

Evaluation of the Thermal and Mechanical Properties of Poly(ϵ -caprolactone), Low-Density Polyethylene, and Their Blends

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ABSTRACT: The thermal and mechanical properties of low-density polyethylene (LDPE), poly(ϵ -caprolactone) (PCL), and their blends were evaluated. Differential scanning calorimetry showed that increasing the PCL content of the blend did not change the LDPE melting temperature, but reduced the crystallinity by up to 16.8%. This behavior was related to interactions between the PCL chains and the crystalline phase of LDPE. Tensile strength and elongation at break values for the blends were lower than those for the

pure polymers, which suggested an incompatibility between the polymers. The values for Young's modulus under tensile increased when PCL was added to LDPE. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3909–3914, 2004

Key words: biodegradable; low-density polyethylene (LDPE); poly(ϵ -caprolactone) (PCL); thermal properties; mechanical properties

INTRODUCTION

Polymers are widely used because of their easy processability; low density; and desirable physical, chemical, mechanical, thermal, and electrical properties. Since World War II, the polymer industry has grown enormously and has developed many important products. One of the most used polymers is polyethylene, which has a high chemical resistance and low cost. However, synthetic thermoplastic polymers are known for their resistance to biological degradation.¹ Polyethylene, the polymer present in the highest proportion in modern waste, is degraded in the presence of oxygen and ultraviolet radiation,² but its extremely slow rate of degradation is a problem after disposal. The increasing environmental problems caused by the disposal of plastic waste have renewed interest in the development of environmentally degradable and "environmentally friendly"

polymers.^{3,4} One solution for this problem is to develop new biodegradable polymers.

According to Chandra and Rustgi,⁵ there are three main classes of biodegradable polymers: (1) synthetic polymers, with vulnerable groups susceptible to hydrolysis by microbes, (2) naturally occurring processable bacterial polymers that are truly biodegradable and are attacked by a wide variety of bacteria, and (3) blends of polymers in which one or more components are readily consumed by microorganisms.

The use of biodegradable polymers has contributed to a reduction in environmental problems, but the cost of producing these materials is still high. As a result, there has been a trend toward the production of degradable natural and synthetic polymers and natural/synthetic polymer blends.

Materials such as starch, poly(vinyl alcohol), polyacetals, poly(β -hydroxybutyrate) (PHB), and poly(ϵ -caprolactone) (PCL) are examples of biodegradable polymers. Among biodegradable synthetic polymers, PCL is one of the most attractive because of its availability, variable biodegradability, and good mechanical properties.⁶ PCL, which has been studied as a substrate for biodegradation and as a matrix for the controlled release of drugs,^{7,8} is generally prepared from the ring-opening polymerization of ϵ -caprolactone.⁹

Studies have been done using starch in blends with polyethylene.^{10–13} Blends of low-density polyethylene (LDPE) containing up to 30% starch show increased

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TABLE I
Processing Conditions Used During Blending

LDPE/PCL (w/w)	Temperature (°C)			Matrix
	Zone 1 ^a	Zone 2 ^b	Zone 3 ^c	
100/0	120	130	140	140
90/10	120	130	140	140
75/25	110	120	130	130
50/50	100	100	110	110
0/100	100	100	110	110

^a Initial region of the screw.

^b Plastification region.

^c Extrusion die region.

tensile strength and elongation at break, whereas Young's modulus decreased as the starch was substituted by a hydrophobic derivative (starch phthalate, stath) through phthalation.¹⁴ The LDPE/stath blends showed greater degradation in soil compared to LDPE/starch blends.

PCL is compatible with many polymers, including poly(vinyl chloride), chlorinated polyethylene, polycarbonate, polyamide 6, poly(styrene-*stat*-acrylonitrile), and ethylene terephthalate-caprolactone copolyester.^{15–20}

Studies of the compatibility and degradation of blends of PCL/poly(ethylene glycol) block copolymer and polypropylene have been shown that PCL tends to disperse as discrete particles in the polypropylene (PP) matrix of the PP/PCE blend 75/25.

The aim of this work was to prepare blends of PCL with LDPE and to evaluate their properties using differential scanning calorimetry, dynamic mechanical thermal analysis, tensile tests, and biodegradability in soil compostage.

