

Mechanical Behavior and Biodegradation of Poly(ϵ -caprolactone)/Starch Blends with and without Expansor

Derval S. Rosa (✉), Cristina G. F. Guedes, Fabricio Casarin

Universidade São Francisco, Programa de Pós-Graduação *Stricto Sensu* em Engenharia e Ciência dos Materiais, Laboratório de Polímeros Biodegradáveis e Soluções Ambientais, Rua Alexandre Rodrigues Barbosa, nº 45, CEP 13.251-900, Itatiba, SP, Brazil
E-mail: derval.rosa@saofrancisco.edu.br; Fax: 55 11 4524-1933

Received: 3 March 2005 / Revised version: 3 May 2005 / Accepted: 20 May 2005
Published online: 3 June 2005 – © Springer-Verlag 2005

Summary

The use of biodegradable polymers has provided an alternative to the problem of polymer-based products discarded in the environment. Poly(ϵ -caprolactone) (PCL) is a biodegradable polymer that has been used industrially, but it is very expensive. Starch is a potentially useful material for biodegradable plastics because of its natural abundance and low cost. The aim of this work was to examine the effect of adding azodicarbonimide (ADC) as an expansor to blends of PCL with corn starch. Different proportions, of ADC (0.1%, 0.2% and 0.3%, w/w) were added to pure PCL and to PCL/starch (50/50) blends and their properties were studied. Biodegradable blends of PCL with starch had a higher density than PCL alone and the addition of ADC reduced the density of the materials. The incorporation of starch increased the water absorption and ADC did not significantly alter this property. The incorporation of starch into PCL reduced the tensile strength and the elongation at break; ADC enhanced these reductions and also decreased the Young's modulus of PCL. SEM showed that blends prepared with starch were immiscible, had a homogeneous dispersion of starch, and poor interfacial adhesion. The addition of ADC resulted in cells in the interior of the polymers. The 50/50 PCL/starch blends biodegraded faster than PCL, and ADC had no significant influence on the biodegradation of the blends but inhibited the biodegradation of PCL.

Introduction

Plastics contribute most to surface litter, which is now a serious problem even in the least developed countries. The disposal of non-degradable waste plastic packaging now pose challenges to the developed and developing world [1]. Poly(ϵ -caprolactone) (PCL) (Figure 1a) is biodegradable, synthetic, aliphatic polyester made by the ring-opening polymerization of caprolactone. PCL has a low melting point (58-60°C), a low viscosity and is easy to process. Until recently, PCL was not widely used in biodegradable polymer applications because of its expensiveness. However, the cost of PCL has been overcome by blending PCL with corn starch [2,3].

Starch is a potentially useful material for biodegradable plastics because of its natural abundance, low-cost, renewable and it is a biosynthesized polymer [4]. Native starch

occurs as granules in the roots, seeds and stems of a variety of plants, including corn and potatoes. Unfortunately, native starch has poor mechanical properties and poor long-term stability caused by the water absorption [5,6]. The polymerization of glucose in starch results in two types of polymers, amylose (Figure 1b) and amylopectin (Figure 1c). Amylose is an essentially linear polymer, although there is evidence, to suggest that some branches are present in this polymer [7]. In contrast, amylopectin is much larger and branched. Amylose and amylopectin do not exist free in nature, but as components of discrete, semicrystalline aggregates known as starch granules. The size, shape, and structure of these granules vary substantially among plants [2]. The structural differences between these two polymers contribute to significant differences in the properties and functionality of starch [2]. Starch is highly hydrophilic and readily disintegrates on contact with water. This can be overcome through blending, since starch has free hydroxyl groups that can readily undergo a number of reactions such as acetylation, esterification and etherification [2].

