

The influence of the structure of starch on the mechanical, morphological and thermal properties of poly (ϵ -caprolactone) in starch blends

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Abstract In this work, the influence of three starches (A_1 , A_2 and A_3) on the mechanical, morphological and thermal properties of poly(ϵ -caprolactone) (PCL) was investigated in PCL/starch blends of 0/100, 75/25, 50/50 and 25/75 w/w%. The addition of starch to PCL reduced the tensile stress at break, the elongation at break and Young's modulus. The starches with linear chemical structures (A_1 and A_3) had lower values of tensile strength and higher values of elongation at break. Light microscopy indicated that the starches and PCL were immiscible. Thermal analysis showed that the 75/25, 50/50, and 25/75 w/w% blends containing linear starches had greater crystallinity than branched starch, an arrangement that may favor their biodegradation.

Introduction

The use of plastics has increased markedly in recent years, primarily because of their durability (plastics usually require more than 100 years for complete degradation), low cost and chemical inertness [1, 2]. This high durability creates a serious environmental problem because of the large amount of plastic waste produced, especially in urban centers [3].

Biodegradable products are one solution for the management of plastic waste [2]. As defined by ASTM D 883-99, biodegradable polymers are polymers that are initially degraded by the action of microorganisms such as bacteria, fungi and algae [4, 5]. Interest in the development of biodegradable polymers has grown in recent years and has resulted in considerable technological progress in the development of biodegradable products [6]. Consequently, the tendency for the future is to substitute polymeric synthetic materials for biodegradable polymers because of the lower environmental impact of the latter [2, 7]. However, the high cost of producing biodegradable polymers compared to conventional plastics is still a major problem to be solved [8]. The development of low-cost, biodegradable polymers for industrial use has been widely studied [9, 10]. In particular, the development of blends of biodegradable polymers containing a natural polymer would represent an important technological advance and be of considerable economical value, in addition to being environmentally friendly [11, 12].

Most high molecular weight biodegradable polymers are polyesters that contain functional ester groups in their structures that make them more susceptible to attack and hydrolysis by fungi [1, 2]. Poly (ϵ -caprolactone) (PCL) is a synthetic, biodegradable polyester with good mechanical properties that is compatible with many types of polymers and is one of the most hydrophobic biodegradable polymers currently available [2, 13]. PCL is used in pharmaceutical drug release formulations. In soil, extracellular enzymes degrade the extensive chains of PCL, thereby allowing microorganisms to assimilate the polymer [14]. However, the high cost of PCL has prevented its widespread industrial use.

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Natural polymers, such as starch and cellulose, are good base materials for producing rapidly degradable plastics, with the advantages that they are inexpensive and are easily digested by microorganisms. Starch is a particularly useful natural polymer because of its low cost and its abundance in nature [7]. The biodegradability of starch in a wide variety of environments makes it applicable for a wide range of products [15]. Starch consists of amylose, a linear α -D-(1-4)-glucan, and amylopectin, an α -D-(1-4)-glucan that has α -D-(1-6) linkages at the branch point [16, 17]. Figure 1 shows the chemical structures of amylose, amylopectin and PCL.

In this study, we investigated the influence of starches containing different proportions of amylose and amylopectin on the mechanical, morphological and thermal properties of PCL in blends of starch and PCL.

Experimental

Materials

Poly (ϵ -caprolactone) (PCL): PCL was supplied in pellet form by Dow Chemical Company Ltd. (P-767) (Cubatão, SP, Brazil). The melting index was 1.9 ± 0.3 g/10 min (ASTM D-1238) [18], with a density of 1.140 kg/m^3 and a weight average molecular weight (M_w) of 50,000.

