Biodegradation and the Dynamic Mechanical Properties of Starch Gelatinization in Poly(ε-caprolactone)/Corn Starch Blends

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ABSTRACT: Biodegradable polymers have attracted considerable attention because of their use as substitutes for nonbiodegradable polymers in disposable commodity applications. Poly(ε-caprolactone) (PCL) was blended with thermoplastic starch prepared from regular corn starch in PCL/starch ratios of 75/25, 50/50, and 25/75 wt %. The effect of corn starch gelatinization on the properties of these blends was assessed by dynamic mechanical thermal analysis, enzymatic degradation, and biodegradation in simulated soil. Increasing the starch content in the blends, storage modulus (E'') increased and enhanced the rigidity of the blends compared to pure PCL. The presence of starch decreased the polymer chain mobility and the intensity of the tan δ peak. These results probably indicate that PCL/starch blends were thermodynamically immiscible. PCL showed no significant reduction in mass after incubation with α-amylase, whereas blends containing corn starch were more susceptible to this enzyme. The biodegradation seen in simulated soil agreed with the findings for degradation by α-amylase and indicated that the latter was a sensitive method for assessing the degradation of PCL/starch blends and the effect of starch gelatinization over a short period of time. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 825–832, 2006

Key words: dynamic mechanical properties; enzymatic degradation; gelatinization; poly(ε-caprolactone); simulated soil biodegradation; starch

INTRODUCTION

Biodegradable polymers have attracted considerable attention because of their use as substitutes for nonbiodegradable polymers in disposable commodity applications. Among synthetic biodegradable polymers, poly(ε-caprolactone) (PCL), a linear, hydrophobic, and partially crystalline polyester, is susceptible to degradation by microorganisms.[1]

Starch is a natural biopolymer obtained from renewable resources. There has been a growing interest in developing starch-based products because starch is abundant, cheap, and totally biodegradable.[1,2] Native starch contains linear D-glucan amylose, and highly branched, unmodified amylopectin, i.e., unmodified starch.[3] In contrast, in gelatinized starch, the semicrystalline structure of the hydrogen bonds between the polymer chains is disrupted, thereby weakening the starch granule. This alteration results in irreversible changes in properties such as granular swelling, native crystalline melting, loss of birefringence, and starch solubilization.[3]

The main limitation of PCL is its low melting temperature (T_m 65°C), and starch also has some drawbacks, including a poor, long-term stability caused by water absorption, poor mechanical properties, and the processing.[2] Some of these problems can be overcome by physical or chemical modifications, including the blending of these polymers.[2,4,5] Blends of starch with synthetic polymers such as ethylene–vinyl alcohol copolymer,[6] starch/poly(ethylene-*co*-vinyl alcohol),[7] copolymers of ethylene with vinyl acetate, vinyl alcohol, acrylic acid, cellulose derivatives and other natural polymers,[8] recycled HDPE/PE,[9] and compounds with a mixture of glycerin as plasticizer have been studied. Among the environmentally friendly starch-synthetic polymer products currently marketed on a commercial scale are Mater-Bi ™ (Novamont, Italy),[10–13] Bioplast (Biotech, Germany),[10] Biopar (Biop Biopolymer Technologies AG, Germany),[11] and Novon™ (produced by Chisso in Japan and Warner Lambert in the USA).[12]

Starch-based biodegradable polymers have numerous applications in agriculture, industry, waste management, catering, and retailing. Loose-fill, thermoformed containers and transparent films are widely used in the packaging industry; biodegradable bags are used for waste collection and for disposable cutlery, whereas biodegradable films are used for agricultural mulching, pet products, and hygiene (cotton buds, packaging for toilet paper), over wrap, backing material for flushable sanitary products, pencil sharpeners, rulers, cartridges, toys, and plant pots. Starch-based biodegradable polymers can be also used as a biofiller to enhance tire performance because they reduce rolling resistance and greenhouse emissions.[13]

The use of products derived from renewable resources of agricultural origin reduces greenhouse gas emissions, energy consumption, and the exploitation of nonrenewable resources. This cycle of use is completed when the raw materials of agricultural origin return to the earth through biodegradation and composting, without releasing pollutants.

The process of polymer degradation is irreversible and results in a significant change in the structure of the material containing the polymer. These changes typically involve a loss of properties or polymer fragmentation and may occur through photodegradation, mechanical degradation, high-energy degradation, thermal degradation, and biodegradation.[5]

An assessment of polymer stability is important for evaluating polymer degradation[5] and can be determined by a variety of techniques, including dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry, mass loss through degradation, morphology by microscopy,[5] and the extent of surface damage based on surface roughness,[14] among others.

