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Biodegradable blends and composites of polycaprolactone and starch derivatives*

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High-molecular-weight (40000 and 80000 g mol^{-1}) polycaprolactone (PCL) has been blended with high-amylose corn starch (HA-CS, 70% amylose) and waxy corn starch granules, as well as with the non-granular starch acetate derivatives. The properties of films of these blends were evaluated using differential scanning calorimetry, dynamic mechanical thermal analysis and Instron tensile testing, and compared with similar blend films made with poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV, 11.6% HV content). All of the PCL blends and the PHBV blends with granular starch were found to be mechanically compatible but phase-separated. The PHBV/starch acetate blends were also phase-separated, but were too brittle for mechanical testing. The PCL/HA-CS blends were the strongest, with ~15% lower tensile strength and a 50% higher modulus than PCL, up to 25 wt% HA-CS. Optical microscopy showed that the small size of the HA-CS granules (10 μm) and good dispersion of the granules in the PCL matrix were the reasons for the good mechanical properties compared with the other blends. Crosslinking was found to improve the thermal properties of the blends.

(Keywords: biodegradable blends; starch/polycaprolactone; composites)

INTRODUCTION

The goal of this research is to develop rigid, biodegradable blends and composites that can be used for disposable food packaging and/or food service items. Our basic approach has been to use polycaprolactone (PCL) as the matrix material and starch and starch derivatives as a modulus-modifier, extender and gas barrier. This approach has been discussed in some detail elsewhere[1]. PCL was chosen because of its good mechanical properties and its compatibility with many types of polymers, and because it is one of the more hydrophobic of the commercially available biodegradable polymers[2].

Waste disposal is becoming an increasingly difficult problem as available landfill areas diminish. The US Environmental Protection Agency recommends composting and incineration as two methods of waste management, and it is expected that these and other conversion processes will become increasingly important means of reducing our dependence on landfills[3-5]. Degradable polymers that are designed for these methods of waste management are needed to take advantage of this new emphasis on waste conversion. Plastics currently account for about 7% by weight (18% by volume) of municipal solid waste, with half of this plastic waste used in packaging[3]. This plastic represents an important potential resource.

Starch and starch derivatives, both in granular form and destructured, have been blended with various plastics, including polyethylene, poly(vinyl alcohol), poly(vinyl chloride), poly(ethylene-*co*-vinyl alcohol) and poly(ethylene-*co*-acrylic acid)[6-11]. Starch helps to lower the cost of the finished product as well as giving some biodegradable characteristics to the thermoplastic polymer. Most of these starch/polymer blends can support microbial growth and tend to lose tensile strength upon environmental exposure. However, it has not been proven that the blending with starch significantly enhances the degradation rate of the polymer component.

Both PCL and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) have been shown to undergo microbial degradation[12,13]. In the case of PCL, it has been found to be biodegradable even after extensive crosslinking with organic peroxides[13]. However, increased crosslink density does slow the rate of degradation. For these reasons, both blends and crosslinked composites of PCL and starch have been examined. Previous studies of PCL/starch blends have shown that these blends are readily biodegradable[14,15].

EXPERIMENTAL

The PCL used in this study was Tone® polymer from Union Carbide. Two different molecular weights were used: P787 had a molar mass of 80000 g mol^{-1} (80000 *MW*) and P767E had a molar mass of 40000 g mol^{-1} (40000 *MW*). The PHBV was obtained from the US

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Table 1 Instron results for the PCL/starch blends. *E* is the modulus, σ_y is the stress at yield, *PEY* is the percentage elongation at yield, σ_b is the stress at break, *PEB* is the percentage elongation at break, and 'Strength' is the tensile strength, which is defined as the peak load/initial cross-sectional area