Film preparation

The films were prepared by dissolving starches A₁, A₂ and A₃ in 22% (wt%) acetone. Blends of PCL with each

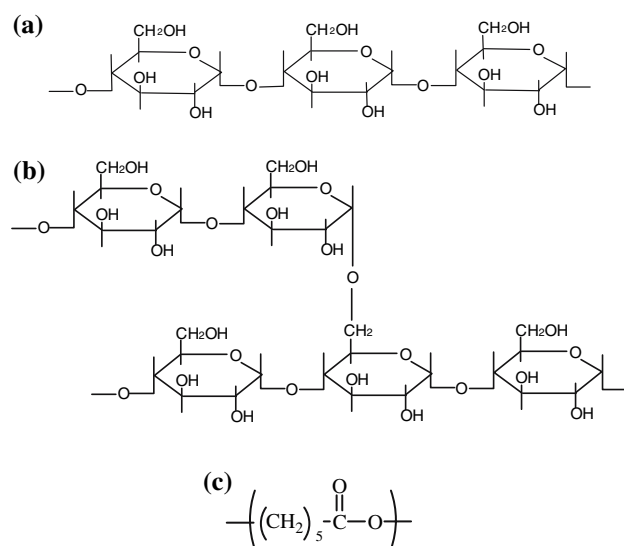


Fig. 1 Chemical structures of (a) amylose, (b) amylopectin and (c) PCL

type of starch were prepared using PCL/starch proportions (w/w) of 100/0, 75/25, 50/50 and 25/75. The solutions were stirred thoroughly at 60 °C and then poured into culture dishes, after which the solvent was allowed to evaporate in a saturated atmosphere. Table 1 shows the composition of the formulations that were prepared.

Samples for mechanical tests

The samples for the mechanical tests were prepared using a cutting knife in a model MA 098 hydraulic press (Marconi Equipamentos e Calibração para Laboratórios, Piracicaba, SP, Brasil). Fifteen type IV samples were prepared for each formulation [19].

Mechanical properties

Tensile tests were done on a model DL 2000 EMIC Universal Testing Machine. Five samples of each composition were strained at a rate of 50 mm/min at room temperature, using a gap distance of 50 mm, and the average values of tensile strength at break (σ), elongation at break (ϵ) and Young's modulus (E) were subsequently determined [19].

Light microscopy

The morphology and phase separation behavior of PCL blends with starch were assessed by light microscopy (model XP-500 microscope LABORANA, São Paulo, SP, Brazil).

Scanning electron microscopy

The specimens were fractured after freezing in liquid nitrogen and micrographs of the fractured surfaces

Table 1 Pure PCL and blends of PCL with starches A₁, A₂ and A₃

Starches	Formulations	Content, in mass (g)	
		PCL	Starch
A ₁	PCL100/A ₁ 0	7.2	0
	PCL75/A ₁ 25	5.4	1.8
	PCL50/A ₁ 50	3.6	3.6
	PCL25/A ₁ 75	1.8	5.4
A ₂	PCL100/A ₂ 0	7.2	0
	PCL75/A ₂ 25	5.4	1.8
	PCL50/A ₂ 50	3.6	3.6
	PCL25/A ₂ 75	1.8	5.4
A ₃	PCL100/A ₃ 0	7.2	0
	PCL75/A ₃ 25	5.4	1.8
	PCL50/A ₃ 50	3.6	3.6
	PCL25/A ₃ 75	1.8	5.4

were obtained using a JEOL model JSM-5900LV scanning electron microscope (JEOL Ltd., Akishima, Japan) at the Laboratório Nacional de Luz Síncrotron (Campinas, SP, Brazil).

Thermal analysis

Thermal analysis of PCL, starch and the PCL/starch blends was done using a model 204 TASC 414/3A differential scanning calorimeter (DSC) (Netzsch-Gerätebau GmbH, Bavaria, Germany) under a nitrogen atmosphere, at a heating rate of 10 °C/min. Two heating cycles were used for each polymer and their blends. The materials were first heated from room temperature to 80 °C to eliminate the thermal history of the samples, and then cooled to room temperature and immediately reheated to 100 °C. The second scan was done using the same heating rate as the first. All DSC experiments were done in duplicate and the thermograms obtained refer to the second heating. Melting temperatures of the first (T_{m1}) and second heating (T_{m2}) were determined. The crystallinity of PCL was calculated using a heat of fusion value ($\Delta H_{0 \text{ PCL}}$) of 139.5 J/kg for 100% crystalline materials [20].

