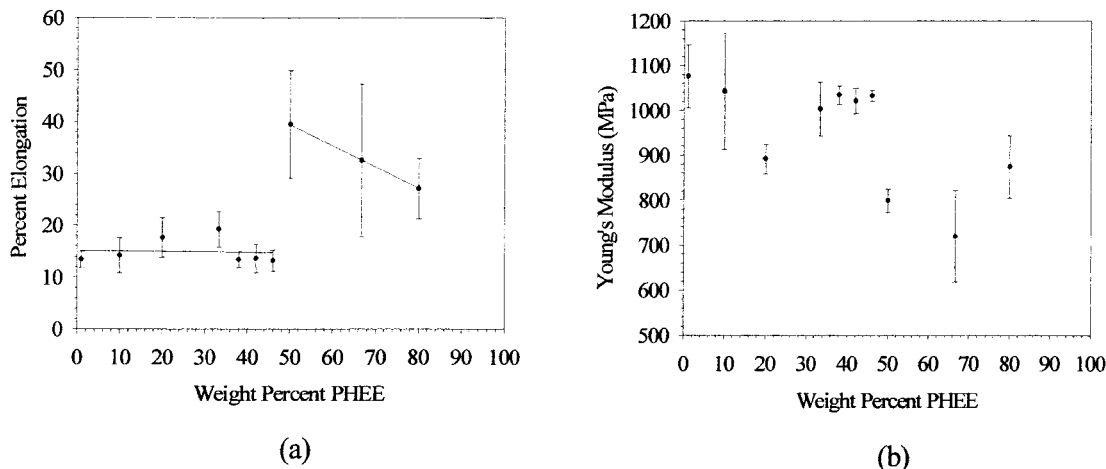


Figure 5 (a) Elongation (%) and (b) Young's modulus versus the percentage of PHEE in a PDLLA/PHEE blend.

greater than predicted. The differences between the predicted and observed values of the elongation and Young's modulus were probably due to differences in the strain rates as well as defects, such as bubbles,

present in the tensile bars. St. Lawrence et al. used compression-molded tensile bars to minimize any defects. It is extremely difficult to injection-mold bubble-free PHEE tensile bars. The approximate values of the