During polymer biodegradation, enzymes are frequently involved in the cleavage of chemical bonds. However, biodegradation will only occur in a favorable environment, and a lack of degradation may reflect an absence of growth factors essential for organisms to degrade the compound.[4,15]

Enzymatic digestion has also been used to examine the biosusceptibility of starch and PCL under specific conditions. Starch polymer is susceptible to enzymatic oxidation,[16] which means that it is particularly easy to hydrolyze during degradation by amylases, often referred to as "starch-splitting " enzymes.[3] Amylases and other enzymes have been used commercially for many years to modify the average weight molecular weight of starch. Many chemically modified starch products can be made with native starch granules as the starting material.

In this study, we used DMTA, enzymatic degradation, and biodegradation in simulated soil to investigate the effect of corn starch gelatinization on properties of blends with PCL.

These studies were carried out with the purpose of to investigate the changes on mechanical properties resulted by starch gelatinization and to obtain material with improved biodegradability, as a solution to the environmental problems caused by the accumulation of waste plastic materials on the landfill.

EXPERIMENTAL

Materials

PCL (Tone P-767) was supplied in pellet form by Union Chemical Carbide Ltd. (Cubatão, SP, Brazil), and had a melting index of 7.0 g/10 min (125°C/2.16 kg) (ASTM D-1238), a density of 1.145 g/cm^3 at 23°C, and an weight average molecular weight (M_w) of 50,000 g/mol.

Cornstarch (Amidex 3001) was supplied in powder form by Corn Products Brasil Ingredientes Industriais Ltda. (Jundiaí, SP, Brazil), and contained 27 wt % amylose and 73 wt % amylopectin, with a weight average molecular weight (M_w) of 486,000 g/mol.

Gelatinized corn starch (RD-337) was also supplied in powder form by Corn Products Brasil Ingredientes Industriais Ltda. (Jundiaí, SP, Brazil), and contained 27 wt % amylose and 73 wt % amylopectin, with an weight average molecular weight (M_w) of 486,000 g/mol.

Blend preparation

Blends of PCL containing 25, 50, or 75 wt % gelatinized and nongelatinized starch were prepared in an MH-100 homogenizer (MH Equipamento Ltda., São Paulo, SP, Brazil), operated at 1880–3600 rpm. The starch was dried in an oven at 60°C for 1 h before mixing the components and placing them in the homogenizer. All of the blends were processed using the same conditions.

Molding

Pure PCL and the blends were compression-molded into sheets (180 mm × 180 mm × 1 mm) using a model MA 098 Marconi press (Marconi Equipamentos e Calibração para Laboratórios, Piracicaba, SP, Brazil). The mold containing the desired material (PCL or blend) was initially placed in the press and heated for 5 min without applying any pressure to ensure uniform heat flow through the material. For all of the blends, the temperature was kept at 110 °C ± 5°C for 5 min at 5 t. The resulting sheets were removed from the press after cooling to room temperature.

Scanning electron microscopy

Micrographs of starch granules and gelatinized starch were taken using a JEOL model JSM-5900LV scanning electron microscope (SEM; JEOL, Akishima, Japan).

The arrows correspond to the dimensions of the grains of starch and starch after gelatinization and the circles to the diameter of the same ones.

Dynamic mechanical thermal analysis

DMTA was done using a dynamic mechanical analyzer, model MK III (Rheometric Scientific, Piscataway, NJ), fixing the samples in single cantilever clamps, with 20 cN m torque and using banding mode with 64 μm p-p of strain and frequency of 1 Hz. The scan was done over the temperature range of -65 to 40°C, with a heating rate of 5°C/min. The analyses were done in duplicate using specimens 30 mm $\times$ 10 mm $\times$ 1.5 mm.

Enzymatic degradation

Samples of PCL and PCL/gelatinized or granular starch were placed in a vial containing 10 mL of acetate buffer, pH 6, with 2.7 g of α-amylase. The vials were placed in a thermostatted oven at 60°C and the buffer/enzyme system was changed every 48 h to maintain the original level of enzymatic activity. The samples were removed from the incubation medium, washed with distilled water, wiped dry, and then weighed and examined by light microscopy. Control samples contained buffer without enzyme. The weights of the samples were recorded and used to determine the percentage of mass retention.