Sample	*E* (MPa)	σ_y (MPa)	*PEY* (%)	σ_b (MPa)	*PEB* (%)	Strength (MPa)
PHBV (11.6% HV)	378	24.0 (0.6)	10.4 (0.8)	21 (2)	13 (1)	24.0 (0.6)
+25% HA-CS	1180	11 (2)	1.1 (0.3)	10 (2)	1.1 (0.3)	11 (2)
+25% WCS	1200	13.2 (0.1)	2.2 (0.3)	12.1 (0.6)	3.2 (0.7)	13.2 (0.1)
PCL (40 000 *MW*)	318	17.4 (0.3)	13 (1)	19 (3)	850 (100)	19 (3)
+25% HA-CS	474	11.3 (0.4)	5 (2)	15 (4)	880 (100)	16 (3)
+25% SA(3)	438	6.0 (0.8)	1.5 (0.3)	6.0 (0.7)	1.6 (0.2)	6.0 (0.7)
+25% WCS	495	9.2 (0.5)	3.2 (0.2)	3.4 (1)	19 (5)	9.2 (0.5)
+25% SA-WCS(3)	495	9.5 (0.3)	2.5 (0.3)	3 (2)	12 (5)	9.5 (0.3)
PCL (80 000 *MW*)	258 (5)	15.3 (0.2)	17 (1)	none	>1100	>33
+25% HA-CS	500 (20)	13.4 (0.3)	5.4 (0.2)	23 (2)	1020 (60)	33 (2)
LDPE[a]	170–280	9–15		8–31	100–650	
HDPE[a]	1070–1090	26–33		22–31	10–1200	
PS[a]	2300–3400	36–52		36–52	1.2–2.5	

[a] Values from ref. 16 for low-density polyethylene, high-density polyethylene and polystyrene

Army Natick RD&E Center in Natick, MA. It was extracted from bacteria and had a hydroxyvalerate content (HV) of 11.6%. The high-amylose corn starch (HA-CS, 70% amylose content) and waxy corn starch (WCS) are sold as amylose and amylopectin by Sigma Chemical. Both were in granular form and were practical grade. Dicumyl peroxide (DCP) and t-butyl peroxide (TBP) were used to crosslink the composites, and were obtained from Aldrich.

Starch acetate derivatives were made by reaction of destructured starch with acetic anhydride in acetic acid at 40°C, using H_2SO_4 as a catalyst[7]. Destructured starch was prepared by refluxing the starch granules for at least 1 h in a mixture of 10 vol% dimethyl sulfoxide (DMSO) in distilled water to break up the granular structure. Starch triacetates were made both from HA-CS (SA(3)) and from WCS (SA-WCS(3)). *FT*i.r., ^1H n.m.r. and ^{13}C n.m.r. were used to verify the degree of substitution of the starch acetates. Thermal properties were measured using a Dupont model 910 DSC and model 951 TGA.

Mixing of the components for the polymer/starch blends and composites was accomplished by using a Brabender Prep Center, model D-71. The starch acetate blends were also made by solution blending with methylene chloride. Thin films for testing (0.5 mm thick) were pressed at 120–160°C and 6 metric tons of pressure (0.91 MPa). Films containing peroxides were cured at 120 or 160°C for 1 h, depending on the peroxide used. Mechanical properties were measured using an Instron model 1011 tensile tester and a Polymer Laboratories DMTA dynamic mechanical analyser. The tensile testing was performed using 150 mm × 10 mm × 0.5 mm and 100 mm × 10 mm × 0.5 mm rectangular strips, in accordance with ASTM Standard D882. The results from three to seven specimens were averaged for each value determined. The d.m.t.a. analysis was performed using 35 mm × 10 mm × 0.5 mm strips in the tensile analyser. The frequencies used were 1, 3, 10 and 30 Hz with a 0.04% strain over a temperature range of −100 to +150°C. The initial tensile force was 1 N, which was reduced at elevated temperatures to maintain a constant displacement. Optical microscopy was performed using a Nikon MetaPhot in the reflecting mode. Films analysed in the transmission mode were wiped gently with a lint-free cloth and sprayed with a compressed air duster prior to analysis.