TABLE I
Mechanical Property Data of Starch-Filled PDLLA/PHEE Composites

PDLLA/PHEE weight ratio	Cornstarch (%)	Ultimate tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)
1/4	0.00	28.00 ± 4.06	17.89 ± 13.23	875.00 ± 69.34
	15.6	31.20 ± 0.772	8.45 ± 3.12	774.00 ± 40.00
	27.57	33.00 ± 4.06	5.95 ± 1.66	871.20 ± 129.70
	43.44	38.754 ± 3.70	5.094 ± 0.741	1164.17 ± 135.00
	60.54	48.00 ± 4.30	4.13 ± 0.836	1456.00 ± 66.80
1/2	69	40.00 ± 3.02	3.157 ± 0.300	1645.00 ± 72.00
	0.00	29.85 ± 3.21	32.49 ± 14.67	719.45 ± 102.09
	39	37.90 ± 1.48	4.433 ± 0.713	1237.00 ± 129.00
	49	57.00 ± 5.77	4.65 ± 0.513	1657.00 ± 116.00
1/1	59	44.00 ± 4.16	4.54 ± 0.470	1369.00 ± 81.40
	0.00	31.76 ± 2.45	39.49 ± 10.34	798.30 ± 26.30
	39	57.00 ± 5.02	5.946 ± 0.379	1473.00 ± 68.00
	49	43.40 ± 2.83	5.116 ± 0.572	1268.00 ± 39.00
2/1	59	46.00 ± 8.50	5.04 ± 0.615	1599.00 ± 37.00
	0.00	49.00 ± 6.40	19.25 ± 3.44	1003.00 ± 60.29
	19	57.00 ± 8.98	6.712 ± 0.209	1217.00 ± 199.00
	39	47.30 ± 4.22	6.351 ± 0.845	1124.00 ± 53.00
	59	38.00 ± 1.80	3.92 ± 0.17	1452.00 ± 25.60
	64	41.00 ± 3.62	5.080 ± 0.239	1345.00 ± 94.00
4/1	69	37.00 ± 1.62	3.60 ± 0.80	1576.00 ± 185.00
	0.00	55.22 ± 1.88	17.67 ± 3.80	891.00 ± 33.25
	35.25	59.00 ± 7.09	6.355 ± 0.521	1410.00 ± 165.00
	49	45.00 ± 2.68	5.37 ± 0.177	1278.00 ± 61.00
	59	48.88 ± 2.01	4.38 ± 0.56	1690.00 ± 77.00
PDLLA	69	43.00 ± 2.31	3.60 ± 0.197	1817.00 ± 64.00
	0.00	66.33 ± 4.02	11.22 ± 1.38	899.00 ± 87.10
	10	59.76 ± 0.86	7.208 ± 0.582	1173.52 ± 81.43
	19	62.29 ± 6.97	8.674 ± 0.447	1145.00 ± 124.00
	25	53.189 ± 2.062	6.173 ± 0.233	1241.17 ± 28.29
	39	45.45 ± 4.41	5.244 ± 0.495	1233.00 ± 185.00
PHEE	59	42.56 ± 2.94	3.701 ± 0.239	1514.00 ± 73.90
	0.00	17.739 ± 4.008	83.343 ± 6.313	568.451 ± 36.623
	10	24.894 ± 2.016	27.564 ± 2.307	755.972 ± 39.122
	30	45.831 ± 2.96	5.098 ± 0.423	1311.45 ± 49.84
	50	38.037 ± 2.68	3.878 ± 0.729	1406.57 ± 78.185

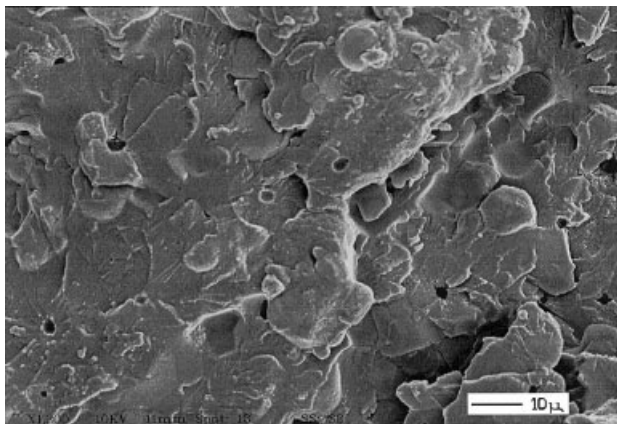


Figure 6 SEM micrograph of a starch/PHEE composite.

tensile strength, elongation, and Young's modulus at a strain rate of $3.3 \times 10^{-2} \text{ s}^{-1}$ and at a degree of undercooling of -6°C were 17.4 MPa, 225%, and 485 MPa, respectively.³⁵

Mechanical properties of the starch-filled PDLLA/PHEE composites

Composites of starch/PDLLA/PHEE were prepared, and their mechanical properties were investigated as a function of PDLLA/PHEE weight ratios. Five different PDLLA/PHEE weight ratios were investigated in addition to starch-filled PDLLA. The PDLLA/PHEE weight ratios were 0.25, 0.5, 1, 2, and 4 (Table I). The starch contents ranged from 0 to 69 wt %. All formulations contained 1% wax OP as an external lubricant. Because of difficulties with the injection molding, composites with PHEE levels of 0 and 20% at a starch level of 69% were not investigated. For the starch-filled PDLLA composites, as the starch content increased, the ultimate tensile strength and elongation to break of the composites decreased, whereas Young's modulus increased. This was likely due to a decrease in the load-bearing area within the polymer composites (Table I).