Light microscopy

The morphology and behavior of the materials during enzymatic degradation were also assessed by light microscopy (Model XP-500 microscope, Laborana Ltda., São Paulo, SP, Brazil) fitted with a CCD camera (resolution of 330/460 lines). The photographs shown here were taken before and after the enzymatic degradation.

Simulated soil

The simulated soil consisted of 23% loamy silt, 23% organic matter (cow manure), 23% sand, and 31% distilled water (all w/w).

Biodegradability based on mass retention

The specimens were weighed and buried, in triplicate, in simulated soil at room temperature (24°C). Biodegradation was monitored every 15 days for 105 days by measuring the mass retention. The buried specimens were recovered, washed with distilled water, and dried at room temperature until there was no further variation in weight, after which they were then
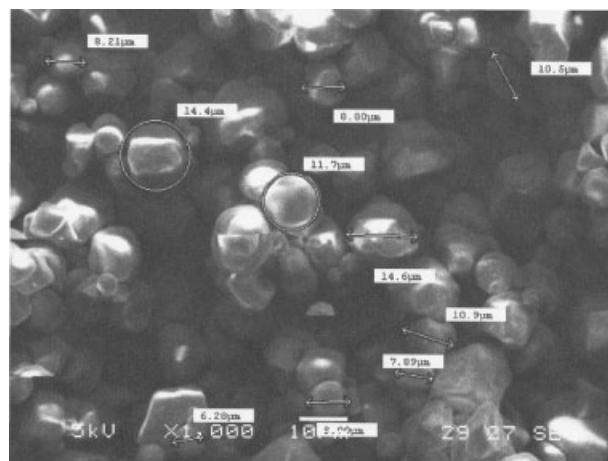
(a)
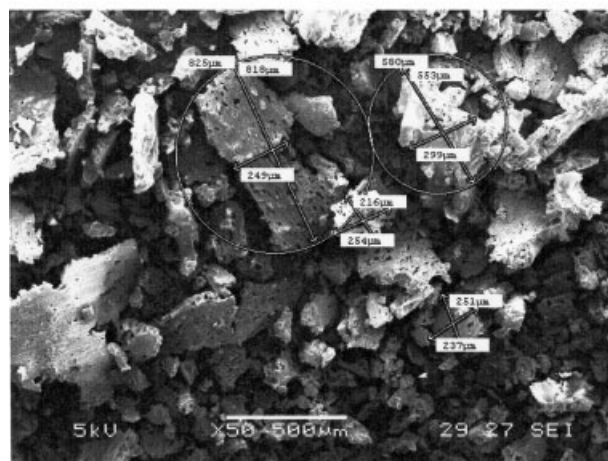
(b)

Figure 1 SEM images of (a) dimensions of starch granules ($\times$1000) and (b) dimensions of gelatinized starch ($\times$50). The arrows correspond to the dimensions of the grains of starch before and after gelatinization, and the circles correspond to the diameter of the same ones.

weighed. Following weighing, the specimens were buried again in their respective trays.

RESULTS AND DISCUSSION

Morphology

Figure 1(a) shows SEM images variation in the shape and size of the starch granules. Starch granules are spherical and range from 5 to 30 μm in diameter.[3] Figure 1(a) shows that the size of the starch granules used in this work varied by nearly 15 μm.

The gelatinized starch had no regular shape [Fig. 1(b)] and the granules were >850 μm in diameter. Starch gelatinization led to granule swelling, loss of crystallinity,[17] and leaching of amylose and amylopectin.[18] The disrupted granules of gelatinized starch ex-

posed the amylose and amylopectin and increased the mobility of these molecules that could have increased the interaction with the PCL chains.

Dymamic mechanical thermal analysis

Figures 2 and 3 show the storage modulus (E'), loss modulus (E''), and tan δ curves provided by DMTA analysis of PCL/nongelatinized starch blends and PCL/gelatinized starch blends, respectively.

In dynamic mechanical studies, changes occur close to the T_g of the polymer, with the dynamic modulus (E') decreasing rapidly, and the loss modulus (E'') and tan δ showing maximal values. All of these effects have been used as measures of T_g.[19]

In the transition region, these changes referred to as the primary dispersion (the α-peak). The magnitude of the α-peak in the amorphous polymer was much higher than in the semicrystalline polymer, primarily because the chain segments of the amorphous polymer were free from restraints imposed by crystalline polymers in the glass transition region. Although the crystallinity of the blends decreased,[17] the intensity of the α-peak decreased because the secondary forces increased with the incorporation of the starch (Fig. 2).