RESULTS AND DISCUSSION

Starch blends

Table 1 contains the Instron results for the PCL/starch and PHBV/starch blends. All of these blends were made using the Brabender Prep Center. It can be seen that the blending of either polymer with 25 wt% starch or starch acetate causes three main changes compared with the original polymer: an increase in modulus; a decrease in percentage elongation at both yield (*PEY*) and break (*PEB*); and a decrease in tensile strength. For the two PHBV/starch blends shown, HA-CS or WCS had the same effect, and the changes in these three parameters were very nearly the same in each of the two cases: a threefold increase in modulus, an order-of-magnitude decrease in *PEY* and *PEB*, and a 50% reduction in tensile strength. The PHBV/starch acetate blends were too brittle for mechanical testing, and were noticeably phase-separated. For the four blends with 40000 *MW* PCL, the increase in modulus (1.5 times) and decrease in *PEY* (roughly an order of magnitude) were the same. The decrease in *PEB* (about two orders of magnitude) and tensile strength (50–75%) was different only in the case of the PCL/HA-CS blend, which had only a slight (5%) decrease in *PEB* and tensile strength (20%). The PCL/HA-CS blend with 80000 *MW* PCL also shows an increase in modulus (twofold), a high strength and a large *PEB*. These results imply some type of interaction of the HA-CS with the PCL that is different from that of the PHBV or the other starch derivatives.

Figure 1 graphically displays the Instron results that were obtained from PCL/HA-CS blends over a range of HA-CS content from zero to 50 wt% HA-CS. These results show that a higher percentage of HA-CS can be blended with the 80000 *MW* PCL (~25–30 wt%) than

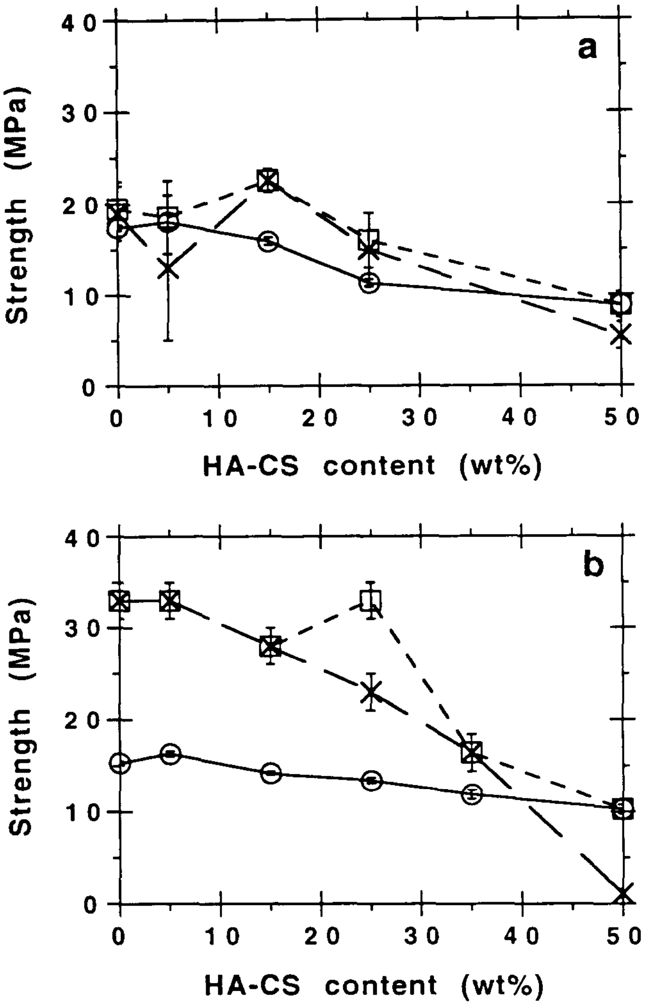

Figure 1 Instron tensile results for the PCL/HA-CS blends, using (a) 40000 *MW* PCL and (b) 80000 *MW* PCL: (□) tensile strength, (×) stress at break, and (○) stress at yield

with the 40000 *MW* PCL (~15–20 wt%) before a significant decrease in tensile strength is seen. These values are somewhat below the theoretical critical value of 31 vol% (~40 wt%) predicted by percolation theory[11]. This value is the point at which the blend system changes from a discontinuous filler phase in a continuous matrix phase to a system containing two interpenetrating continuous phases. Since the starch continuous phase is much weaker than the PCL continuous phase, it is above this critical concentration that one would expect a rapid decline in mechanical properties. The fact that the strength of the PCL/HA-CS blends falls off sooner than predicted implies that either the HA-CS is not uniformly distributed throughout the blend, or the size of the HA-CS domains is not random.