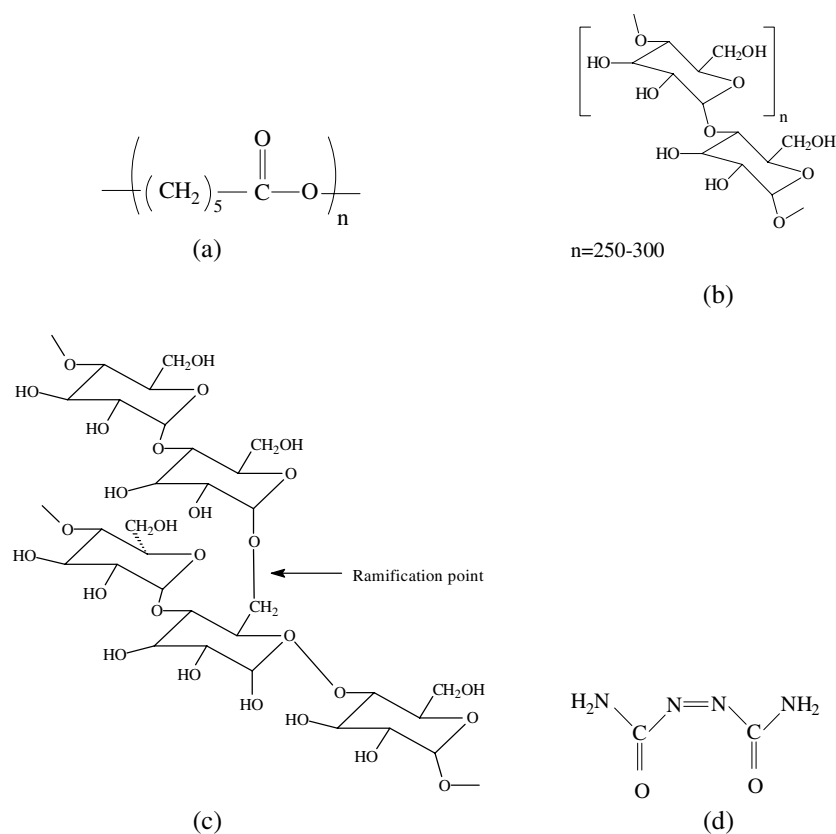


Figure 1. Chemical structures of (a) PCL, (b) amylose, (c) amylopectin, and (d) ADC.

Rutkowska et al. (2000) examined the influence of different additives on the biodegradation of PCL film in compost with plant treatment active sludge [2]. Azodicarbonamide (ADC) (Figure 1d) is a nucleating agent commonly used to reduce the density of plastics and to lower costs by using less raw material. ADC has been used to reduce the weight and modify the texture and mechanical, thermal and

acoustic properties of plastics. The expanders currently available can be classified as exothermic. The ADC is the active agent, and endothermic, when citrates and citric acid are the active initiators. The use of ADC as expansion during polymer biosynthesis results in the formulation of tiny cells of gas through the plastic [8]. The aim of this study was to examine the influence of ADC as an expander on the density, water absorption, tensile properties, morphology and biodegradation in simulated soil of PCL/starch blends.

Experimental

Materials

PCL was supplied in pellet form by Union Chemical Carbide Ltd. (P-767) (Cubatão, SP, Brazil). The melting temperature was 60°C, and the melting flow at 80°C was 1.9 ± 0.3 g/10 min (ASTM D-1238), with a density of 1,145 kg/m³ and a weight average molecular weight (M_w) of 50,000 g/mol.

Corn starch (Amidex 4001) was supplied in powder form by Corn Products Brasil - Ingredientes Industriais Ltda. (Jundiaí, SP, Brazil), and contained 0-3 wt.% amylose and 97-100 wt.% amylopectin, with an average molecular weight (M_w) of 486,000 g/mol and a density of 0.5-0.7 g/cm³.

Azodicarbonamide (ADC; type CS-4M) was obtained from INBRA Indústrias Químicas Ltda. (Diadema, SP, Brazil), and had an average granulometry of 3.2 µm, a point of decomposition of 208°C, a weight average molecular weight (M_w) of 116.08 and an apparent density of 0.4 g/cm³.

Blend preparation

The starch was dried in an oven at 60°C for 1 h before mixing the components and placing them in the homogenizer. Pure PCL and PCL/starch 50/50 blends containing 0.0, 0.1, 0.2 and 0.3 wt.% ADC were prepared in an MH-100 homogenizer (MH Equipamento Ltda., São Paulo, SP, Brazil).

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 3 min without applying any pressure in order to ensure uniform heat flow through the material. For all of the blends, the temperature was kept at $130 \pm 3^\circ\text{C}$ for 3 min at 15 t. The resulting sheets were removed from the press after cooling to room temperature.

Density

PCL and PCL/starch blends were equilibrated at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity for not less than 40 h prior to the test (ASTM D 792-98). The densities were measured using an analytical balance with a precision of 0.1 mg, and equipped with a stationary support for the immersion vessel above the balance pan. The specimens were weighed in air and completely immersed in ethyl alcohol at $23 \pm 2^\circ\text{C}$.

Water absorption

Three specimens of each material were dried in an oven with circulating air for 24 h at $50 \pm 3^\circ\text{C}$, cooled in a desiccator, and immediately weighed to the nearest 0.1 mg. The specimens were then rested on their edge and completely immersed in a container of distilled water maintained at $23 \pm 1^\circ\text{C}$ (ASTM D 570). After 2 h, the specimens were removed from the water one at a time, wiped with a dry cloth to remove all surface water, and immediately weighed to the nearest 0.1 mg. The samples were then returned to the water and weighed again at 2 h intervals during the first 10 h. Thereafter, the specimens were weighed every 24 h for seven days.

Tensile properties

The tensile properties were assessed with an EMIC model DL 2000 universal testing machine (EMIC Equipamentos e Sistemas de Ensaio Ltda., São José dos Pinhais, PR, Brazil) using specimens (Type IV) cut from compression-molded sheets, according to the ASTM D-638 standard. The control program used was Mtest LBP version 3.00 and the load cell had a capacity of 20 kgf. The specimens were initially 25 mm long and the speed of stretching was 5.0 mm/min. The average and standard deviation values of tensile strength, elongation at break and Young's modulus were determined for each formulation.