Avérous et al.[10] reported that the evolution of the tan δ of thermoplastic starch plasticized with glycerol showed two relaxations. The main relaxation (α) was associated with a large tan δ peak and an important decrease in the storage modulus that was attributable to the TPS glass relaxation, while the secondary relaxation (β) was consistent with the glycerol glass transition. Avérous et al.[20] observed the same behavior for PCL/TPS blends. In the present study, only one α-peak was observed because the starch was used without glycerol.

The maximum heat dissipation per unit deformation normally occurs at the temperature where E'' is maximum.[19] The peak of E'' occurred at -54, -51, and $-50°C$ for the PCL/gelatinized starch blends of 75/25, 50/50, and 100/0, respectively, [Table I, Fig. 3(c)]. Starch gelatinization increased the loss modulus in the 75/25 blends, but reduced this modulus in the 50/50 blends [Fig. 3(b)]. This probably reflected the fact that in gelatinized starch the amylase and amylopectin chains are free, thereby allowing better energy dissipation through the polymeric system.

The movements of long chain segments in the polymeric structure have a profound effect on the loss factors (tan δ and loss modulus) of the dynamic mechanical properties. The tan δ value at the α-peak (the glass transition) was greater than at the dissipation peaks for lower temperatures, and was accompanied by the greatest decrease in dynamic modulus with increasing temperature (Figs. 2 and 3).

Above the T_g, the dynamic modulus (E') increased markedly while the α-peak (T_g) shifted to a higher
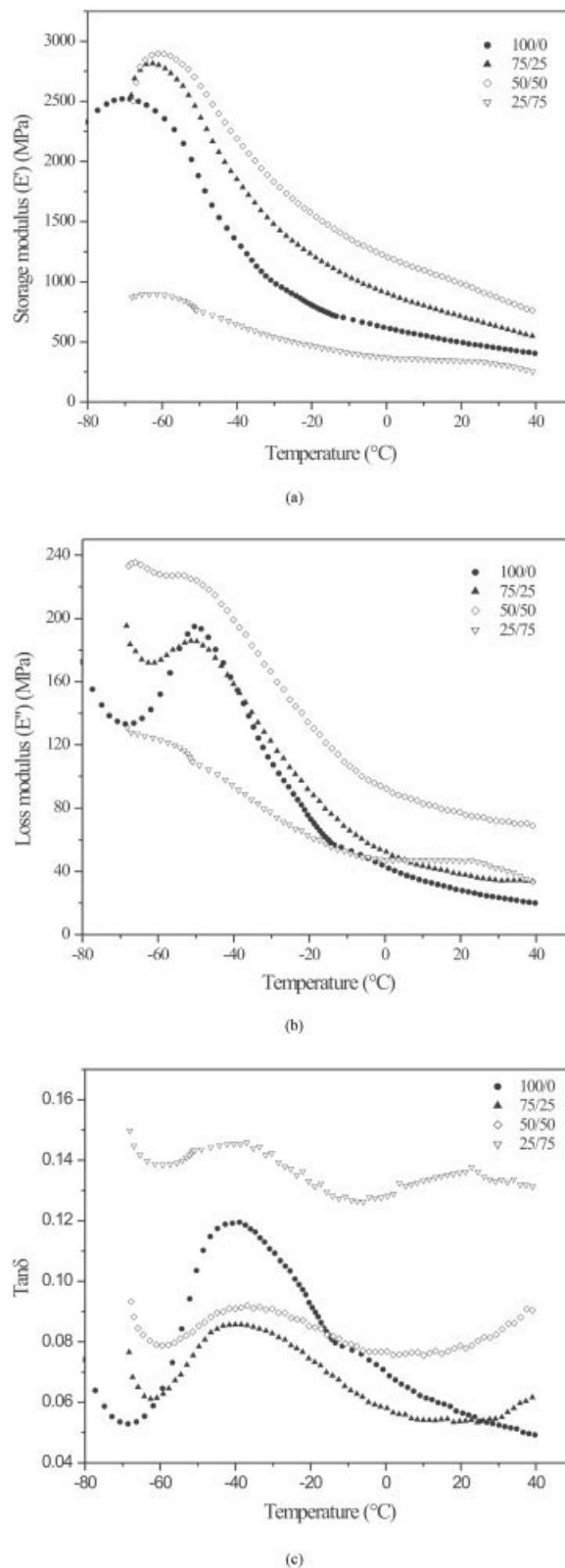

Figure 2 DMTA curves for PCL/nongelatinized starch blends: (a) storage modulus (E'), (b) loss modulus (E''), and (c) tan δ.