EXPERIMENTAL

Polymers

Poly(ϵ -caprolactone) (PCL)

This polymer was provided by Union Chemical Carbide Ltd. (P-767; Cubatão, SP, Brazil). The melting index was 1.9 ± 0.3 g/10 min (ASTM D 1238), with a density of 1.140 ± 0.007 g/cm³ and a weight-average

molecular weight (M_w) of 80,000. PCL was supplied in pellet form.

Low-density polyethylene (LDPE)

This polymer was supplied by Union Carbide Química (Brazil; DUCB 6000 NT), and was previously used in extrusion processes. The polyethylene was designated as Type I, Class A-5 (ASTM D 1248) with a melting index of 0.3 ± 0.1 g/10 min (ASTM D 1238), a density of 0.920 ± 0.003 g/cm³ (ASTM D 1505), and M_w of 36,415 g/mol.

Blend preparation

LDPE and PCL were thoroughly mixed and extruded using a one-screw extruder (Miotto ELM 25 Extrusion). The extrusion conditions were as follows: temperatures as shown in Table I, L/D = 25, and screws 40/40/40 with a 5 kg capacity.

Molding

The blends were molded by compression into sheets 2 mm thick using 180 × 180-mm window frame molds in a U.M. Cifali Construções Mecânicas (Brazil). Press, model 2762. The plates of the press were kept at $165 \pm 5^\circ\text{C}$ for 5 min for all blends. The resulting sheets were removed from the press after cooling to room temperature.

Soil compostage with different pH values

Soil compostage consisted of 23% loamy silt, 23% organic matter (cow manure), 23% sand, and 31% distilled water (wt %). Calcium hydroxide was added to provide pH values of 7, 9, and 11.

Mechanical properties

Tensile specimens (ASTM D638; Type III) were cut from each sheet. Tensile tests were done in an Emic universal testing machine (Model DL 2000). Five samples of each composition were strained at a rate of 50 mm/min at room temperature, using a gap distance of

TABLE II
Mechanical Properties of LDPE, PCL, and Their Blends
Obtained from Tensile Testing

LDPE/PCL (w/w)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
100/0	12.3 ± 1.1	460.9 ± 29.0	292.7 ± 40.8
90/10	9.2 ± 1.5	377.6 ± 26.0	468.5 ± 57.2
75/25	6.9 ± 0.3	39.4 ± 9.7	352.8 ± 27.2
50/50	4.4 ± 0.4	9.9 ± 5.3	673.7 ± 144.6
0/100	16.9 ± 1.2	393 ± 25.0	429.1 ± 24.8

