



## Abiotic degradation of poly(DL-lactide), poly( $\epsilon$ -caprolactone) and their blends

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### ABSTRACT

An effective hydrolytic degradation of PDLLA, PCL and their blends in a phosphate-buffered solution of pH 4.0 at 37 °C for 18 weeks was achieved, observing a considerably faster degradation of PDLLA as compared to PCL due to the hydrophobic and semicrystalline nature of PCL matrix, able to partially prevent water diffusion into the bulk specimen.

DSC and FTIR results indicated that PCL phase, in compositions rich in PCL, was very stable against hydrolysis, but the presence of PDLLA in the PDLLA/PCL blends seemed to catalyze the hydrolytic degradation of the PCL phase, probably associated to easier diffusion of water into the PCL domains by the presence of PDLLA amorphous regions. This last trend was proportional to the content of PDLLA in the blends, excepting for the composition 64%PDLLA/36%PCL. It was confirmed that PCL molecules partially delayed hydrolysis of PDLLA molecules, according to FTIR analysis, and the water diffusion prevention level was proportional to the content of PCL in the blends, except for the system 64%PDLLA/36%PCL, which presented a lower extent of degradation than neat PDLLA but higher than the blend 80%PDLLA/20%PCL. This indicated that PCL molecules did not significantly impede hydrolysis of PDLLA molecules in this blend, possibly due to the achievement of a particular structure of the PDLLA/PCL interphase in this blend. In general, hydrolysis of PDLLA/PCL blends was found to be a complex phenomenon depending not only on the content of both polymer phases, but also on the polymer phase crystallinity and morphology.

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### 1. Introduction

Research in degradable polymers has gained considerable interest in recent years due to the increasingly attractive environmental, biomedical and agricultural applications. Aliphatic polyesters are one of the most promising materials to be used (as e.g., packaging materials and mulch films) to solve the problems related to plastic waste accumulation. The development of biodegradable products such as fishing lines and nets could solve the problems caused by the several hundred thousand tons of non-degradable plastic products discarded into marine environments every year, causing death of numerous marine animals [1].

Poly(lactide) (PLA) is perhaps the most frequently used polyester in biomedical applications due to its many favorable characteristics, e.g., high strength and biocompatibility. Environmental concern has led to escalated interest in using polylactide and other biodegradable polymers as an alternative to traditional commodity plastics [1].

PLA is a linear thermoplastic polyester produced by the ring-opening polymerization of lactide. Lactide is a cyclic dimer prepared by the controlled depolymerization of lactic acid, which is obtained from the fermentation of sugar feedstocks, *i.e.* corn, etc [2,3]. In general, commercial PLA grades are copolymers of poly(L-lactic acid) and poly(D,L-lactic acid), which are produced from L-lactides and D,L-lactides respectively. The ratio of L-enantiomers to D,L-enantiomers is known to affect the properties of PLA [4,5], *i.e.* if the materials are semicrystalline or amorphous; until now all the efforts reported in order to improve the properties of PLA are focused on the semicrystalline material [4], e.g., D-content less than 6%. Nevertheless, in this work the poly(lactic acid) chosen to study was an amorphous grade containing 12% D-lactide, denoted here as PDLLA, because amorphous polymers are easier to transform into actual packages by thermoforming, which is a common technology in the food packaging sector [1]. Even more, the resulting amorphous material has more desirable mechanical characteristics and is more easily degraded than semicrystalline PLLA, allowing its use in resorbable plating, artificial cartilage or bone, chemotherapeutics implants and pharmaceutical devices like tablets for oral drugs administration [6], however their physical and some mechanical properties are often not good enough for some end-use applications

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[5]. The most important limitations in its application in the food packaging industry are: medium gas barrier properties and brittleness. In this way, a feasible strategy to decrease the brittleness of PLA is by blending it with polycaprolactone (PCL).

Polycaprolactone (PCL) is also a biodegradable polyester obtained by ring-opening polymerization from the  $\epsilon$ -caprolactone. This is a semicrystalline polymer with a degree of crystallinity around 50%, low glass transition temperature (by *ca.*  $-60$  °C) and melting point of *ca.*  $60$  °C. The PCL chain is flexible and exhibits high elongation at break and low modulus and processing temperatures similar to PLA [1], therefore it is expected to act as a plasticizing agent when blending it with the amorphous PLA matrix. Actually, this plasticizing effect has been studied by Cabedo [7] and Newman [6], showing the influence in phase morphology and the partial miscibilization of PDLA/PCL blends.

Concerning to the degradation of aliphatic polyesters, this has been reported [1] to proceed by one or several mechanisms including chemical hydrolysis, microbial/enzymatic and thermal degradation. The degradation proceeds either at the surface (homogeneous) or within the bulk (heterogeneous) and is controlled by a wide variety of compositional and property variables, *e.g.*, matrix morphology, chain orientation, chemical composition, stereochemical structure, sequence distribution, molecular weight distribution, the presence of residual monomers and the environmental degradation conditions.