Results and discussion

Mechanical properties

Figure 2 shows the tensile strength at break, the elongation at break and Young's modulus for pure PCL and its blends with starches A_1 , A_2 and A_3 . Mechanical tests were not done for the pure starches because it was not possible to prepare suitable films with the casting process used here. Compared to pure PCL, all of the PCL/starch blends showed a decrease in their mechanical properties with increasing starch content, indicating that corn starch behaved as a non-reinforcing filler.

In relation to the chemical structure of the starches, the tensile strength at break for the blend containing 25% of type A_2 starch was greater than for the same blend containing the linear starches A_1 and A_3 ; the latter showed reductions of only 11% and 10%, respectively. The branched structure of A_2 , which allowed smaller concentrations to be used, probably favored greater packing of the starch chains with PCL because of the secondary interactions between the hydroxyl groups of starch and the carbonyl groups of PCL. For the other blends, the values were practically the same as for branched starch (A_2). Thus, for PCL50/ A_50 , the reduction compared to pure PCL was 59% for

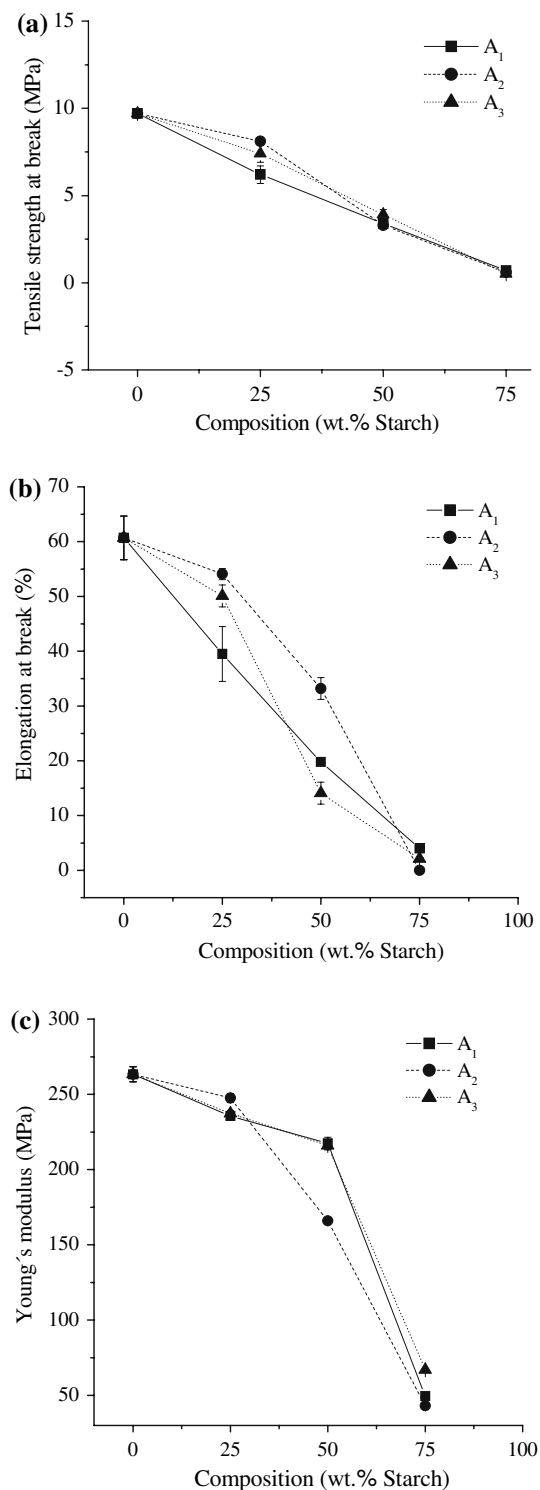


Fig. 2 Mechanical properties of pure PCL and PCL/starch blends: (a) tensile strength at break, (b) elongation at break and (c) Young's modulus