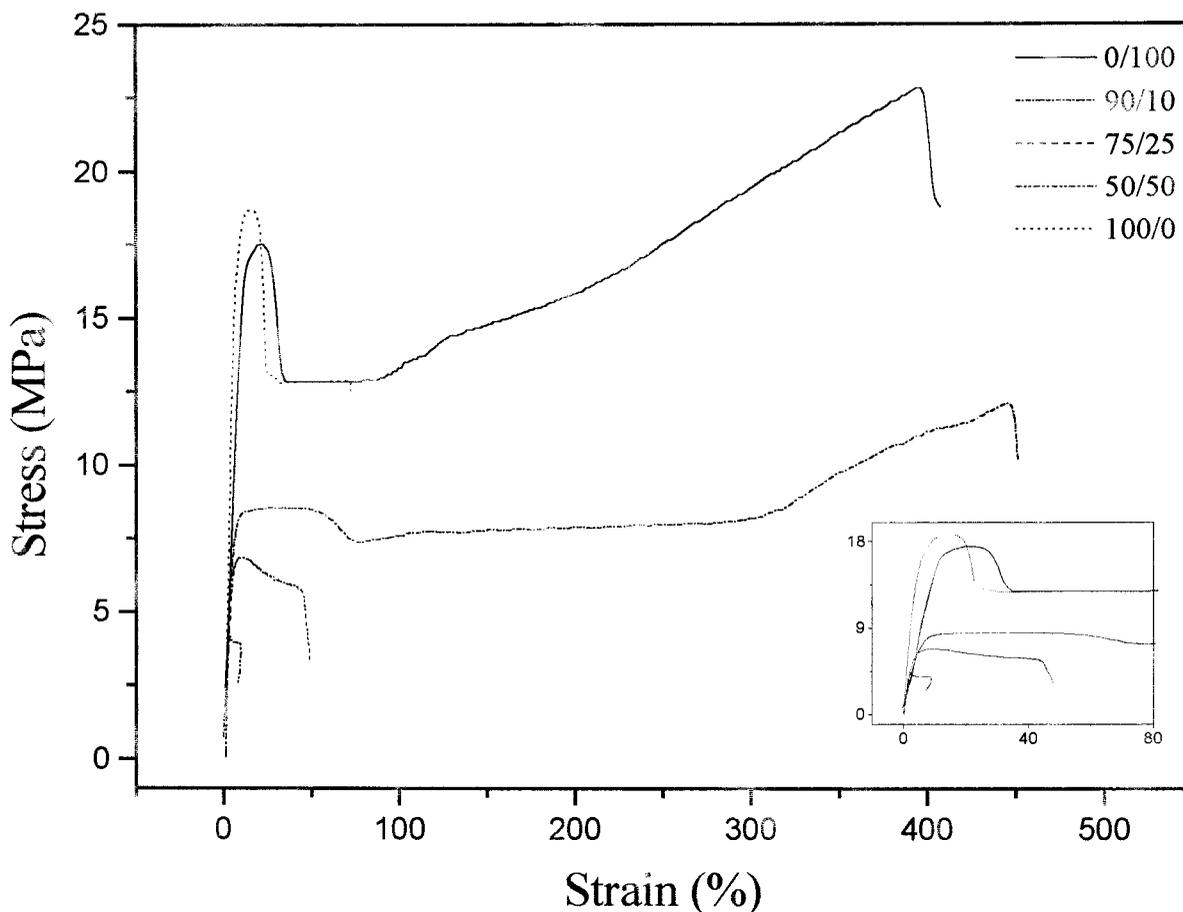


Figure 1 Stress-strain curves for LDPE, PCL, and their blends.

115 mm. Average values of elongation at break, tensile strength, and Young's modulus were determined.

Thermal analysis

DSC analysis

Thermal analysis was done with a differential scanning calorimeter (DSC) model 204 TASC 414/3A (Netzsch-Gerätebau GmbH, Bavaria, Germany) under a nitrogen atmosphere, at a heating rate of 10°C/min. Two heating cycles were used for each film. The LDPE films were first heated from room temperature to 160°C to eliminate their thermal history, and then cooled to room temperature and immediately reheated to 160°C. The second scan was done at the same heating rate. All DSC experiments were done in duplicate and the thermograms shown refer to the second heating.

The degree of crystallinity of LDPE was obtained from the ratio between the fusion heat of the samples (ΔH) and the fusion heat of 100% crystalline LDPE. A heat of fusion value (ΔH_0) of 290 J/g was used for 100% crystalline LDPE.²¹

DMTA analysis

Dynamic mechanical thermal analysis (DMTA) was done using a model MK III dynamic mechanical analyzer (Rheometric Scientific, Piscataway, NJ) over the temperature range of -60 to 60°C at a frequency of 1 Hz. The temperature ramping rate was 2°C/min. The

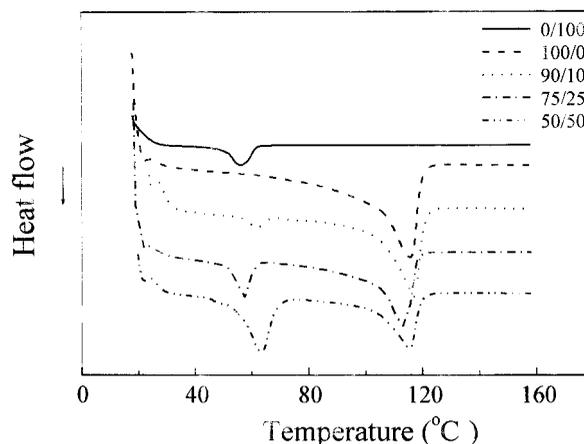


Figure 2 DSC curves for different composition LDPE/PCL blends.