Scanning electron microscopy (SEM)

The specimens were fractured after freezing in liquid nitrogen and micrographs of the fracture surfaces were obtained using a JEOL model JSM-5900LV scanning electron microscope (JEOL Ltd, Akishima, Japan).

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

Results and discussion

Density

The incorporation of starch into PCL increased the density of the blends compared to pure PCL, as shown in Figure 2, in spite of the starch to be denser than PCL. However, the addition of ADC reduced these densities by 8.0% for PCL and 25.8% in average for PCL/starch blends, when added 0.3% ADC in both samples.

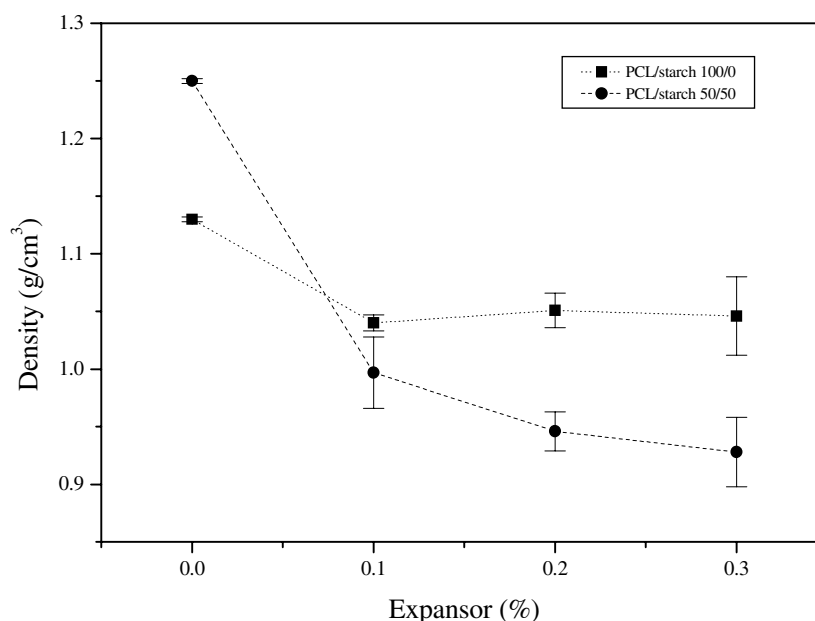


Figure 2. Densities of PCL and PCL/starch 50/50 blends with or without ADC. The points are the mean \pm S.D. of three determinations.

Regardless of the amount of ADC (0.1%, 0.2% or 0.3%) incorporated, the effect on the density of PCL was almost the same. However, the density of the 50/50 blends decreased with increasing ADC content, and became less dense than PCL with the highest concentration of expansor. This effect could be attributed to the poor interfacial adhesion between PCL and starch, resulting in blends more porous than pure PCL, as shown by the morphology of the materials (Figures 6b and 7b). The blowing gas produced during the thermal decomposition of ADC that was adsorbed on to the surface of the particles during phase separation and the poor interfacial adhesion between the polymers facilitated the form action of cells during the foaming process and allowed the ADC to expand more in the PCL/starch blends than in pure PCL. Blends containing 0.2% and 0.3% of expansor had a lower density than water, reducing the weight of these materials which also favors their application in products that float under the water.

Water absorption

Figure 3 shows the water absorption by PCL and PCL/starch blends after seven days of immersion.

PCL showed practically no increase (1.0%) in weight during the period of immersion in water. However, the incorporation of starch into PCL significantly increased the water absorption of the blends. There was an initial increase in the weight of the blends that was higher for 50/50 blends containing 0.2% ADC, until approximately the first 60 days.

The plateau regions with little or no change in weight as a function of the immersion time represented the water saturation limit of PCL and the PCL/starch blends. For PCL, the plateau region occurred after 48 h of immersion, while for PCL containing