temperature as the secondary forces between the phases increased. The addition of 25 and 50% starch to PCL increased the storage modulus (E') by enhancing
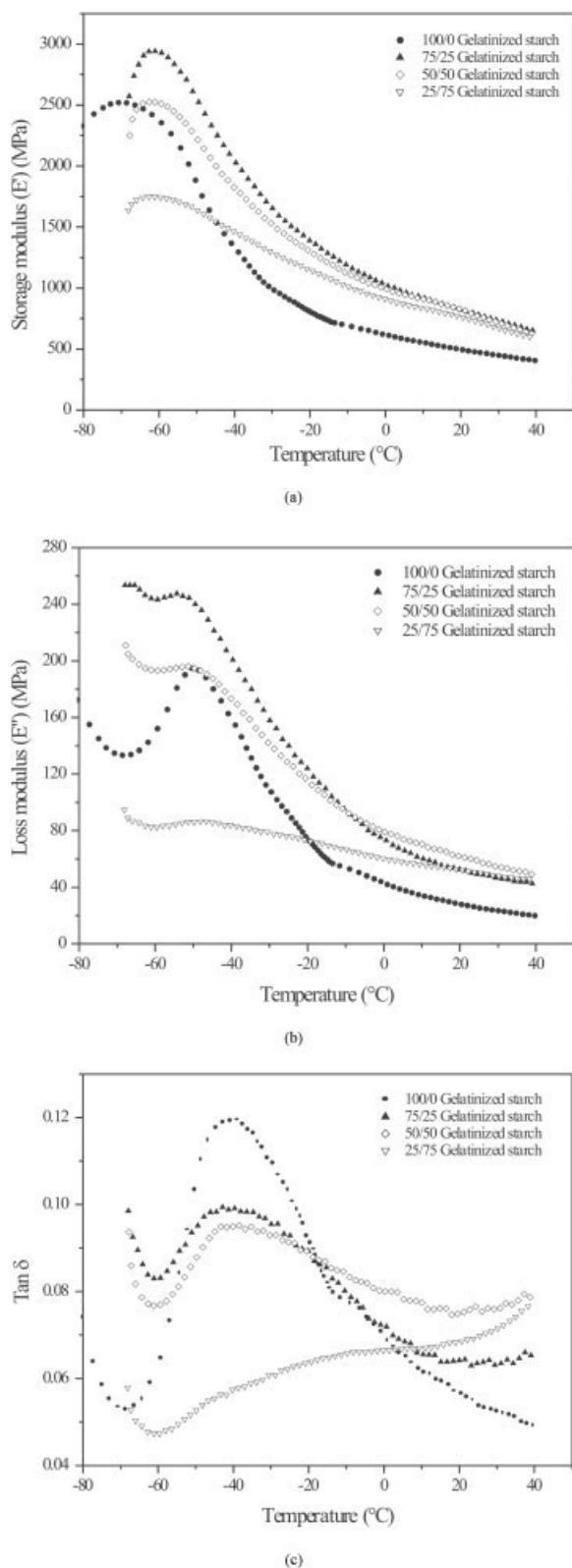
Figure 3 DMTA curves for PCL/gelatinized starch blends: (a) storage modulus (E'), (b) loss modulus (E''), and (c) tan δ.

the secondary forces of the PCL/starch blends [Fig. 2(a)]. This was particularly the case with 50% starch, which increased these secondary forces most and

made the blends more rigid than pure PCL by decreasing the polymer chain mobility. Gelatinized starch showed the same behavior, but the effect was less marked. The addition of 75% starch significantly reduced the E' [Fig. 2(a)], whereas the addition of 25% gelatinized starch increased the secondary forces by enhancing the interaction of the free hydroxyls of the starch with PCL in the blends; 50% gelatinized starch did not alter this property, in relation to pure PCL [Fig. 3(a)].

The damping curve for the dynamic properties of heterogeneous copolymers reflects the border of the transition region between immiscible substances, and this transition is generally broad for such copolymers. As shown here, the intensity of the tan δ peak decreased with the incorporation of starch, and the broad transition region observed indicated that PCL and starch were insoluble in each other [Figs. 2(c) and 3(c)].

The lower intensity of tan δ seen in the blends indicated less movement of the molecular chains in the blends compared to pure PCL. The 75/25 blend was more rigid and, although gelatinization also had increased the rigidity of the material, this increase occurred on a shorter scale, with the starch acting as a load. For 25/75 blends, it was not possible to determine the temperature at which tan δ was maximal, since there was no corresponding peak [Figs. 2(c) and 3(c)].