A_2 , 47% for A_3 and 45% for A_1 . For PCL25/ A_75 , the reductions compared to blends containing 50% starch were 79.5% for A_1 , 82% for A_2 and 87% for A_3 . The

decrease in tensile strength at break after the addition of starch probably reflected the heterogeneous distribution of starch in PCL and the low interfacial interaction between components of the blend that resulted in mechanical rupture at the blend interface.

The elongation at break values was greater with A_2 than with the other starches in blends containing 25% and 50% starch. For blends containing 50% starch, the reductions were 51% with A_2 , 68% with A_1 and 69% with A_3 compared to pure PCL. Likewise, the smallest reduction in the elongation at break was obtained with blends containing type A_2 starch, probably because this starch contained only branched chains, thereby allowing the formation of a larger number of secondary linkages and hence increasing the time to rupture.

The blends containing 75% starch showed a 94% reduction in the elongation at break when compared with pure polyester. In this blend, there was no significant difference among the three types of starch in the tensile strength at break and other mechanical properties.

In the blends containing a lower content of starch, the inclusion of type A_3 starch, which is derived from type A_1 by acid hydrolysis and has a smaller M_w , resulted in greater values for the elongation at break compared to starch without acid treatment (type A_1). The structure of type A_3 starch probably allowed greater interaction with the side groups of PCL; this behavior was not seen in blends containing 50% starch.

Young's modulus was reduced in all blends containing starch, regardless of the type. In blends containing 25% starch, type A_2 produced a smaller decrease in rigidity when compared to PCL alone. For blends containing 50% starch, the decreases were 18% for A_3 , 18% for A_1 and 37% for A_2 . Hence, the greater the degree of branching, the greater the decrease in rigidity compared to PCL. The smaller decrease in modulus seen in blends containing linear structures indicated that the blend was more rigid. These findings suggested a limited physical interaction between the starch molecules and PCL, except for blends containing 50% starch in which there was apparently marked interaction between the carbonyl groups of PCL and the hydroxyls of the starch. Such interaction resulted in better packing of the polymeric chains. At a concentration of 50%, type A_2 starch generally had the least effect on the parameters analyzed, indicating greater compatibility with PCL compared to linear starches.

Light microscopy

Figure 3 shows a light micrograph of PCL in which spherulites are visible. Figure 4 shows that there was

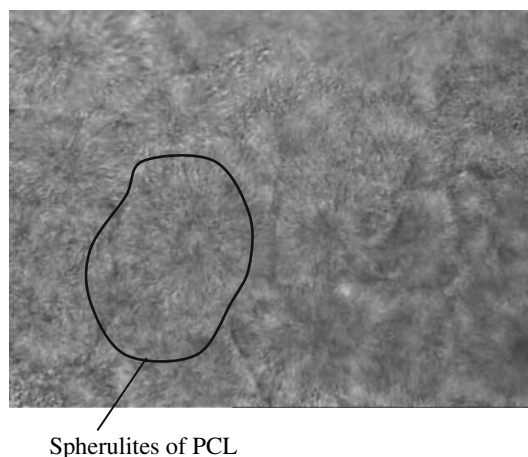


Fig. 3 Light photomicrographs of pure PCL. 200 \times

no significant variation in the grains of the three types of starch studied, probably because all were derived from the same source (corn). However, since the grains did not undergo gelatinization, they showed incomplete opening. The small difference in size suggested by the photomicrographs of Fig. 4 most likely reflected the swelling of some grains in water during preparation of the blends or during microscopic analysis.