Optical microscopy was used to examine the starch granules and the PCL/starch blends. *Figures 2a* and *2b* are photomicrographs of HA-CS and WCS granules, respectively. From these photos and others taken at higher magnification, the sizes of the starch granules were estimated to be about 10 μm for the HA-CS and about 25–30 μm for the WCS. *Figures 2c* and *2d* are photomicrogaphs obtained from pressed films of the PCL/HA-CS blends with 25 and 50 wt% HA-CS, respectively. *Figure 2c* shows that the PCL/HA-CS film with 25 wt% HA-CS is phase-separated, i.e. the starch granules have not dissolved into the PCL during processing of the film, but the granules do appear to be well dispersed within the PCL matrix. At 50 wt% HA-CS, however, *Figure 2d* shows that the starch has clumped or coalesced into larger aggregates of about 30–40 μm in diameter. Aggregates were also seen in the 25 wt% starch acetate samples when mixed in the Brabender. From these microscopy data, it can be deduced that the reason that the PCL/HA-CS blends have better mechanical properties than the other PCL/starch blends is because of the small granule size and good dispersion of the HA-CS granules in the PCL matrix. This is supported by a recently published article by Lim *et al.*[17] that showed a linear reduction in tensile strength of linear low-density polyethylene (LLDPE)/starch films as the granule size of the starch increased from 2 to 35 μm. At 15 wt% starch content, the loss in strength of LLDPE for 10 μm diameter granules was about 15%, while that for 35 μm granules was 50%. These percentages are very close to those found here for PCL films containing 25 wt% starch.

D.m.t.a. data (*Figure 3*) comparing the tan δ peaks from PCL, the PCL/25 wt% HA-CS blend and the PCL/25 wt% SA(3) blend show no shifting or change in the shape of this peak after blending. Likewise, no change was evident in the loss modulus for either of these two blends (*Figure 4*). The loss modulus (E'') is said to be less influenced by crystallization effects during the analysis of semicrystalline polymers[18]. These results imply no change of the PCL glass transition temperature (T_g), and hence no thermodynamic compatibility between PCL and HA-CS or between PCL and SA(3). The modulus for both of these blends was found to be increased over the entire temperature range tested, namely −100 to about +60°C, the melting temperature of the PCL.

Table 2 lists the d.s.c. data obtained for two of the PCL/HA-CS blends. The T_g transition was not discernible, so only the melting transition could be evaluated. Comparisons of the films as pressed, after quenching from the melt at 200°C min^{-1} and after slow cooling from the melt to −70°C at 10°C min^{-1} showed little change in the crystalline melting temperature (T_m), the heat of fusion of the melting transition (ΔH_f), or the degree of crystallinity of the PCL in the films. The

Table 2 D.s.c. results for the PCL/HA-CS blends at two different compositions. T_m is the crystalline melting temperature, ΔH_f is the heat of fusion for the PCL melting transition, and 'Cryst.' is the percentage crystallinity of the PCL

Sample	T_m[a] (°C)	ΔH_f (J g^{-1})	Cryst. (%)
Pressed films			
PCL (80000 *MW*)	58.0	72.6	52
+25% HA-CS	58.5	41.5	40
+50% HA-CS	57.6	31.6	45
After quenching			
PCL (80000 *MW*)	51.5	59.8	43
+25% HA-CS	52.1	41.7	40
+50% HA-CS	51.8	25.1	36
After slow cool			
PCL (80000 *MW*)	52.1	63.8	46
+25% HA-CS	52.8	45.0	43
+50% HA-CS	52.3	27.8	40