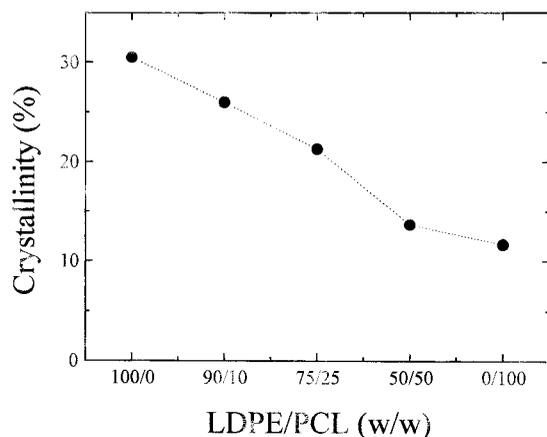


Figure 3 Crystallinity of LDPE as a function of LDPE/PCL composition.

analyses were done in specimens measuring $35 \times 9 \times 1$ mm. DMTA was done in duplicate and the glass-transition temperature (T_g) was determined using the maximum peak of loss modulus (E'').

Measurement of biodegradability

Films of LDPE, PCL, and their blends were weighed and buried, in triplicate, in soil compostage at pH 7, 9, and 11. Biodegradation was monitored every 15 days for approximately 10 months by measuring the residual mass. For this, the buried samples were recovered, washed with distilled water, and dried at room temperature before being weighed and then buried again in their respective trays. The residual mass was calculated as the ratio between the final and the initial weights.

RESULTS AND DISCUSSION

Mechanical properties

The average values and estimated standard deviations of elongation at break, tensile strength, and elasticity modulus for LDPE, PCL, and their blends are shown in Table II. Figure 1 shows the stress-strain curves for LDPE/PCL and their blends.

TABLE III
Temperature and Enthalpy of Fusion of LDPE, PCL, and their Blends Obtained from DSC

LDPE/PCL (w/w)	LDPE		PCL	
	T_m (°C)	ΔH (J/g ⁻¹)	T_m (°C)	ΔH (J/g ⁻¹)
100/0	113.9	88.6	—	—
90/10	113.7	70.1	57.1	3.6
75/25	113.4	59.9	57.6	8.8
50/50	112.4	37.2	57.8	18.5
0/100	—	—	56.0	9.5

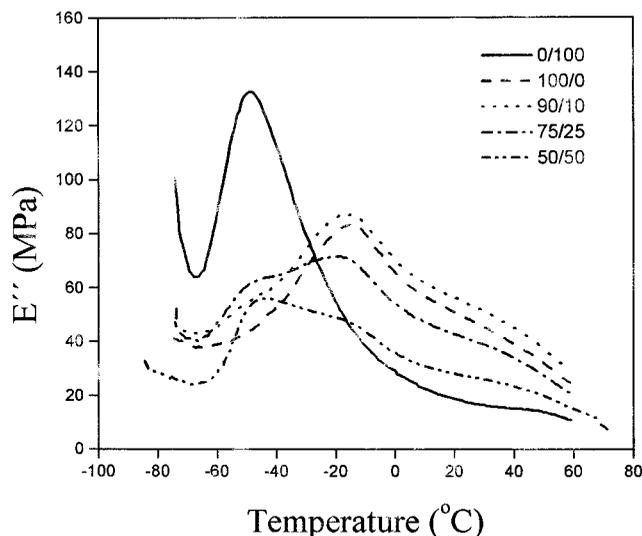


Figure 4 Loss modulus curves for LDPE, PCL, and their blends.

In LDPE/PCL blends, the addition of PCL to LDPE reduced the tensile strength and elongation at break, but increased the elasticity modulus, probably because PCL was stiffer than LDPE. This property showed the highest standard deviations ($\sim 21.5, 13.9,$ and 12.2%) for the 50/50, 100/0, and 90/10 blends, respectively. The 50/50 blend had the lowest tensile strength and elongation at break. These findings suggested a strong incompatibility between LDPE and PCL in the mixture, leading to a lack of interfacial adhesion between the polymers. Despite the elevated standard deviations, the mean values obtained for the mechanical properties indicated that the blends could be useful for applications, such as packaging.