General trends of the mechanical properties of the starch-filled PDLLA/PHEE composites were analyzed with the data in Table I. There was a general increase in the tensile strength with increasing starch contents for PDLLA/PHEE composite ratios of 1/4, 1/2, and 1/1. As previously stated, this was most likely due to the starch granules, behaving as rigid fillers, having a higher tensile strength than the matrix. This also suggests that the adhesion of the starch granules to the matrix was highly probable when the matrix contained a significant amount of PHEE and, therefore, an increase in the tensile strength with the starch content. This adhesion could be due to hydrogen bonding between the starch granules and the matrix. As expected, there was a decrease in the tensile strength with increasing starch contents for PDLLA/PHEE

composite ratios of 2/, and 4/1. There was a large decrease in elongation for all PDLLA/PHEE composite ratios, once starch was added. The elongation dropped below 10% when starch was added to the composites, regardless of the polymer or ratio, and continued to decrease as the starch content increased (Table I). There was an increase in Young's modulus with increasing starch contents for all PDLLA/PHEE composite ratios. The increase in Young's modulus with respect to the starch content was fairly constant for all PDLLA/PHEE composite ratios (similar slopes), except for the PDLLA/PHEE composite ratio of 2/1. The increase in Young's modulus with respect to the starch content was not as steep as for the other four composite ratios. It is unclear why this was observed. Generally, at any particular starch loading, an increase in the PDLLA/PHEE composite ratios resulted in an increase in the modulus. This was expected because PDLLA has a higher modulus than PHEE.

The decrease in the elongation to break with an increase in the starch content arose from the fact that the actual elongation experienced by the polymer matrix was much greater than the measured elongation of the specimen. Although the specimens were part filler and part matrix, all of the elongation came from the matrix. Simple models give a qualitative and often semiquantitative understanding of experimental results. If there is good adhesion between the matrix and the starch, and if the fracture path tends to go from particle to particle, as observed by SEM for these starch-filled composites, rather than giving a perfectly smooth fracture surface, the elongation to break of the starch-filled composites can be approximated by the Nielsen equation:^{42,43}

$$\varepsilon_{\text{comp}} = \varepsilon_0 [1 - (\phi_f)^{1/3}] \quad (2)$$

where $\varepsilon_{\text{comp}}$ and ε_0 are the elongations to break of the composite and the matrix, respectively. The volume fraction of the filler (starch) is ϕ_f . The Nielsen equation assumes that the filler particles are spherical, that the matrix is homogeneous, and that there exists perfect adhesion between the filler particles and the matrix. The volume fraction of starch was determined with the following equation:

$$\phi_f = \frac{W_s / \rho_s}{\sum (W_i / \rho_i)} \quad (3)$$

where W_s is the weight fraction of the cornstarch; W_i is the weight fraction of each individual component in the blend, including the starch; ρ_s is the density of the cornstarch (1.40 g/mL); and ρ_i is the density of each individual component in the blend. ρ_{PDLLA} and ρ_{PHEE} were both 1.25 g/mL, and $\rho_{\text{wax OP}}$ was 1.01 g/mL.

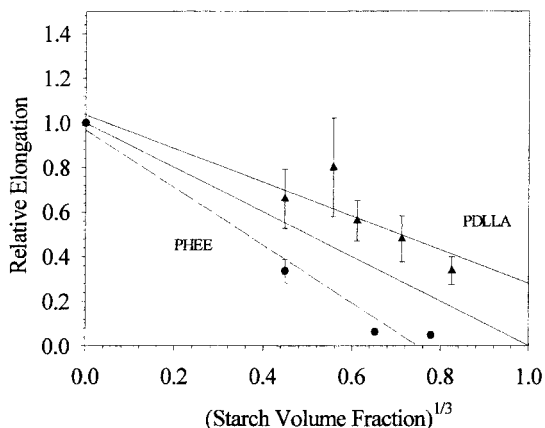


Figure 7 Nielsen equation plot of starch-filled adipic PHEE and PDLLA.