[a] Peak temperature

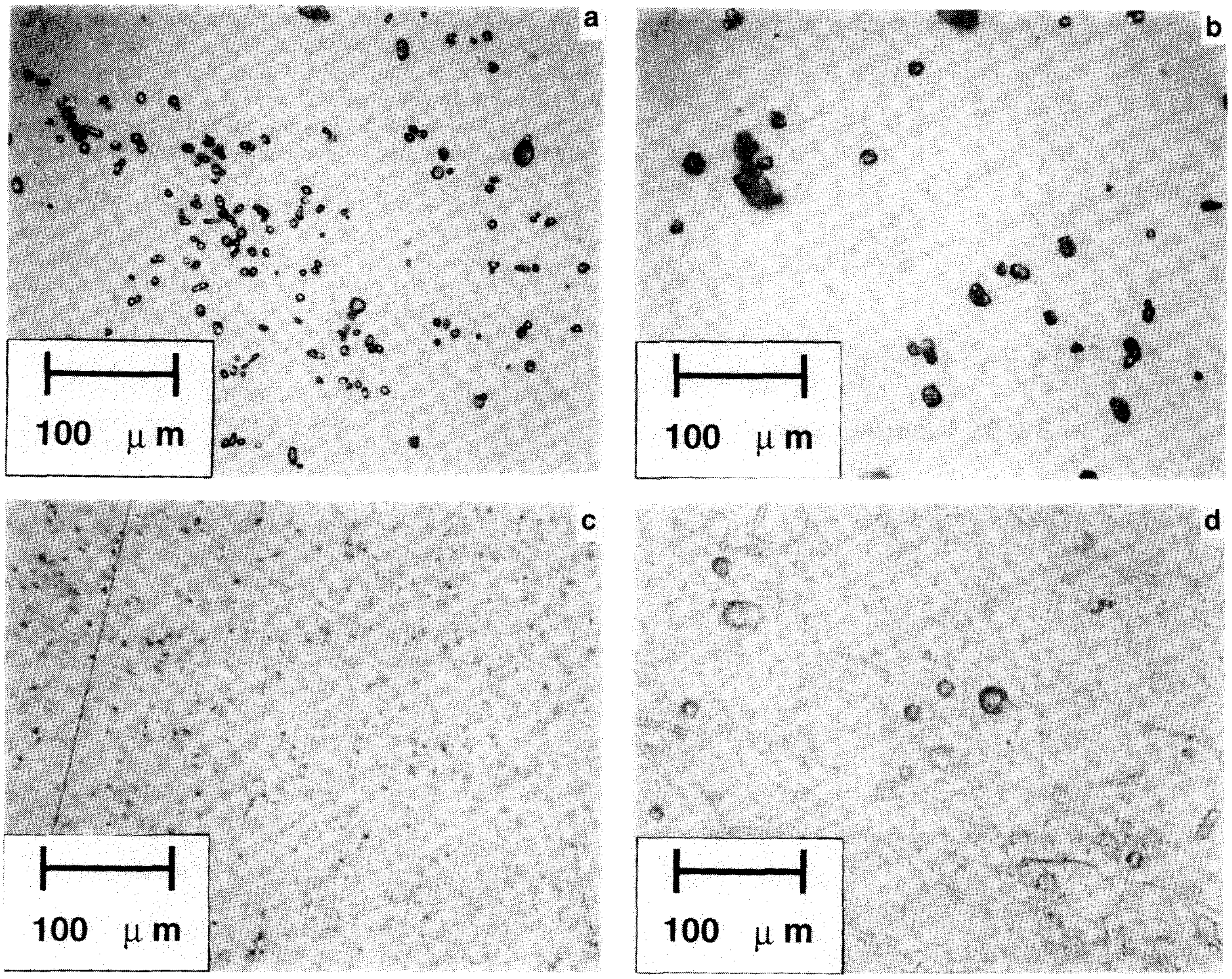

Figure 2 Optical photomicrographs obtained at 200 × magnification: (a) HA-CS granules, (b) WCS granules, (c) PCL/25 wt% HA-CS blend, and (d) PCL/50 wt% HA-CS blend