PCL and the 75/25 and 50/50 blends showed curves with a single peak that was attributed mainly to PCL [Figs. 2(c) and 3(c)]. The addition of starch did not influence the temperature at which the peak T_g was observed, except for the 50/50 blend containing nongelatinized starch, for which the corresponding value was $-37°C$ [Table I, Fig. 2(c)]; this temperature was not considered different because of its broader transition.

Starch gelatinization increased the values of tan δ [Fig. 3(c)]. Gelatinized starch produced no shift and no T_g was seen in the temperature range measured. The glass transition temperature (T_g) of starch cannot be determined experimentally because starch polymers start to decompose at a lower temperature.[21]

The side chains of PCL reorganized more easily in the presence of gelatinized starch than with granules starch because the former behaved as a polymer in the polymer blend. Hence, a mixture of thermoplastic starch and PCL could potentially behave in a manner similar to more conventional polymer–polymer blends. The addition of starch granules to PCL showed the general trend for filler effects on polymer properties, with gelatinized starch acting as rigid filler in films, thereby reducing the mobility of the chains.[22]

TABLE I
T_g for PCL and PCL/Starch Blends as Determined by DMTA

Formulation (wt %)	T_g (°C)/tan δ		T_g (°C)/E'' (MPa)	
	Nongelatinized	Gelatinized	Nongelatinized	Gelatinized
100/0	−42/0.12	−42/0.12	−50/195	−50/195
75/25	−41/0.09	−42/0.10	−51/186	−54/248
50/50	−37/0.09	−43/0.10	−53/227	−51/196
25/75	−	−	−	−

Enzymatic degradation

PCL and its blends with starch granules or gelatinized starch were subjected to degradation tests using α-amylase. The mass retention was monitored and the results are shown in Figure 4. PCL showed no significant reduction in mass during 240 h of incubation with the enzyme, probably because PCL is not a substrate for α-amylase.

PCL is degraded by the hydrolytic cleavage of its ester groups and is affected by the chemical structure and molecular arrangement of the chain polymer and by the state of the polymer surface, since contact with microorganisms represents the first step in degradation.[23] PCL is a semicrystalline polymer and its crystallinity protects against the action of α-amylase. The higher mass retention of PCL compared to its blends with starch indicated that α-amylase was unable to cleave the ester groups of PCL. In contrast, the action of α-amylase on starch resulted in the fragmentation of PCL and, consequently, a greater area of contact with the enzyme that made it easier to degrade the blends. There was a decrease in the crystallinity of PCL with increasing granular starch content as reported by Rosa et al.,[17] which could favor degradation of the polymer.
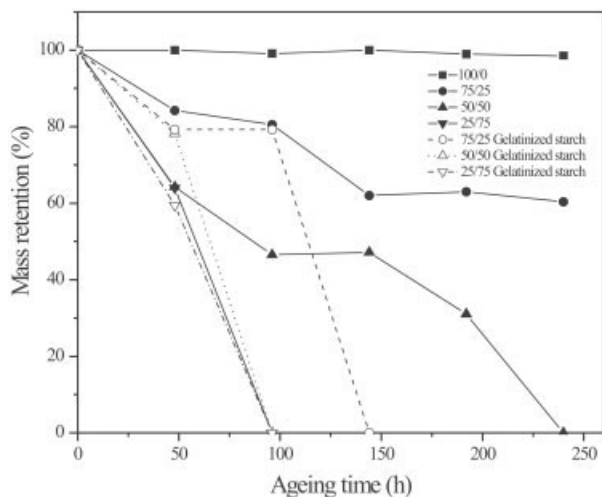
Blends containing corn starch were more susceptible to α-amylase, with complete degradation occurring after 240 h. Starch is generally totally biodegradable, and the amylase and amylopectin present in starch are readily hydrolyzed by α-amylase at their α-1–4-linkages.[24] In many cases, association of the enzyme molecule with a polymer chain results in the hydrolysis of several units before dissociation.[24]

α-Amylase randomly hydrolyzes the α-1–4-glucosidic bonds of starch into dextrins, and this hydrolysis can significantly reduce the mass retention of blends.[24] The release of starch from the surface to the bulk of the blends is also limited by the porosity of the material. Starch gelatinization promoted by the more porous surface between the polymers[15] favors degradation to the bulk of the blends and contact of the enzyme with the polymer.