Nielsen equation plots were constructed for starch-filled PDLLA and PHEE (Fig. 7) and starch-filled PDLLA/PHEE blends (Figs. 8 and 9). For starch-filled PDLLA (Fig. 7), the observed slope is greater than the theoretical slope. This is most likely due to fair to poor adhesion of starch granules to the PDLLA matrix.⁴² This can be observed in the SEM micrograph for a starch/PDLLA composite [Fig. 10(a)]. For the starch-filled PHEE (Fig. 7), the observed slope is less than the theoretical slope. This suggests there was good adhesion of starch granules to the PHEE matrix (Fig. 6).⁴² For the starch-filled PDLLA/PHEE composite with a resin ratio of 1/4, the observed slope is greater than the theoretical slope, but the standard deviations are so large that this plot is statistically insignificant from the theoretical plot. This suggests that these composites underwent a brittle–ductile failure under a tensile load. This is evident in the stress–strain curves. Therefore, it is difficult to say, with any degree of certainty, whether or not there was poor adhesion of the starch granule to the PDLLA/PHEE matrix. For the starch-filled PDLLA/PHEE composites with resin ratios of 1/2 and 1/1 (Fig. 8), the observed slopes are less than the theoretical slope. This suggests that there was good adhesion between the matrix and the starch granules. For the 1/1 PDLLA/PHEE ratio, the plot becomes statistically significant from the theoretical plot at starch volume fractions greater than about 0.60. At starch volume fractions in excess of 0.60, there was good adhesion of the starch granule to the matrix. For the starch-filled 2/1 and 4/1 PDLLA/PHEE ratios, the slopes are essentially unity (Fig. 9). The data are statistically insignificant except for starch volume fractions greater than 0.6 for the 4/1 PDLLA/PHEE ratio, for which the relative elongation is greater than the theoretical elongation. These data suggest that there existed some adhesion between the matrix and the starch granules.

Nicolais–Narkis equation plots were constructed for starch-filled PDLLA/PHEE composites (Figs. 11 and

12). The Nicolais–Narkis equation can be stated as follows:

$$\sigma_{\text{comp}} = \sigma_0[1 - 1.21(\phi_f)^{2/3}] \quad (4)$$

where σ_{comp} and σ_0 are the tensile strengths of the composite and matrix, respectively. The Nicolais–Narkis equation assumes that the filler particles are spherical, that the matrix is homogeneous, and that there exists no adhesion between the filler particles and the matrix. For the starch-filled PDLLA/PHEE composites with resin ratios of 1/4, 1/2, and 1/1, differences in the data were statistically insignificant (Fig. 11). The Nicolais–Narkis plots suggest there was some degree of adhesion, if not good adhesion, of the matrices to the starch granules. This is evident in the positive slopes of these plots. The starch granules appear to adhere better to PHEE than to PDLLA/PHEE matrices, as evidenced by a greater slope, even though this plot is statistically insignificant from the other three plots. This is suggested by the tensile strength data in Table I. For the starch-filled PDLLA/PHEE composites with resin ratios of 2/1 and 4/1 and for PDLLA, differences in the data were statistically insignificant. The Nicolais–Narkis plots suggest there was some degree of adhesion, if not good adhesion, of the matrices to the starch granules (Fig. 12). This is evident in the slopes of these plots being greater than the theoretical plot. In other words, adhesion between the PDLLA/PHEE matrices and starch improved as the PHEE content increased, and this is consistent with Figures 11 and 12. It is apparent that the best adhesion of the starch granule to the matrix occurred when the matrix had a PDLLA/PHEE ratio ranging from zero to unity.