Table 3 Instron results for crosslinked PCL and the PCL/starch composites. E is the modulus, σ_y is the stress at yield, PEY is the percentage elongation at yield, σ_b is the stress at break, PEB is the percentage elongation at break, and 'Strength' is the tensile strength, which is defined as the peak load/initial cross-sectional area

Sample	E (MPa)	σ_y (MPa)	PEY (%)	σ_b (MPa)	PEB (%)	Strength (MPa)
PCL (80 000 MW)	258 (5)	15.3 (0.2)	17 (1)	none	>1100	>33
+ 1% TBP	265 (8)	14.2 (0.3)	17 (2)	none	>1100	>33
+ 5% TBP	230 (10)	12.8 (0.4)	16 (2)	22 (3)	800 (70)	22 (3)
+ 5% DCP	187 (9)	11.9 (0.4)	22 (2)	24 (3)	840 (70)	24 (3)
+ 15% DCP	–	4.7 (0.2)	42 (4)	9 (1)	380 (50)	9 (1)
+ 25% HA-CS	500 (20)	13.4 (0.3)	5.4 (0.2)	23 (2)	1020 (60)	33 (2)
+ 25% HA-CS + 5% TBP	330 (30)	13.8 (0.6)	9.3 (0.9)	11 (1)	70 (40)	13.8 (0.6)
+ 25% HA-CS + 5% TBP + 5% $CaCO_3$	270 (70)	9.0 (0.1)	10 (2)	8.8 (0.8)	140 (100)	9.3 (0.4)

percentage crystallinity was calculated by using a value of 33.3 cal g^{-1} (139.3 J g^{-1}) for the heat of fusion of crystalline PCL, and adjusted for the amount of PCL present in the blend[19]. This analysis showed no effect of the HA-CS on the PCL in the blend, and hence no apparent miscibility between the two components.

Starch composites

The Instron results for the crosslinked PCL and PCL/starch composites are presented in *Table 3*. From these data, several trends are apparent. Increased crosslinking of the PCL with organic peroxides causes a decrease in modulus and a decrease in strength of the

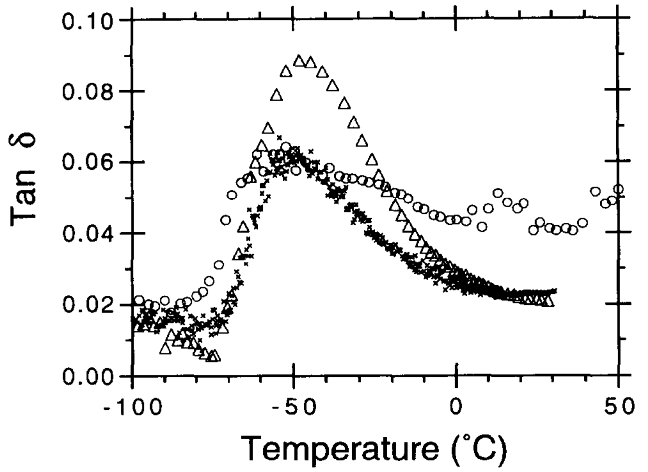

Figure 3 D.m.t.a. tan δ peaks obtained at 1 Hz for (△) PCL, (×) PCL/25 wt% HA-CS blend, and (○) PCL/25 wt% SA(3) blend

Table 4 D.s.c. results for crosslinked PCL at two different crosslink densities. T_m is the crystalline melting temperature, ΔH_f is the heat of fusion for the PCL melting transition, and 'Cryst.' is the percentage crystallinity of the PCL

Sample	T_m[a] (°C)	ΔH_f ($J g^{-1}$)	Cryst. (%)
Pressed films			
PCL (80 000 *MW*)	58.0	72.6	52
+1% TBP	56.7	69.9	50
+5% TBP	48.4	63.0	45
After quenching			
PCL (80 000 *MW*)	51.5	59.8	43
+1% TBP	49.6	53.1	38
+5% TBP	42.4	51.7	37
After slow cool			
PCL (80 000 *MW*)	52.1	63.8	46
+1% TBP	50.1	52.4	38
+5% TBP	42.9	53.7	39

