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Influence of crystallinity on the biodegradation rate of injection-moulded poly(lactic acid) samples in controlled composting conditions

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ABSTRACT

One of the most attractive characteristics of poly(lactic acid) (PLA) is the fact that, following the international standards for polymer biodegradation, it can be potentially degraded in soil or compost. The potential of this material, however, requires additional investigations in order to understand the PLA behaviour during composting, including the main factors that affect the biodegradation phenomena. In this work, the degradation of PLA was investigated in both distilled water and controlled composting conditions at a temperature of 58 °C. PLA samples with different morphologies were prepared by injection moulding and successive annealing at high temperature. As expected, the crystallinity was found to decrease the PLA degradation rate, but it was also found that the crystallinity affects only partially the first stages of water diffusion in the polymer matrix, whereas it has a significant effect on the final swelling of the samples and on their biodegradation rate. It could therefore be concluded that the denser structure of the initially crystalline sample was more impermeable to the enzymatic attach and to oligomer diffusion. This was also testified by the fact that if the characteristic dimension of the crystalline sample is reduced, degradation rate becomes much faster and close (although still slower) to that of the amorphous sample.

1. Introduction

Recently, Poly(lactic acid) (PLA) has attracted considerable interest for applications in several fields [1,2]. In fact, its excellent mechanical properties, transparency and compostability have promised intense utilization in packaging as well as consumers goods sector [2].

One of the most attractive characteristics of PLA is the fact that it can be potentially degraded in soil or compost and thus the products made by this material at the end of their life cycle can be diverted from landfill to composting. However, in order to understand the real perspective of this material, it is crucial to understand its behaviour during composting, including the main factors that affect the biodegradation phenomena.

While the hydrolytic degradability [3] and the enzymatic degradability [4] of PLA have been studied in several papers, reports on the biodegradation in compost of PLA are still few. The process is considered consist in a sequential mechanism in which the first step is the hydrolysis which reduces the molecular weight of the PLA, and the second step is the assimilation by the microorganisms [5]. Apart from this general understanding, biodegradability of plastics in composting conditions is affected by several interconnected physical and environmental factors that cannot be simulated in simple laboratory tests. As matter of fact, the only way to determine the compostability of a plastic is to carry out biodegradation test methods [6,7].

Another complicating factor in plastics biodegradation is the complexity of these materials with regard to their possible structures and compositions. Differences in structural conformations, molecular weight, orientation and crystallinity have been reported to control the degradation behaviour [8–10] apart from the shape and the dimensions of the specimens themselves.

Reeve et al. [11] prepared various PLA stereo copolymers from mixtures of (D)- and (L)-lactide. The resulting materials exposed to a fungal protease showed a degradation rate dependent by the (L) repeat unit content. In a more recent paper [12], the same authors have showed as the film crystalline order, the chain stereochemical composition, and the repeating unit sequence distribution affected interactions between PLA films and proteinase K.

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Cai et al. [13] studied the influence of morphology on the degradation of PLLA in aqueous media. They found that the highly crystalline residues appear to be very resistant to degradation.

Rudnik and Briassoulis [14] analysed the effect of sample thickness on the degradation of PLA in soil and found that the effect of degradation was more pronounced for thinner samples.

Even if the importance of morphology on degradation of PLA has been established, more detailed information on this subject is needed for the correct interpretation the biodegradation behaviour of PLA prepared from different processing techniques.

In this paper we report the effect of sample morphology on biodegradation of PLA samples obtained by injection moulding.

2. Experimental

2.1. Materials

The material adopted in this work is a commercial PLA from Natureworks (2002D), with a D-enantiomer content of approximately 4%. The molecular weight distribution was characterized by chromatography: $M_n = 145{,}000$ and $M_w = 235{,}000$. The crystallization kinetics and the viscosity of the material were assessed in a previous work, also considering the effect of previous thermo-mechanical histories [15].

Cellulose powder with fibres length between 0.02 and 0.25 mm was purchased from Sigma Aldrich.