The addition of PHEE to a starch/PDLLA composite enhanced the injection-molding processing of the starch/PDLLA/PHEE/wax OP composite. For example, a sample containing 59% starch and 40% PDLLA

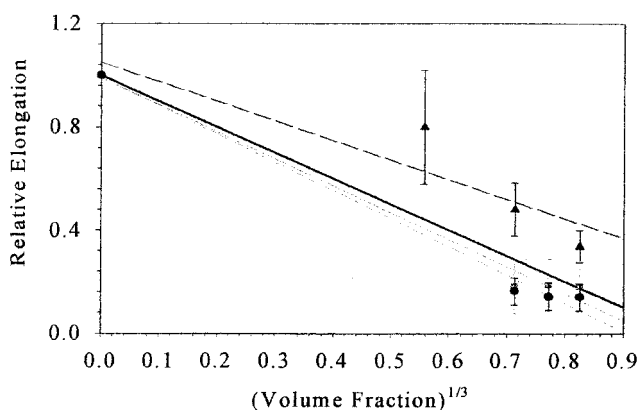


Figure 8 Nielsen equation plot of starch-filled PDLLA/PHEE composites: (—) theoretical relative elongation, (▲) relative elongation for PDLLA, (■) 1/2 PDLLA/PHEE ratio, and (●) 1/1 PDLLA/PHEE ratio.

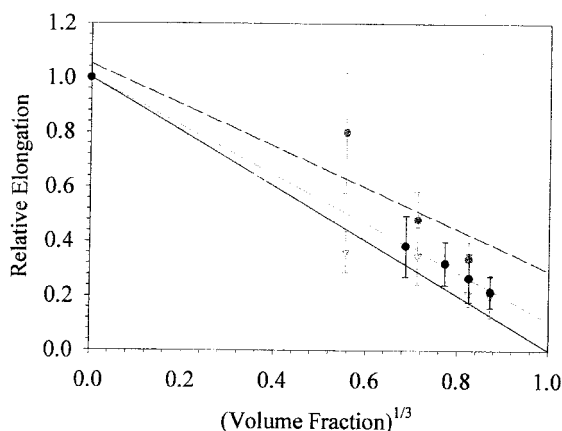


Figure 9 Nielsen equation plot of starch-filled PDLLA/PHEE composites: (—) theoretical relative elongation, (⊙) relative elongation for PDLLA, (▼) 2/1 PDLLA/PHEE ratio, and (●) 4/1 PDLLA/PHEE ratio.

could not be completely injected into molded tensile bars. The mold was approximately 90–95% full at sprue and mold temperatures of 204 and 102°C, respectively. The injection pressure was at the maximum of 27,500 psi. A sample containing 69% starch, 29% PDLLA, and 1% PHEE could be fully injected into molded bars at sprue and mold temperatures of 200 and 99°C, respectively. The injection pressure was at the maximum of 27,500 psi. It was presumed that a small addition of PHEE to the starch/PDLLA composite significantly reduced its viscosity. It is believed that PHEE imparted a plasticizing effect to the composite. Therefore, the processing of starch/PDLLA/wax OP composites would be greatly facilitated by a small addition of PHEE.