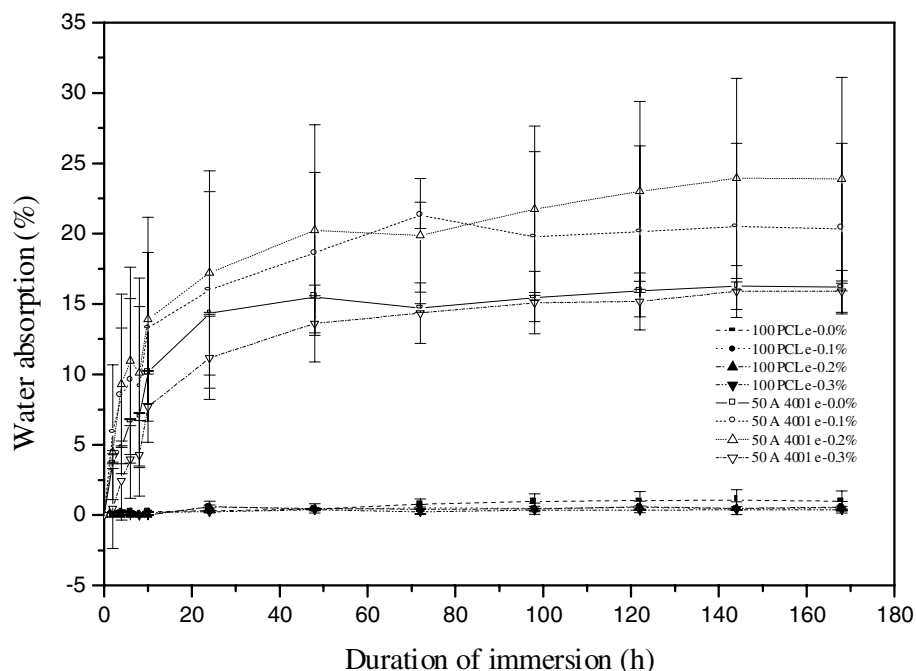


Figure 3. Water absorption of PCL and PCL/starch 50/50 blends. The points are the mean \pm S.D. of three determinations.

expansor, the plateau occurred after 10 h. PCL/starch blends containing cells formed by expansor showed greater variation in their results, except for the formulation without ADC. These deviations were attributable to the ability of the cells within the polymers to retain different amounts of water.

The slight decrease in the weight of 50/50 blends containing 0.2% ADC after 72 h of immersion could be attributed to the loss of soluble matter, following the rupture of starch grains during immersion since pure PCL showed no similar reduction in weight.

The increase in water absorption favoured polymer biodegradation because the retention of water within the polymer enhanced the onset of hydrolysis.

Tensile properties

Figure 4 shows the tensile strength and elongation at break, and Young's modulus values and Figure 5 shows the stress versus strain behavior for PCL and PCL/starch blends in the absence and presence of ADC.

As shown in Figure 4a, tensile strength at break drastically decreased with the incorporation of starch into PCL, indicating that corn starch behaved as non-reinforcing filler. The tensile strength decreased 67%, 73% and 62% for PCL containing 0.1%, 0.2% and 0.3% ADC, respectively, in relative to PCL without additive, and for PCL/starch 50/50 blends without ADC, the reductions were 61%, 69% and 76%, respectively.

Figure 4b shows that the elongation at break was higher for PCL and decreased markedly with the addition of ADC (up to 90% for 0.1% ADC). The incorporation of

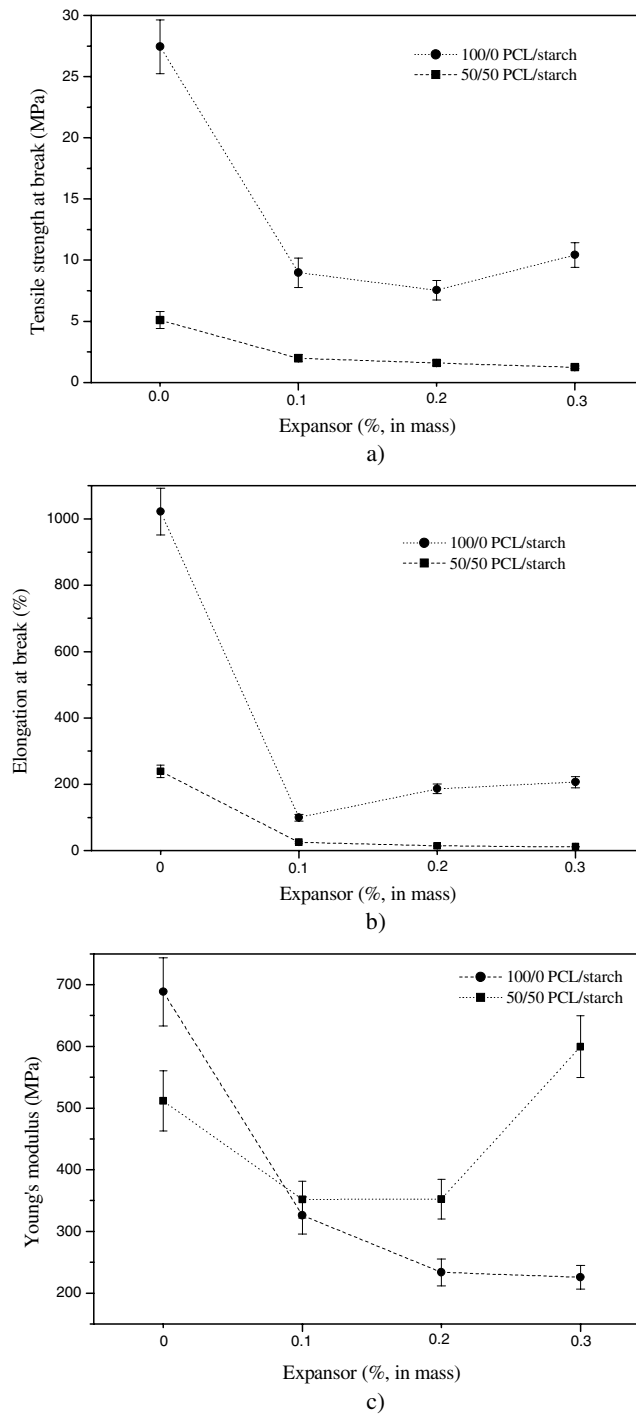


Figure 4. Mechanical properties of PCL and PCL/starch blends. (a) Tensile strength at break, (b) Elongation at break and (c) Young's modulus. The points are the mean \pm S.D. of ten determinations.