Thermal analysis

The DSC curves for the LDPE/PCL blends and the pure polymers are shown in Figure 2. Endothermic peaks were observed for LDPE and PCL, indicating that there was a crystalline phase in both materials. The degree of crystallinity was calculated from the enthalpy values^{21,22} (Fig. 3). The crystallinity of pure PCL was lower than that of pure LDPE because the

TABLE IV
Glass-Transition Temperature (T_g) of LDPE, PCL, and their Blends Obtained from E'' Maximum

LDPE/PCL w/w	T_g (°C)
100/0	-15
90/10	-16, -44
75/25	-22, -46
50/50	-18, -44
0/100	-47

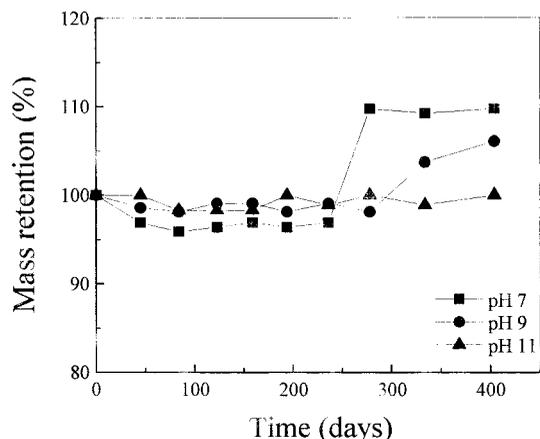


Figure 5 Biodegradation curves for 100/0 LDPE/PCL at pH 7, 9, and 11.

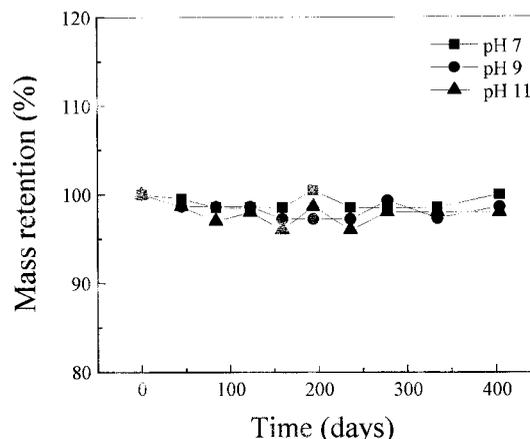


Figure 7 Biodegradation curves for 90/10 LDPE/PCL at pH 7, 9, and 11.

carbonyl groups in the main chain made packing of chains difficult.²³

The effect of adding PCL to LDPE is shown in Figure 2. For all three LDPE/PCL ratios, the DSC curves showed two endothermic peaks at temperatures very close to melting points for LDPE and PCL (113.9 and 56°C, respectively). No significant peak shifts were noted with increasing PCL concentration. Thus, the decrease of 1.5°C for LDPE and the small increase of 1.1°C for PCL can be attributed to inherent variation in the method used to obtain the thermal measurements or to the slight degrees of mixing. The DSC results for the pure polymers and the blends are summarized in Table III.

DMTA analysis

Figure 4 shows the loss modulus (E'') versus temperature for PCL, LDPE, and their blends, and Table IV shows the T_g values obtained using the E'' maximum. The loss modulus curves did not clearly show the

transitions of the two polymers, given that the transition ranges of LDPE and PCL were relatively close, and they were hard to discern from the E'' curves. However, in the 50/50 and 75/25 blends the approximation of the T_g peaks of both polymers was visible (see Fig. 4 and Table IV), and suggested a slight miscibility between the pure polymers. However, it is possible to superimpose the transitions peak of both polymers.

