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Comparative thermal, biological and photodegradation kinetics of polylactide and effect on crystallization rates

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ABSTRACT

A comparison is made between available literature and present results of the three major types of polylactide (PLA) degradation giving a compiled view on the details of degradation mechanisms with relation to explicit factors affecting degradation. The temporal decrease of molar mass has been analyzed under isothermal conditions at 220 °C, biological and photodegradation conditions using a polylactide (PLA) with ~4 mol% D units. The decrease of molar mass with time during biodegradation follows a first order process ($M = M_o e^{-kt}$) while the molar mass of specimens tested during thermal and photodegradation follows a second order law ($1/M = (1/M_o) + kt$) Literature data obtained in similar degradation conditions were also adequately fitted with these equations. This allows us to conclude that the main step in the three types of degradation is a random chain excision, with some differences in the algebraic functionality. Under the degradation conditions tested, the degradation rate follows the progression thermal > photo > biological. For equivalent molar mass, the effect of degradation type on cold crystallization and melting is significant indicating that degradation cannot be explained by a solely outcome of chains breakage and molar mass reduction. This feature is especially prominent when the linear growth rates of specimens subjected to bio or photo degradation are compared. Anhydride groups that are formed during photodegradation decrease the crystallization rate compared to biodegraded specimens of equivalent molar mass. The molar mass dependence of the maximum growth rate follows a power law with exponents 1.3 for bio and 1.0 for photodegraded specimens, representative of semi-entangled systems. The temperature coefficient of the growth rate, analyzed according to secondary nucleation leads to a linear dependence for bio and photodegraded specimens, and to values of the surface free energy of crystallites that decrease from ~85 to 55 erg/cm^2 with decreasing molar mass. Combinations of molar mass characterization, FTIR, and thermal and crystallization rate analysis are proven useful strategies to assess and discriminate macroscopic changes of PLA structure induced by different types of degradation. This work also underlines the importance of analyzing the linear growth rates as a parameter that uncovers specific structural changes during degradation.

1. Introduction

Polylactide, PLA, has attracted much attention as a candidate for biomedical applications due to its inherent biocompatibility. Under this view, most of the PLA degradation studies during the last two decades have been focused on hydrolytic stability [1–4]. Although the inherent brittleness of PLA may prevent its use in applications where toughness and impact resistance are critical, biodegradable polylactides, its random copolymers and blends, have been raised as potential substitutes of poly(propylenes) and other polyolefins in applications where optimized tensile properties are not required, such as packaging and agricultural uses, among others [5–7]. Implementing PLA in such new applications requires understanding structural changes during processing and post-processing due to aging, and in the different degradation processes that can undergo during its life cycle, namely, thermal, bio or outdoor degradation [8–12].

Particularly, it is important to characterize the structural modifications due to *thermal degradation* at all stages of processing and for modeling service life. On the one hand, PLA may degrade during a first extrusion or compression molding process depending on the operation temperature and residence time, leading to a rapid reduction of molar mass and mechanical strength [13]. On the other

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hand, the service life of the material can be modeled by submitting the polymer to controlled temperature cycles [14] which may accelerate the degradation process.

The mechanisms of thermal degradation have been widely studied. In brief, prior studies have revealed that at temperatures below 230 °C the polymer backbone cleavage is mainly caused by non-radical intramolecular transesterification, leading to the formation of oligomeric rings, acetaldehyde and carbon monoxide units as by-products. Above 270 °C, the occurrence of *cis*-elimination and radical reactions promotes further evolvement of carbon dioxide and methylketene [15–17]. Since the temperature of many PLA processing routes do not exceed 230 °C, it is accepted that thermal degradation occurs via non-radical reactions, leading to significant decrease in molar mass which has an important effect on the crystallization rate, morphology and final performance of PLA.

Concerning the mechanisms of *biodegradation* of PLA and its copolymers under controlled conditions, modes such as *in vitro* degradation with selected cultures or composting have been extensively studied in the literature [18,19]. PLA biodegradation is regulated by a first stage of hydrolysis, either acid or basic. In both cases, it may start at the end groups or by intramolecular random protonation of the carbonyl group, leading to PLA with lower molar mass [2,20]. The bulk hydrolysis of the polylactide is described as a heterogeneous process, initiated at the inner part of the material. With water diffusing through the material, each ester bond cleavage gives a new carboxyl end group that accelerates hydrolysis. In the first stages, only the more soluble produced oligomers may migrate to the surface of the material, with the majority remaining inside the matrix. This diffusion-limited process increases the acidity of the inner regions of PLA and promotes its autocatalytic degradation [21–24]. As degradation proceeds, oligomers with reduced sizes can be assimilated by the microorganisms, completing the biodegradation process.