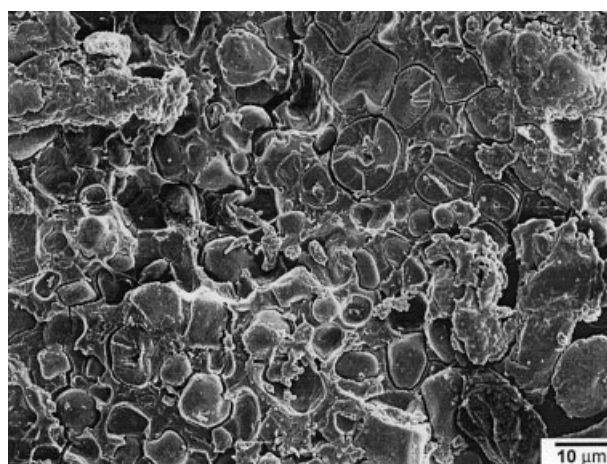
Morphology

SEM was used to analyze the fracture surfaces of tensile bars fractured in the Instron tensile tester. The fracture surfaces of two representative tensile bars are presented. The first fracture surface [Fig. 10(a)] is of a 59% starch, 40% PDLLA, and 1% wax OP composite. As previously mentioned, there was poor adhesion of starch granules to the PDLLA matrix. The second fracture surface [Fig. 10(b)] is of a 69% starch, 20% PDLLA, 10% PHEE, and 1% wax OP composite. The starch/PDLLA/wax OP composite contained numerous voids, intact starch granules, interfacial debonding between the starch granules and matrix, and few fractured granules. The starch/PDLLA/PHEE/wax OP composite contained some interfacial debonding and good adhesion between the starch granules and matrix. A majority of the granules were bound to the matrix. There were very few intact starch granules, with the majority of the granules being fractured. This suggests that the fracture path tended to go from granule to granule and around the granules. It was presumed that the good adhesion between the starch

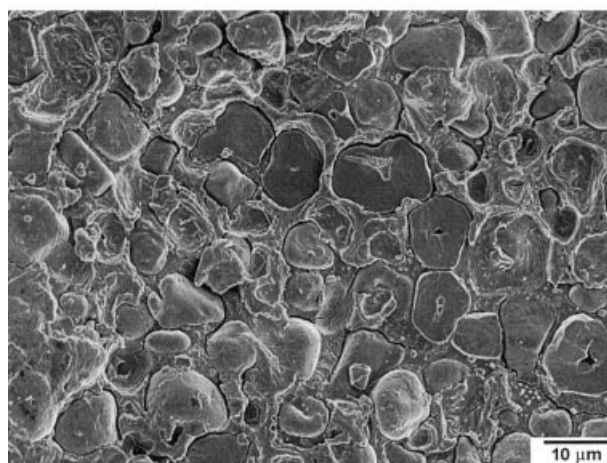
granules and the matrix was mainly due to hydrogen-bonding interactions between the starch granules and the matrix but presumably between the starch granules and PHEE. This explains the presence of fractured starch granules in the starch/PDLLA/PHEE/wax OP composites. SEM cannot distinguish PDLLA from PHEE. TEM has previously been employed to distinguish PDLLA from PHEE. As previously mentioned, TEM micrographs of starch/PDLLA/PHEE composites showed that at PDLLA/PHEE ratios of greater than 2, PHEE was the domain dispersed in the PDLLA matrix. At a ratio of 2, there was a lamellar array of PDLLA and PHEE, which suggested that a phase inversion was taking place [Fig. 4(a,b)].

CONCLUSIONS

DSC results showed two distinct T_g 's for all of the PDLLA/PHEE and starch/PDLLA/PHEE/wax OP compositions, indicating that PDLLA and PHEE



(a)



(b)

Figure 10 SEM micrographs of (a) a starch-filled PDLLA composite and (b) a starch/PDLLA/PHEE/wax OP composite.

formed immiscible blends. In addition, the reheating thermograms for starch/PDLLA/PHEE/wax OP composites exhibited a double melting endotherm for PDLLA, indicating the formation of morphologically different crystal structures, the formation of higher melting crystals, or both. Finally, DSC data suggested that starch accelerated the PDLLA crystallization, in addition to acting as a nucleating agent for PDLLA, in starch-filled PDLLA/PHEE composites. For the PDLLA/PHEE blends, an increase in the PHEE content led to an increase in the elongation at PHEE levels greater than 50% but a decrease in the ultimate tensile strength and Young's modulus. For the starch/PHEE composites, an increase in the starch content led to an increase in Young's modulus and an increase in the ultimate tensile strength up to a starch content of 30%. There was a decrease in elongation with an increase in the starch content. For the starch/PDLLA/PHEE/wax OP composites, an increase in the starch content led to an increase in Young's modulus but a decrease in the ultimate tensile strength for composites with a 2/1 and 4/1 PDLLA/PHEE ratio. The elongation dropped below 10% when starch was added to the composites, regardless of the polymer or ratio, and continued to decrease as the starch content increased. This behavior was mainly due to a decrease in the load-bearing area of the matrix. Variations in the PHEE levels at a particular starch loading had no significant effect on the elongation of the blends. The decrease in the elongation with an increase in the starch content was consistent with the Nielsen equation. The increase in the tensile strength with an increase in the starch content was consistent with the Nicolais–Narkis equation. The Nielsen and Nicolais–Narkis plots suggested that the best adhesion of the starch granules to the matrix occurred when the PDLLA/PHEE ratio ranged from zero to unity.