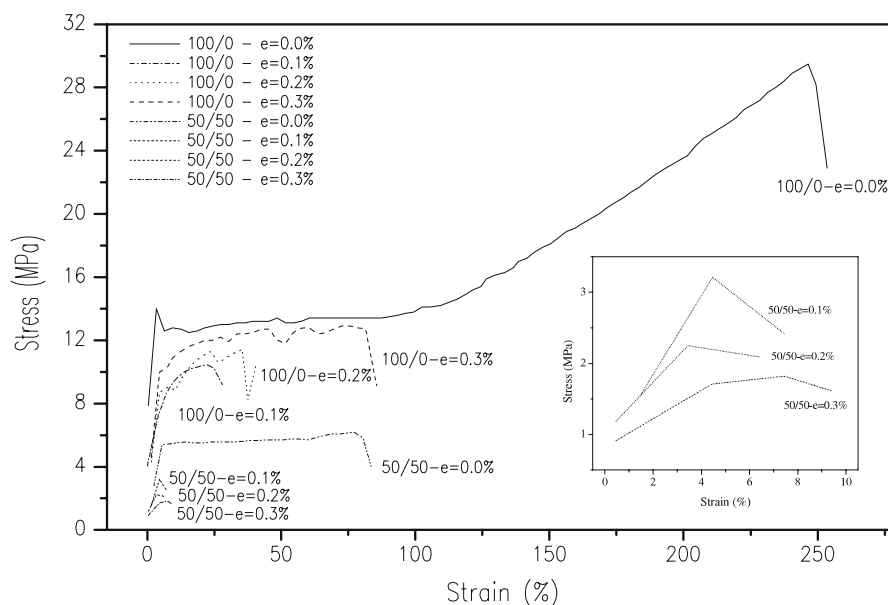


Figure 5. Stress versus strain curves for PCL and PCL/starch blends. The inset shows the responses at low strain.

starch into PCL/starch blends also reduced the elongation by 76%. The addition of starch granules to PCL followed the general trend for filler effects on polymer properties; ADC reduced this property by up to 95% compared to blends without ADC.

In synthetic polymer blends with a ductile matrix, the elongation at break is considered to be highly sensitive to the state of the interface [9]. The reduction in the elongation at break of the PCL/starch blends could be attributed to the poor interfacial adhesion between PCL and starch, as shown in SEM (Figure 7b).

Young's modulus for the blends (Figure 4c) decreased markedly (by up to 67%) with the addition of ADC, except when 0.3 wt.% was added to PCL, in which case there was a significant increase in this property. The addition of 0.1% and 0.2% ADC to the PCL/starch blends reduced Young's modulus. However, this effect was the opposite with 0.3% ADC, which increased Young's modulus and made the blends more rigid.

Figure 5 shows that there was a marked reduction in the tensile strength and elongation at break of the polymers containing starch, and that the addition of ADC decreased these parameters even further.

Morphology

Figures 6 and 7 show SEM images of PCL and PCL/starch blends, respectively, with or without ADC.

The incorporation of ADC into PCL resulted in the appearance of cells within the polymeric matrix. These cells were higher and more frequent in PCL/starch blends, and their occurrence increased as the content of ADC increased (Figure 7c–h).

Starch was homogeneously dispersed throughout the polymeric matrix of PCL, and starch granules retained their typically spherical shape and act as fillers (Figure 7a and b). PCL and starch were immiscible, as shown by the different phases seen in SEM,