2.2. Samples preparation

Before any tests, the PLA pellets were dried in a vacuum oven at 60 °C for 8 h. The pellets were injection moulded using a 70 Ton Negri-Bossi injection moulding machine with a single cavity, which was specifically designed to produce under controlled conditions injection-moulded specimens with 120 × 30 × 2 mm dimensions. Injection moulding was carried out at a melt temperature of 200 °C, injection pressure of about 70 MPa and packing time of 40 s. Details of the geometry adopted can be found elsewhere [16,17].

The total residence time of material inside the machine was calculated to be about 15 min. The pressure curves measured during injection moulding confirmed that no significant changes in material viscosity took place during the 20 consecutive cycles corresponding to the residence time of material inside the machine. In addition, the moulded samples showed no signs of degradation and still presented both the odour and transparency of the virgin material.

Due to the very slow crystallization kinetics of this grade of PLA [18], the injection-moulded samples resulted to be fully amorphous. These samples will be referred to as amorphous PLA. In order to obtain fully crystalline samples, some moulded samples were kept in an oven at 105 °C (namely the temperature of maximum crystallization rate for this material) for 8 h. A calorimetric characterization of these samples revealed a crystallinity degree of about 30%, which is the maximum reachable for the chosen polymer [15]. These samples will be referred to as crystalline PLA. A third sample was prepared by milling the crystalline PLA to a characteristic dimension of 0.2 mm, so that the effect of geometry could be assessed. This sample will be referred to as “crystalline PLA – milled”.

2.3. Biodegradation tests

Biodegradation tests on PLA samples were carried out in a homemade respirometric system, as assessed by ASTM D 5338 and ISO 14855 standards. A schematic representation of the system is shown in the following Fig. 1.

The system is composed by an air pumping system that provides pressurized air to the bioreactor (Fig. 1.1). The CO_2 present in the pressurized air is removed by passing through 10 N sodium hydroxide (NaOH) solution (Fig. 1.2). A subsequent treatment in a trap and a series of condensers remove the excess of moisture from the pressurized air (Fig. 1.3). The air flow is then divided and maintained at a constant flow rate of 0.5 L/min by means of a flow meter for each bioreactor (Fig. 1.4). The bioreactors were kept in an oven at constant temperature of 58 ± 2 °C (Fig. 1.5). As bioreactors, glass flasks of approximately 3 L internal volume were used (Fig. 1.6).

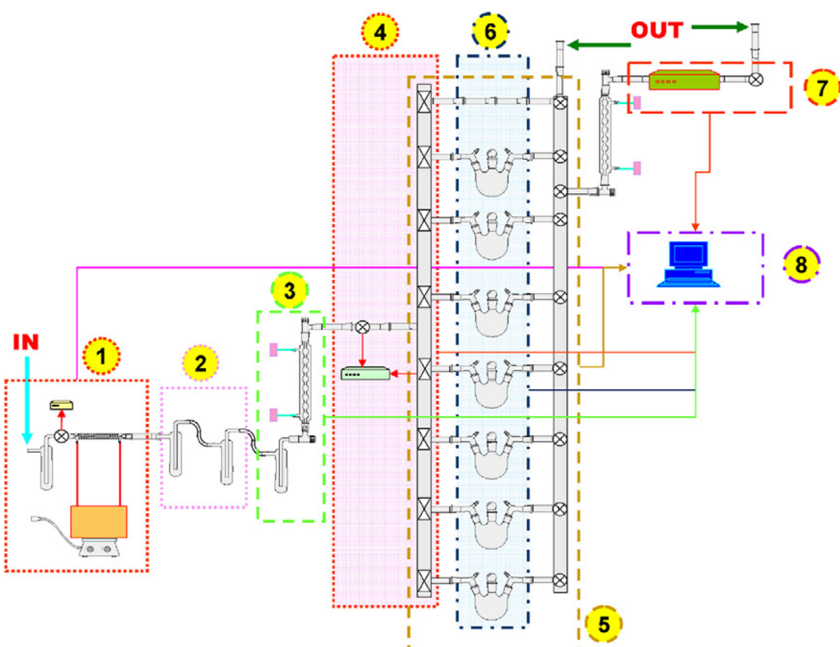

Fig. 1. Schematic representation of the respirometric apparatus.