Most of the studies on PLA degradation have concentrated on abiotic hydrolysis [8–10]. The effects of, *e.g.*, residual monomer and other impurities, molecular weight and copolymerization composition on hydrolysis rate and properties have been studied [10–14]. The hydrolytic degradation of semicrystalline polyesters has been reported to occur in two stages [15,16]. The first stage starts with water diffusion into the amorphous regions, which are less organized and allow water to diffuse more easily. The second stage starts when most of the amorphous regions are degraded. The hydrolytic attack then proceeds from the edge toward the center of the crystalline domains. This explains the much faster hydrolysis rate of the amorphous PDLA compared to semicrystalline PDLA. In a series of papers, Li et al. demonstrated that in the case of specimens of PLA or poly(lactide-*co*-glycolide) (PLG) the hydrolysis is faster in the center than at the surface [8,9]. They suggested that the hydrolysis products are formed both at the surface and in the inner part, but those localized near the surface dissolve in the aging medium, while the concentration of carboxylic end groups increases in the center and catalyze ester hydrolysis, resulting in a surface-center segregation and multimodal molecular weight distributions for both polymers.

As far as biodegradability is concerned, it has been confirmed that PLA is naturally degraded in soil or compost [17–19], reporting that the resulting products of the PLA hydrolytic degradation can be totally assimilated by microorganisms such as fungi or bacteria [20–23].

Polycaprolactone is relatively stable against abiotic hydrolysis, but it was shown early that it is degraded by microorganisms [1,24]. The molecular weight of PCL remained unchanged during the degradation and it was stated that the biotic degradation occurred at the surface. Later, polycaprolactone has been shown to biodegrade in many different environments, *e.g.*, in pure fungal cultures [25–27], in compost [24,27–29], in active sludge [27,30], by enzymes [31] and in soil [32]. Generally, it has been shown that the biodegradation of PCL proceeds by rapid weight loss through surface erosion with minor reduction of the molecular weight. In contrast, the abiotic hydrolysis of PCL proceeds by a reduction in molecular weight combined with minor weight loss.

Concerning to the hydrolytic degradation of blends of PLA and PCL, Tsuji et al. [33] investigated the non-enzymatic hydrolysis of

blend films from poly(L-lactide) (PLLA) and poly( $\epsilon$ -caprolactone) (PCL) in a phosphate-buffered solution of pH 7.4 as a model of phase-separated aliphatic polyester blends. They found that the hydrolysis of PLLA was much faster than that of PCL; a small amount of PCL accelerated the hydrolysis of PLLA in the blend films, probably because of the increased concentration of the terminal carboxyl groups in the film by the addition of low-molecular weight PCL molecules; hydrolysis of PLLA in the blend films with high PCL content was greatly retarded probably due to prevention of water diffusion into the PLLA phase dispersed in the PCL matrix; and hydrolysis of PCL was not strongly influenced by the presence of PLLA.

Other researchers [34] have found that the enzymatic hydrolysis of poly(D,L-Lactide) (PLA) and poly( $\epsilon$ -caprolactone) (PCL) phases in different blends proceeded by specific chain end scissions, as the presence of PLA did not affect either the degradation of PCL, concluding that the biodegradation of both polymer phases was independent of each other; however, in previous studies these blends were considered totally immiscible, but according to Newman et al. [6] the blends used in this work showed an important interaction measured by Differential Scanning Calorimetry (DSC) and Thermally Stimulated Depolarization Currents Experiments (TSDC).

In this context, even if blends of PLA and PCL have been extensively studied in terms of their crystallization [35,36], phase behavior [33,37] and mechanical properties [35,38], a key-question that remains to be addressed concerns the possible influence of the mixing ratio of both polymer phases on the hydrolytic degradation of the final composite.

The aim of this work is reporting about the abiotic hydrolytic degradation behavior of blends of PCL and an amorphous PDLA, in order to gain insights into the process of hydrolytic degradation of these materials. Even more, to the best of our knowledge, so far, no works on the effect of amorphous PDLA on the hydrolysis of PDLA/PCL blends have been reported. In a previous work, Cabedo et al. [7] reported the preparation and characterization of the same blends observing that, the PCL addition had a plasticization effect as seen by a decrease in the storage modulus and an increase in the thermal stability. In a further research, Newman et al. [6] followed the structural, dielectric and calorimetric behavior of the same PDLA/PCL blends, demonstrating that these melt-mixed blends presented a certain degree of miscibility as the coexistence of a PCL-rich phase and a PDLA phase, thus making these blends in interesting materials for thermoforming industrial and medical applications.

## 2. Materials and methods

### 2.1. Materials

The amorphous poly(lactic acid) (PDLA) was a commercial grade (Galastic<sup>®</sup>) supplied by Galastic, containing 12 mol% of D-Lactide, with a mean molecular weight of *ca.* 190 kg/mol. The poly( $\epsilon$ -caprolactone) (PCL) was a commercial grade (CAPA<sup>®</sup>FB100) supplied by Solvay, with a mean molecular weight of *ca.* 100 kg/mol.

Prior to the mixing step, PDLA and PCL were dried at 50 °C for 24 h under *vacuum* and then stored in the presence of humidity absorbent. Melt blending of PDLA and PCL polymers was conducted on an internal mixer (Haake PolyLab) with a rotation speed of 60 rpm for 8 min at a temperature of 150 °C [7]. The batch was extracted from the mixing chamber manually, allowed to cool to room temperature in air and grounded in a rotatory mill. Several PDLA/PCL compositions were prepared according to the Table 1. From these materials, polymer sheets (0.1 mm thick) were obtained

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