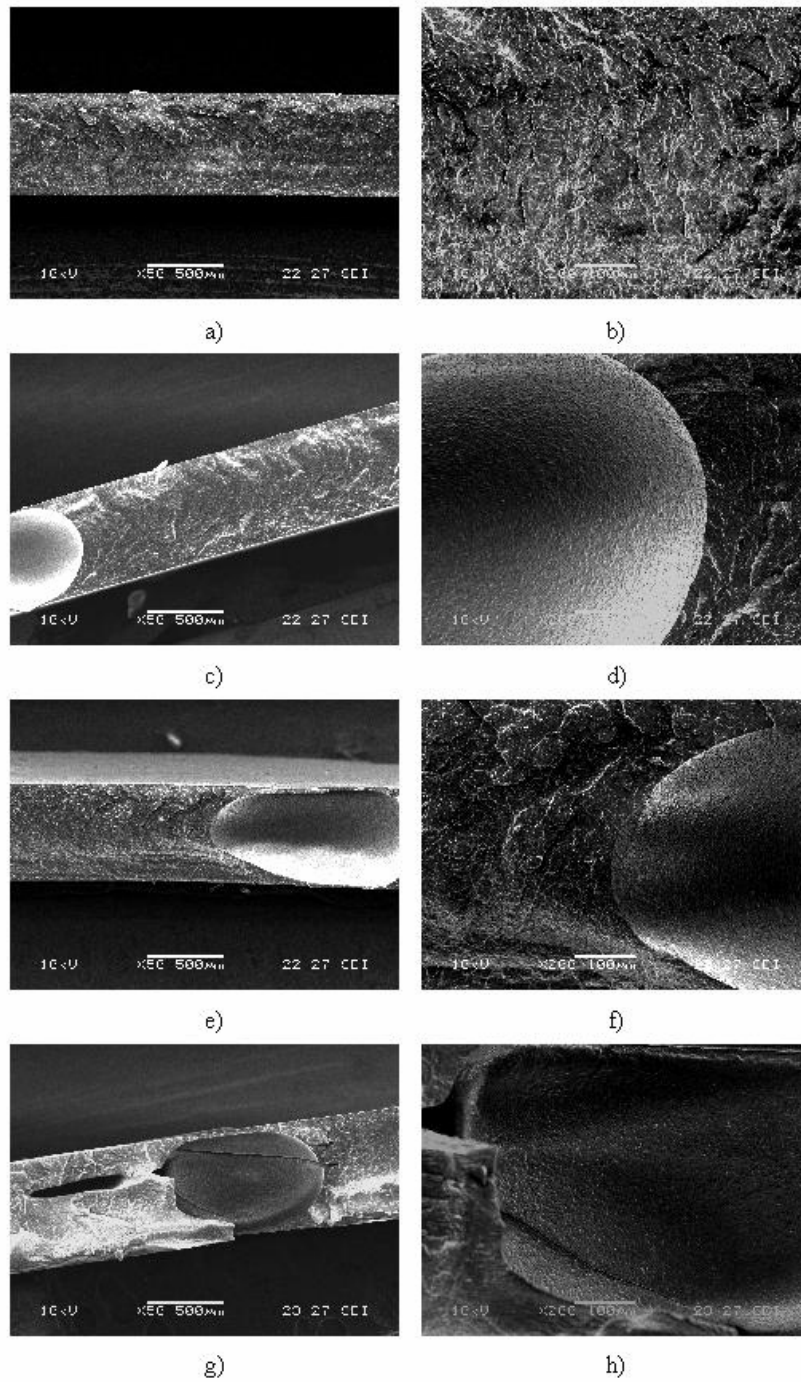


Figure 6. SEM of the fractured surface of PCL containing: (a) 0.0% ADC (50 \times), (b) 0.0% ADC (200 \times), (c) 0.1% ADC (50 \times), (d) 0.1% ADC (200 \times), (e) 0.2% ADC (50 \times), (f) 0.2% ADC (200 \times), (g) 0.3% ADC (50 \times) and (h) 0.3% ADC (200 \times).