Scanning electron microscopy

Figure 5 shows the morphology of PCL/type A_2 starch blends with two distinct phases but a good dispersion of starch in the PCL matrix. This finding suggested that there was no interaction among the materials, in agreement with the thermal analysis results.

Thermal analysis (DSC)

Table 2 shows the thermal analysis of PCL and its blends with starches A_1 , A_2 and A_3 . With the DSC conditions used, it was not possible to determine the melting temperatures of the starches because of the low temperature at which they began to decompose [8].

In blends containing 25%, 50% and 75% starch, linear starches (types A_1 and A_3) produced greater crystallinity of PCL than branched starch, which suggested that blends of the former starches would be more biodegradable than those containing branched starch. Table 2 shows that T_{m1} was greater than T_{m2} for all samples, indicating that after the initial melting the PCL crystals re-organized into a thermodynamically more stable form ($T_{m2} < T_{m1}$) compared to the initial samples.

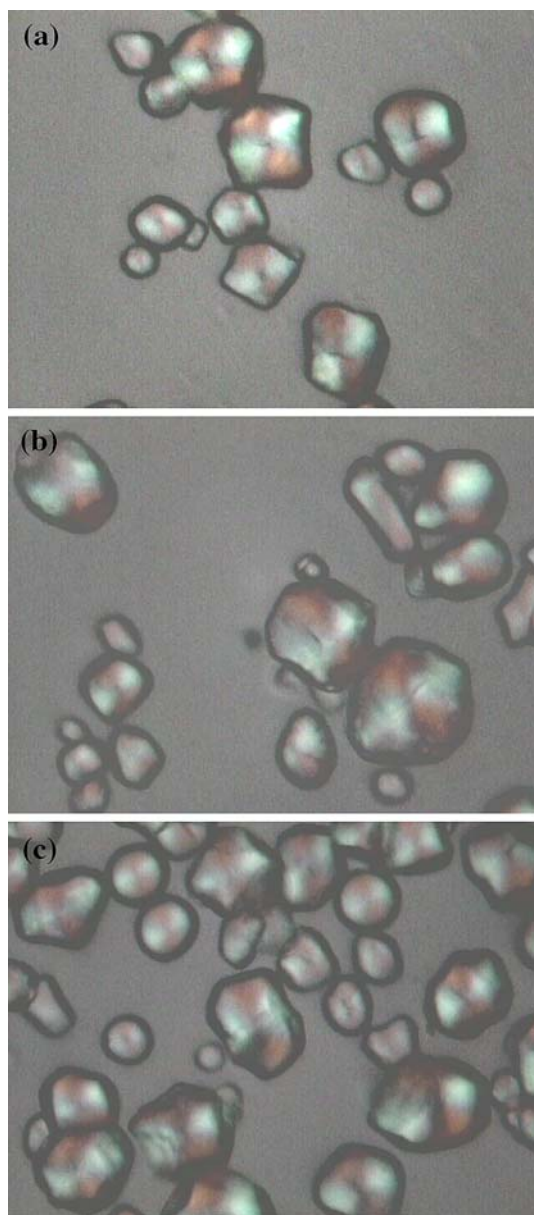


Fig. 4 Light photomicrographs of starches A_1 , A_2 and A_3 in the 50 PCL/50 starch blends (a) A_1 , (b) A_2 and (c) A_3 . 100 \times in all cases

A decrease in the melting temperature and crystallization is directly related to the miscibility of polymer in the blends [21]. Thermal analysis showed that there was no significant difference in the melting temperature of PCL in blends containing one of the three types of starch. The slight increase in the melting temperature seen in the presence of starch (up to 2.6%) was probably attributable to the separation of the two polymeric systems [22]. These results suggested that the mixtures were immiscible [23].

An increase in the starch concentration reduced the crystallinity of PCL in most of the blends by 5–56%.