Biodegradation test

The biodegradation tests were made in alkaline pH because in previous work,²⁴ the samples of biodegradable polymers were subjected to soil compostage at acid and alkaline pH values (2.0 to 11.0). The biodegradation was best at alkaline pH because this made the polymers more susceptible to hydrolysis. The biodegradation curves for pure LDPE and PCL and the LDPE/PCL blends 90/10, 75/25, and 50/50 at pH 7, 9, and 11 are shown, respectively, in Figures 5 to 9. As

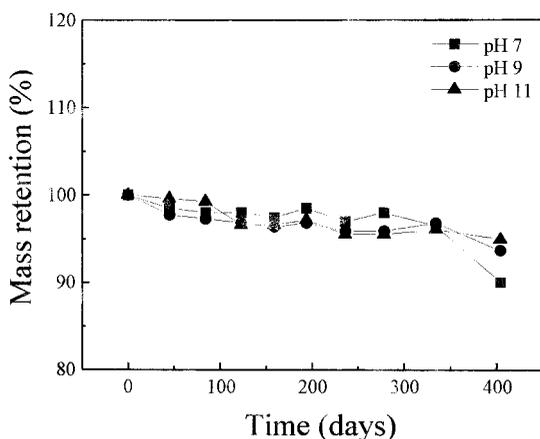


Figure 6 Biodegradation curves for 0/100 LDPE/PCL at pH 7, 9, and 11.

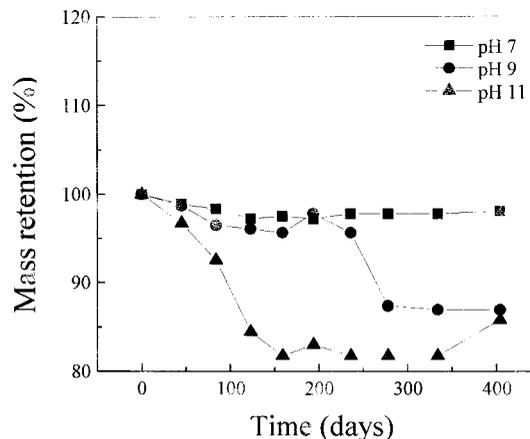


Figure 8 Biodegradation curves for 75/25 LDPE/PCL at pH 7, 9, and 11.

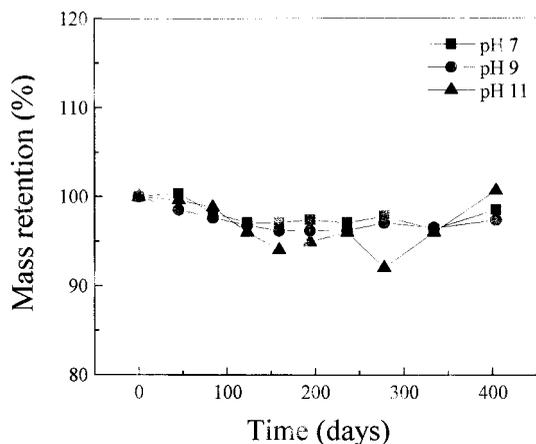


Figure 9 Biodegradation curves for 50/50 LDPE/PCL at pH 7, 9, and 11.

expected, PCL showed some biodegradation, whereas LDPE did not. For the LDPE/PCL blends, the mass loss was greatest for the blend 75/25 that, after aging in soil compostage for around 80 days, showed 15% biodegradation compared to 3% for PCL. The biodegradation of blend 75/25 probably reflected the interactions among the polymer chains, as also suggested by the closeness of the T_g peaks seen in DMTA (see Table IV). Biodegradation was favored by alkaline soil compostage, as shown by the greater loss of mass at pH 11. A similar finding was previously reported for other biodegradable materials.²⁴

The 90/10 blend had the lowest biodegradation, probably because the high crystallinity and low miscibility resulted in reduced interaction of LDPE with PCL. The great amount of LDPE that was likely responsible for an encapsulation of PCL by LDPE, caused by stirring during processing of the mixture, may have hindered the access of water molecules to the polyester. Blend 50/50 showed phase separation, with each component showing its characteristic behavior (Fig. 9). Some studies were carried out with respect to factors that improve the biodegradation tests conditions seeking a reduction of the biodegradation time of the PCL.^{24,25}

CONCLUSIONS

Of the blends studied here, 75/25 showed the best biodegradation. DMTA analysis showed some misci-

bility, whereas the mechanical properties indicated incompatibility, probably because of encapsulation of PCL by LDPE. This effect was reflected in the reduced biodegradation of the blends.

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