Conversely, studies of degradation in soil of the polylactides are more limited and usually based on simple monitoring of the weight loss up to 24 months [6,22,25,26]. In general, all these prior studies yield that biodegradation under composting takes place more rapidly than under degradation in soil, and attribute such difference to the higher temperatures and water content which enhance hydrolysis and assimilation processes [22,25]. This fact highlights the importance to extend the testing time of PLA degradation in soil to reach meaningful correlations for temporal effects of molar mass decay. In this framework, in recent works, we have applied international standards of degradation in soil up to 15 months [27,28]. A decrease on the molar mass with the degradation time was observed. In addition, DSC and DMA studies allowed determining that the cold crystallization temperature decreased with the degradation in soil time and the related enthalpy of crystallization increased. However, a thorough study on the functional temporal dependence of the decay of molar mass, in connection with the variation of thermal parameters, was not provided, due to the relatively short testing period.

Photodegradation is another source of PLA degradation when exposed to outdoor conditions. Prior works have used primarily ultraviolet (UV) radiation, while the effect of sunlight photodegradation on PLA has been less studied, possibly because of the generally lower sensitivity that polymers have to this radiation [29]. Comparative studies of UV and sunlight exposure in aliphatic polyesters concluded that a rapid degradation of films by UV radiation took place with increasing exposure times through the formation of carbon–carbon double bonds and carboxyl end groups [12,30]. However, the formation of these groups was not observed for the films exposed to sunlight, albeit their tensile strength decreased. Other mechanisms proposed for PLA degradation under UV radiation involve photolysis of the ester bond at the backbone or the formation of hydroperoxide derivatives and their subsequent degradation to compounds containing carboxylic acid and diketone end groups [31]. More recently, a sunlight mechanism was proposed for PLA that surmises the formation of anhydride groups [32].

In recent studies, efforts have been made to understand mechanistically chain excision and the temporal evolution of molar mass in the three major types of degradation summarized above, the thermal, biodegradation, or photodegradation of PLA [15,16,30,33]. However, it is difficult to compare the decrease of molar rates among the various degradation types because these prior works used different starting PLA materials.

The objective of the present work is to study specific differences between thermal, biodegradation in soil and photodegradation using the same PLA. The present data and available literature data are analyzed in order to provide the most plausible degradation kinetic laws. Gel Permeation Chromatography (GPC) and viscometry were used to monitor the decrease of molar mass, and Fourier Transformed Infrared Spectroscopy (FTIR) to assess the effect of degradation on the polylactide chemical structure. The effect of decreasing molar mass on the crystallization rate is also studied through a combination of thermal and optical microscopy studies. The overall crystallization of PLA was examined by Differential Scanning Calorimetry (DSC) and the isothermal linear growth rates by Polarized Optical Microscopy (POM). The results offer additional input on the specific nature of each degradation type.

Considering chain excision as the major step in any of the three degradation types with minor changes in the nature of the functional groups, then one expects analogous crystallization rates for PLAs of equivalent molar masses [34,35]. Moreover, differences in rates for equivalent molar mass specimens may arise from dissimilar chemical groups generated in the PLA chain during degradation. Hence, specific differences in degradation mechanisms are inferred in this work from a comparative analysis of linear growth rates of equal molar mass specimens subject to different degradation types. This analysis serves as a test for the proposed degradation mechanisms, and provides further information of the structure of crystallites formed upon solidification of PLA of different molar mass.

2. Experimental section

2.1. Materials

The material studied, PLA2002D, is a commercial polylactide copolymer with ~4% D-lactide content manufactured by Natureworks, Blair, NE, USA. The samples analyzed include the original pellets, thermally degraded pellets, melt-pressed plates, biodegraded plates and photodegraded plates. Rectangular $10 \times 4 \times 0.1$ cm plates for bio and photo degradation studies were prepared from the original pellets by melt compression in a Collin 6300P hydraulic press at 210 °C in five pressure steps: 4 min at 2 bar, 2 min at 30 bar, 3 min at 50 bar, 5 min at 180 bar, and 12 min at 40 bar followed by tap water cooling. Specimens $6 \times 1 \times 0.1$ cm for photo and biodegradation tests were cut from the melt-pressed plates.

2.2. Degradation tests

Specimens subjected to thermal degradation were obtained from the initial pellets, sandwiched between two thin sheets of Teflon©, and maintained in a Carver Press at 220 °C ± 10 °C during 3, 30, 62, 120 or 330 min without pressure. A degradation temperature of 220 °C was chosen as representative of melt extrusion processes. After a given time in the melt had elapsed, the

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