[a] Peak temperature

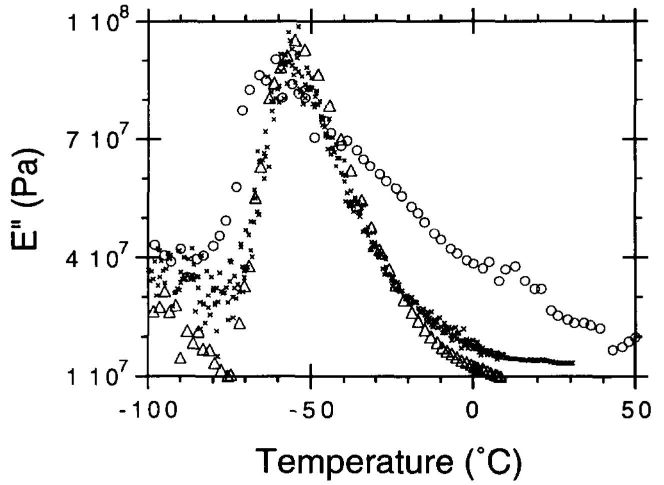

Figure 4 D.m.t.a. loss modulus obtained at 1 Hz for (△) PCL, (×) PCL/25 wt% HA-CS blend, and (○) PCL/25 wt% SA(3) blend

PCL. Also, moderate amounts of peroxide (1–5 wt%) cause only a small (0–30%) decrease in tensile strength. Previous studies found that over 10 wt% of BPO was necessary to slow the rate of biodegradation noticeably in one-month-long exposures to *Cryptococcus laurentii* and *Fusarium*[13]. Therefore, the crosslink density can be used to select the rate of degradation and/or tensile strength needed for a particular application.

D.s.c. data (*Table 4*) show a decrease in crystalline melting temperature with increased crosslinking. This is explained in terms of decreased chain mobility due to the crosslinks, causing smaller, less perfectly formed and hence lower-melting crystallites to be formed. Interestingly, the degree of crystallinity seems not to be affected by this small degree of crosslinking (up to 5 wt% of peroxide). With greater amounts of crosslinking, the degree of crystallinity has been found to decrease[13]. From the Instron data in *Table 3*, it appears that a decrease in crystallinity or crystallite size causes a measurable decrease in tensile strength of PCL.

Referring again to *Table 3*, the PCL/25 wt% HA-CS crosslinked composite shows both a higher modulus, due to the HA-CS granules, and lower strength, due to the crosslinking reaction, than unmodified PCL. The strength is still on the order of that of low-density polyethylene (see *Table 1*), and has dimensional stability above the crystalline melting temperature of PCL. It is expected that starch derivatives containing crosslinkable functional groups could add considerably more strength and rigidity to the PCL composites. This is expected because of the polyfunctionality of starch, resulting in higher degrees of crosslinking, and because of the high melting temperature and thermal stability of starch crystallites (degradation onset temperature of ~285°C was found with t.g.a.).

CONCLUSIONS

Blending granular starch or starch acetate with PCL or PHBV increases the modulus and decreases the overall strength compared to the polymer before blending. PCL can be mixed with up to 25 wt% HA-CS with only a small (20%) decrease in strength. It appears that this is a physical effect due to the small size of the HA-CS granules used in this study (~10 μm in diameter). No miscibility was detected for any of the starch blends in this study by d.s.c. or d.m.t.a.

The tensile strength of PCL decreases as crosslinking increases, owing to a decrease in the crystallite size and degree of crystallinity. However, crosslinking improves the thermal properties of the blends. Starch and starch derivatives can be incorporated into crosslinked PCL composites to increase the modulus. Starch derivatives with crosslinkable side groups may afford increased strength as well as increased modulus owing to their polyfunctionality and high T_m.

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