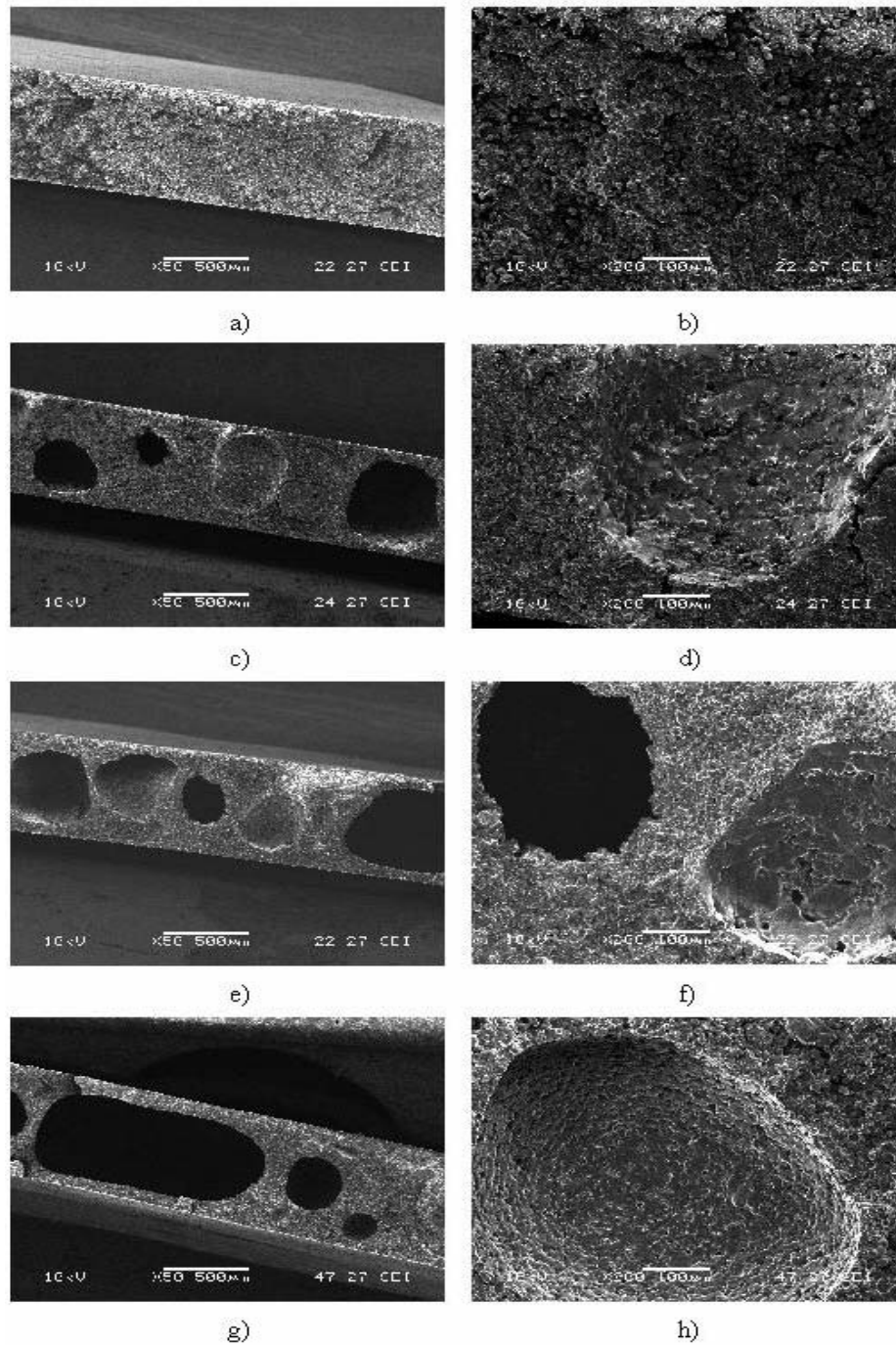


Figure 7. SEM of the fractured surface of PCL/starch blends containing: (a) 0.0% ADC (50 \times), (b) 0.0% ADC (200 \times), (c) 0.1% ADC (50 \times), (d) 0.1% ADC (200 \times), (e) 0.2% ADC (50 \times), (f) 0.2% ADC (200 \times), (g) 0.3% ADC (50 \times) and (h) 0.3% ADC (200 \times).

and indicated a poor interfacial interaction between PCL and starch (Figure 7). Poor interfacial adhesion probably reflects the hydrophilic nature of the blends containing starch [10,11] and could explain the greater increase in weight caused by water absorption and the decrease in the mechanical properties of PCL.

Biodegradability based on mass retention

Figure 8 shows the biodegradation of PCL, PCL/starch blends and their formulation in the absence and presence of ADC in simulated soil.

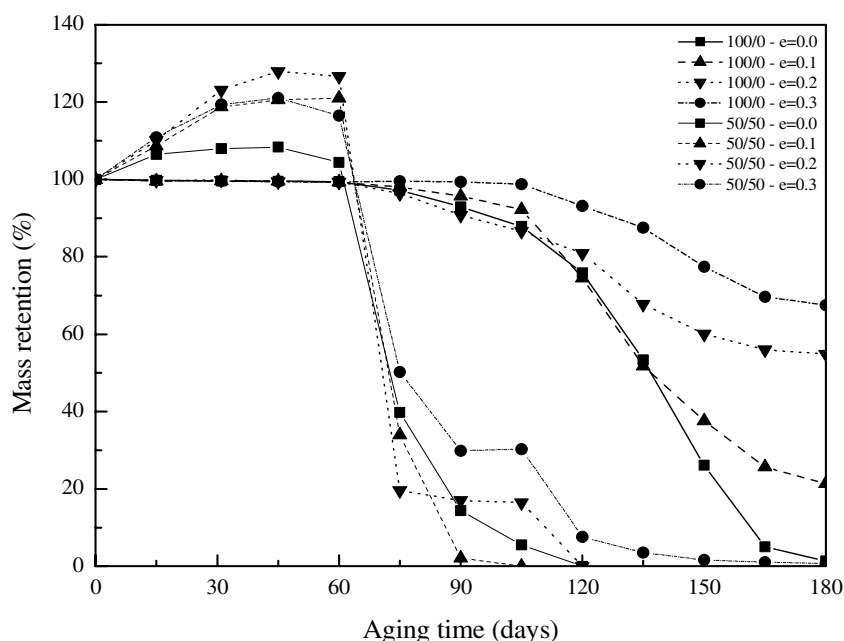


Figure 8. Mass retention of PCL and PCL/starch 50/50 blends with or without ADC. The points are the mean of three determinations.