An increase in the weight percentage of cornstarch in a composite resulted in a decrease in the elongation

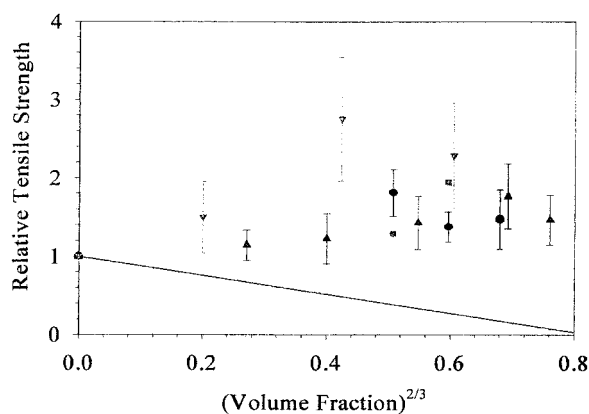


Figure 11 Nicolais–Narkis equation plot of starch-filled PDLLA/PHEE composites: (—) theoretical relative tensile strength, (▲) 1/4 PDLLA/PHEE ratio, (●) 1/1 PDLLA/PHEE ratio, (■) 1/2 PDLLA/PHEE ratio, and (▼) starch-filled PHEE.

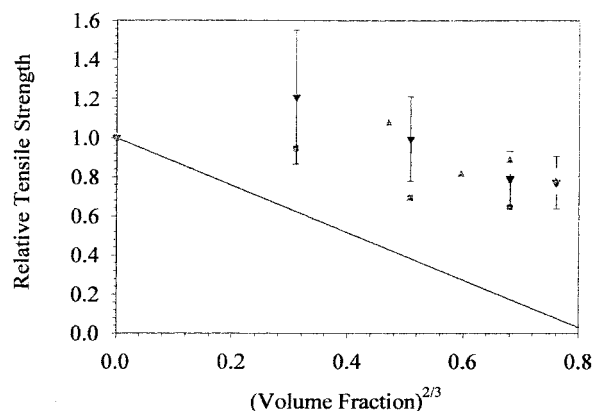


Figure 12 Nicolais–Narkis equation plot of starch-filled PDLLA/PHEE composites: (—) theoretical relative tensile strength, (■) starch-filled PDLLA, (▲) 4/1 PDLLA/PHEE ratio, and (▼) 2/1 PDLLA/PHEE ratio.

(%) along with an increase in Young's modulus, no matter what the PDLLA/PHEE ratio was. An increase in the tensile strength, with increasing starch content, was observed for PDLLA/PHEE matrices with ratios of 1/4, 1/2, and 1/1. This was most likely due to the good adhesion between the starch granules and PHEE. The decrease in the composite strength with an increase in the starch content was due to a decrease in the load-bearing area of the matrix. Another contributing factor to the decrease in the tensile strength and elongation was that there possibly was an increase in the interfacial void concentration between the starch granules and matrix. This was indicative of poor adhesion between the matrix and filler.

SEM revealed that composites of starch/PDLLA exhibited fair to poor adhesion between the starch granules and PDLLA. The addition of PHEE to the composites led to good adhesion between the starch granules and matrix. This was due to the favorable interactions between the starch granules and PHEE, presumably via hydrogen bonding. Finally, the addition of PHEE to starch-filled PDLLA enhanced the injection molding of these blends, presumably because of the plasticization effect of PHEE.

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