There was no significant variation in the action of amylase on the two types starch (gelatinized or granules) in 25/75 blends. However, for the 75/25 and 50/50 blends, the presence of gelatinized starch significantly enhanced the action of the enzyme. This finding probably reflected the fact that starch gelatinization results in physical and chemical alterations and the rupture of polymeric chains that subsequently expose amylose and amylopectin, thereby allowing the enzyme to act directly on these molecules.

The cleavage of starch leads to the fragmentation of PCL and provides a larger surface area for the enzyme to act on, thereby accelerating the degradation of the blends. As shown in Figure 4, there was an abrupt reduction in the percentage of mass retention at the beginning of the incubation with enzyme (48 h) in blends containing 75% starch and reflected the action of amylase on the starch.

Light microscopy

Figure 5 shows photomicrographs of PCL/gelatinized and nongelatinized starch blends obtained before and after enzymatic degradation. Initially, all of the samples showed similar morphologies [Figs. 5(a), 5(c)–5(e), 5(i)–5(k)]. However, after incubation with α-amylase, numerous small particles were seen and were more frequent with increasing starch content [Figs.
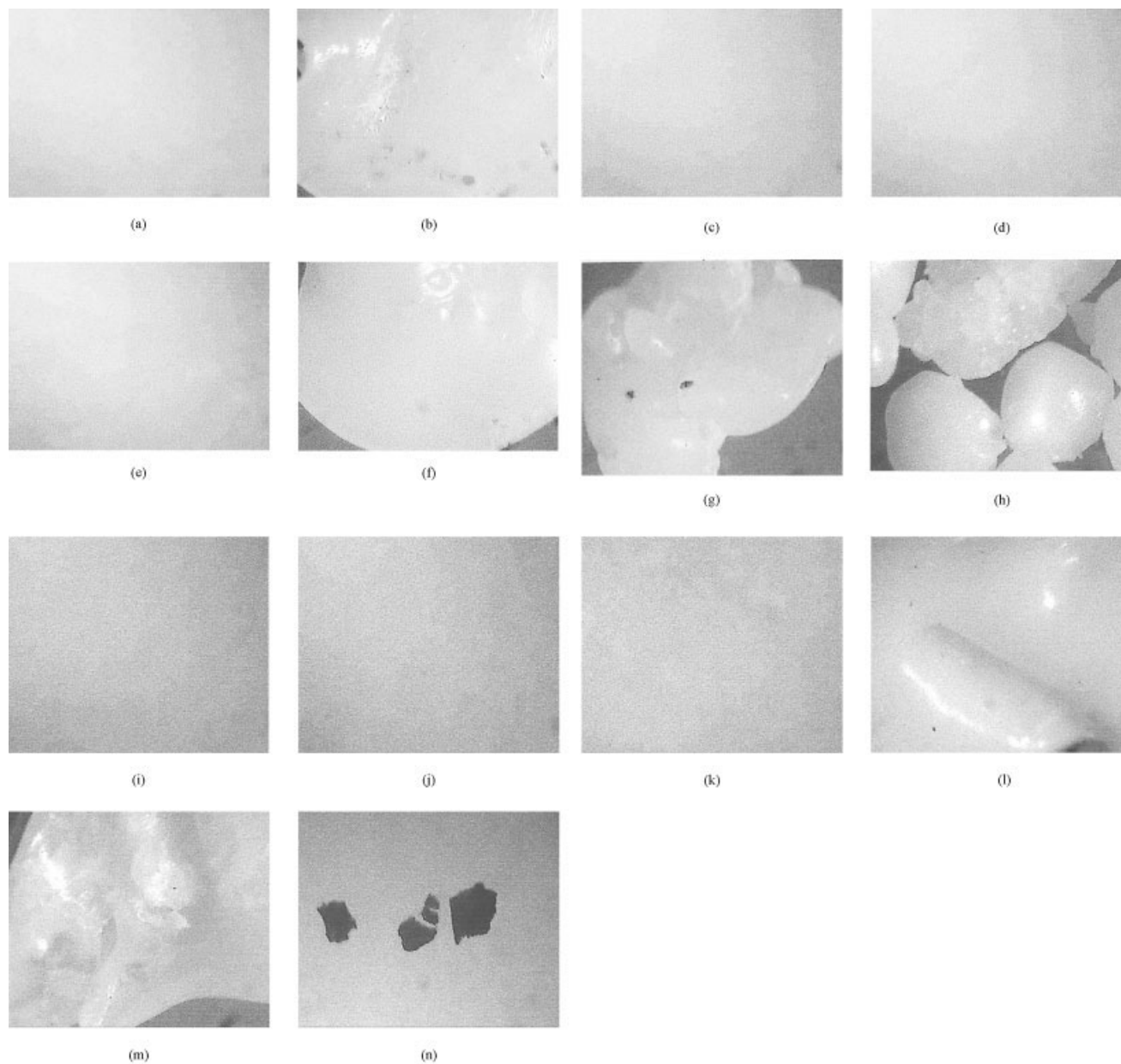

Figure 4 Mass retention for PCL/gelatinized and nongelatinized starch blends in α-amylase.