PCL/starch blends biodegraded faster than the formulations with PCL. The curves showed three main phases for this biodegradation. The first phase was a lag phase defined as the time (days) from the start of the test until adaptation and selection of the degrading microorganisms. The second or biodegradation phase corresponded to the time (days) from the end of the lag phase until about 90% of the maximum level of biodegradation had been reached. The last phase was the plateau phase that extended from the end of the biodegradation phase until the end of the test [12]. This behavior was similar to that described in the International Standard ISO 14855:1999, which also includes three phases.

Initially, during the lag phase (first 60 days of aging) in simulated soil, there was an increase in the mass retention of PCL/starch blends, especially of 50/50 blends containing 0.2% ADC. This finding agreed with the water absorption results. Starch is highly hydrophilic and absorbed water throughout the first 60 days. However, since the simulated soil contained less water than in the water absorption assay, a longer time was required to achieve the peak of mass retention. This water absorption

avored the onset of hydrolysis, with the cleavage of hydrogen bonds making the polymers more susceptible to biodegradation by microorganisms in a shorter time compared to PCL (degradation phase). The addition of ADC expander did not influence the biodegradation of 50/50 blends, except in the presence of 0.3% ADC. This finding probably reflected the fact that the temperature used to produce the PCL/starch blend was lower than the point of total decomposition for ADC, the blowing agent. The residual ADC probably acted as a partial expander that served as a stabilizing anti-microbial agent, which also inhibited the biodegradation of PCL.

The retention of mass by 50/50 blends decreased significantly (from 2% to 30% for 0.1% and 0.3% ADC, respectively) after 90 days of aging and corresponded to the plateau phase of biodegradation. PCL and its formulations showed no significant water absorption or loss of mass after 75 days (biodegradation phase) of aging in simulated soil in the presence of ADC, but this degradation became more accentuated after 100 days. Although the addition of ADC expander inhibited the biodegradation of PCL, the extent of mass retention increased proportionally with the amount of ADC added.

The plateau phase of PCL started after 150 days of aging, with a significant difference in mass retention after 180 days (1%, 21%, 55% and 68% of mass retention with 0.0%, 0.1%, 0.2% and 0.3% of ADC, respectively), thereby reinforcing the greater importance of ADC for PCL than for starch and, consequently, the higher biodegradation of PCL/starch blends. These results also showed that the addition of a small amount of ADC (0.1% and 0.2%) had less of an effect on the biodegradation of 50/50 blends than on pure PCL.

Conclusions

Biodegradable blends of PCL containing starch had a higher density compared to PCL and the addition of ADC reduced the density of the materials. The incorporation of starch increased the water absorption and ADC did not significantly alter this property. The incorporation of starch into PCL reduced the tensile strength and the elongation at break; and ADC enhanced these reductions and also decreased the Young's modulus of PCL. SEM showed that blends prepared with starch were immiscible, had a homogeneous dispersion of starch, and poor interfacial adhesion. The addition of ADC resulted in cells in the interior of the polymers. The 50/50 PCL/starch blends biodegraded faster than PCL, and ADC had no significant influence on the biodegradation of the blends, but inhibited the biodegradation of PCL.

References

1. Ishiaku US, Pag KW, Lee WS, Ishak M. (2002) *European Polymer Journal*, 38, 393-401.
2. Environment Australia *Biodegradable Plastics – Developments and Environmental Impacts*. (2002). Environment Australia, out.
3. Rosa DS, Guedes CG, Pedroso AG. (2004) *Polímeros: Ciência e Tecnologia*, 14, 3, 180-185.
4. Zoua J-J, Liua C-J, Eliassonb B. (2004). *Carbohydrate Polymers*, 55, 23–26.
5. Chena L, Nia Y, Biana X, Qiua X, Zhuanga X, Chena X, Jinga X. A novel approach to grafting polymerization of 3-caprolactone onto starch granules. *Carbohydrate Polymers*, 1-7, 2004.

6. Mano J F, Koniarova D, Reis RL. Thermal properties of thermoplastic starch/synthetic polymer blends with potential biomedical applicability. *Journal of Materials Science: Materials in Medicine*, 14, 127-135, 2003.
7. Curá JA, Jansson P-E, Krisman CR (1995). *Starch/Staerke*, 47, 207-209.
8. Agencia de Seguridad Alimentaria AESA. Madrid. Available from: <<http://ww1.msc.es/aesa/html/alimentacion/alimentacionN2Art8.html>>. Accessed on: 18/05/2004.
9. Jang BC, Huh SY, Jang JG, Bae YC (2001). *Journal of Applied Polymer Science*, 82, 3313.
10. Koenig M. F., Huang S. J. (1995). *Polymer*, 36, 9, 1877-1882.
11. Kim C-H, Cho KY, Park J-K (2001). *Polymer*, 42, 5135-5142.
12. International Standard ISO 14855:1999. Determination of the ultimate aerobic biodegradability and disintegration of plastic materials under controlled composting conditions - Method by analysis of evolved carbon dioxide. 17 p., 1999.