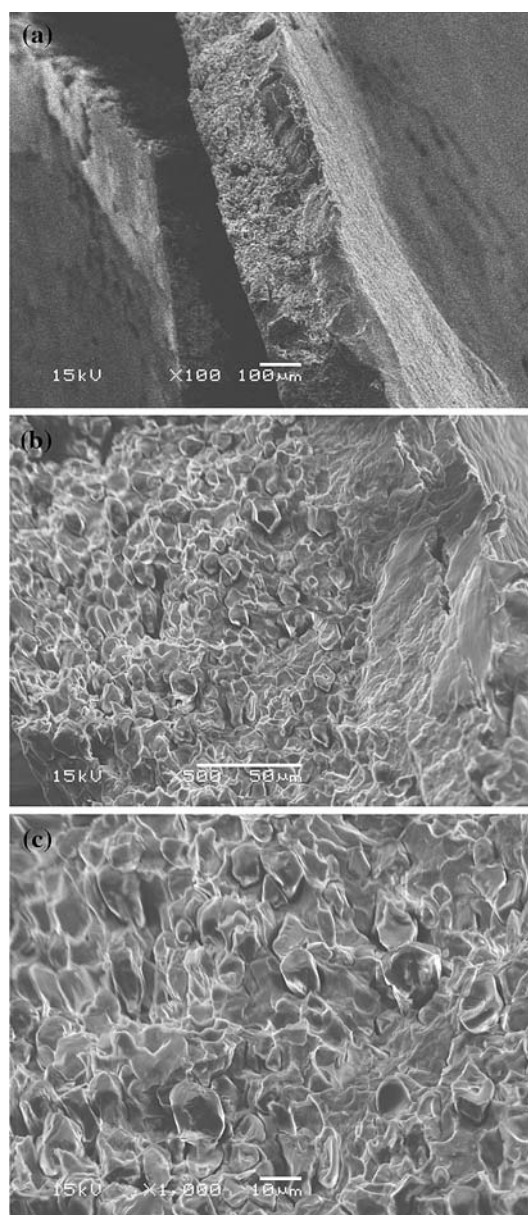


Fig. 5 Scanning electron photomicrographs of PCL50/A50. (a) A_1 , (b) A_2 , and (c) A_3 . 500 \times in all cases

This reduction could favor the biodegradation of the blends, as suggested by Rosa et al. [24]. The crystallization temperature of the blends increased by up to 25% compared to pure PCL and the crystallization of PCL was probably facilitated by the addition of starch.

Conclusions

The presence of increasing amounts of three types of starch (A_1 , A_2 and A_3) in blends with PCL generally reduced the mechanical properties of PCL. Starches

Table 2 Melting temperatures (T_{m1} and T_{m2}), temperature of crystallinity (T_c) and crystallinity of pure PCL and their blend with starches A_1 , A_2 and A_3

Formulation PCL/ Starch	T_{m1} (°C)	T_{m2} (°C)	T_c (°C)	Crystallinity (%)
Pure PCL	70.4	57.2	20.4	45
PCL75/ A_1 25	70.3	59.6	22.9	48
PCL50/ A_1 50	65.3	57.2	25.5	36
PCL25/ A_1 75	67.9	57.2	25.1	34
PCL75/ A_2 25	67.9	59.7	22.9	40
PCL50/ A_2 50	65.3	57.2	25.4	28
PCL25/ A_2 75	77.9	57.3	22.9	27
PCL75/ A_3 25	67.9	59.7	22.9	48
PCL50/ A_3 50	65.3	57.6	25.4	45
PCL25/ A_3 75	67.9	57.2	24.8	28

with a linear structure (A_1 and A_3) had a smaller tensile strength at break and greater elongation at break. Photomicrographs showed that the blends formed a two-phase system with good dispersion. Thermal analysis showed that in blends containing 25%, 50% and 75% starch, linear starches produced greater crystallinity than branched starch. Finally, the addition of starch probably facilitated the crystallization of PCL.

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