Figure 5 Photomicrographs of PCL/starch blends at the beginning (B) and at the end (E) of enzymatic degradation: (a) 100/0 (B); (b) 100/0 (E); (c) 75/25 (B); (d) 50/50 (B); (e) 25/75 (B); (f) 75/25 (E); (g) 50/50 (E); (h) 25/75 (E); (i) 75/25 G (B); (j) 50/50 G (B); (k) 25/75 G (B); (l) 75/25 G (E); (m) 50/50 G (E); and (n) 25/75 G (E).

5(b), 5(f)–5(h), 5(l)–5(n)]. As a result, blends containing gelatinized starch became less compact.

Biodegradability based on mass retention in simulated soil

Figure 6 shows the biodegradation of PCL and blends of PCL with nongelatinized and gelatinized starch.

The incorporation of starch into PCL reduced the mass retention of the blends, with this reduction being proportional to the increase in starch content. Gelatinization of the starch reinforced the biodegradation of

the blends. The blends initially showed an increase in mass retention that agreed with the water absorption test reported by Rosa et al.,[17] whereas pure PCL showed no such increase. Starch is a hydrophilic polymer and the gelatinization of starch disrupted the granules and exposed the amylose and amylopectin chains, thereby enhancing their absorption of water (by up to 20% in 25/75 gelatinized starch after 15 days of ageing). This increased absorption favored hydrolysis of the polymers, with the cleavage of hydrogen bonds making the polymers more susceptible to biodegradation by microorganisms over a shorter time compared to PCL.
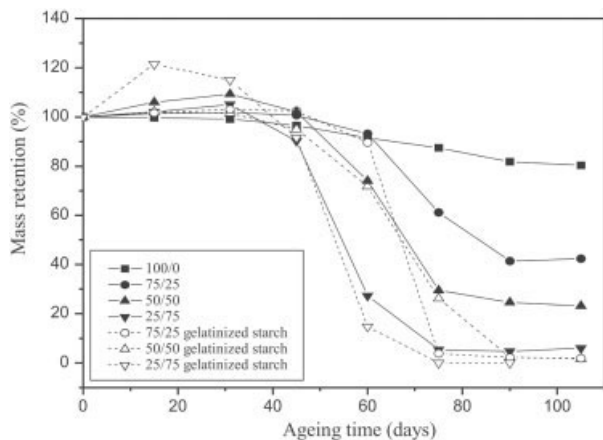
Figure 6 Mass retention for PCL/gelatinized and starch granules in soil simulator.

The biodegradation of polymers in simulated soil starts with a lag phase[25] and during this period the adaptation and selection of the degrading microorganisms varied by up to 45 days for the 25/75 and 50/50 blends, regardless of the type of starch, and by up to 60 days for the 75/25 blend and pure PCL.

The second phase of biodegradation (from the end of the lag phase until about 90% of the maximum level of biodegradation) was characterized by a drastic reduction in mass retention in all of the blends; this reduction was greater in blends with a higher starch content and greater gelatinization.

The last phase was the plateau phase that extended from the end of the biodegradation phase until the end of the test[25] (90 days of ageing in the case of PCL and the blends), with marked variation in the mass retention (from 0% for 25/75 gelatinized starch up to 80% for PCL). This finding confirmed the strong influence of gelatinization in enhancing the biodegradation of PCL/gelatinized starch blends.

Finally, PCL/gelatinized starch blends showed improved biodegradation and were less expensive than materials currently available on the market.

CONCLUSIONS

The results of this study showed that increasing the starch concentration increased the storage modulus (E'') and enhanced the rigidity of the blends compared to pure PCL. Starch decreased the polymer chain mobility and the intensity of the tan δ peak. These results indicated that the PCL/starch blends were thermodynamically immiscible. PCL showed no significant reduction in mass after incubation with α-amylase, whereas blends containing corn starch were more susceptible to this enzyme, with complete degradation occurring after 240 h.

The biodegradation seen in simulated soil agreed with the findings for degradation by α-amylase and indicated that the latter was a sensitive method for assessing the degradation of PCL/starch blends and the effect of starch gelatinization over a short period of time.

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