Material characterisation

Thermal, rheological and microstructural characterisation of commercial biodegradable polyesters

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ABSTRACT

Growing environmental concerns along with new regulations are forcing industries to seek renewable raw materials for their products. This work studies the thermo-rheological properties of commercial biodegradable polyesters: two polylactic acids (PLAs), a poly-caprolactone (PCL) and a PLA/PCL blend. Comprehensive material characterization by means of thermogravimetry/differential thermal analysis (TG/DTA), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), frequency sweep tests and polarized light microscopy was carried out. The results have shown that the material thermal/thermo-rheological properties and, therefore, its microstructure, are strongly dependent on its thermal history. This fact arises from the slow recrystallization kinetics shown by PLA. Interestingly, PCL may play the role of nucleating agent for the PLA crystallization, making it faster. This issue must be carefully considered so that a reliable material characterization is achieved.

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1. Introduction

The classic way to manufacture polymers is based on the polymerization of the lightest fractions of crude oil. However, growing environmental awareness and rising crude oil prices have motivated researchers from industry and academia to develop biodegradable products from renewable resources [1]. Among bio-based polymers, polylactic acid (PLA) is a promising candidate to replace petroleum-based plastics due to its high stiffness and strength, which are comparable to polystyrene, at least at room temperature. PLA is a versatile polymer synthesized by the biological fermentation of renewable resources, such as corn starch and sugar beet, and thus environmentally and ecologically safe [2,3]. Initially, PLA development focused on the production of body implants which would degrade within the human body over time [4]. Over recent decades,

PLA has been used in a variety of consumer goods, such as single use cutlery or food packaging [5]. This approach involves heating the polymer above its melting point, shaping it to the desired forms, and cooling to freeze form and dimensions.

In this work, two commercial polylactic acids (PLAs) produced by NatureWorks LLC (United States), with the trade names Ingeo 2002D and Ingeo 4032D, have been studied. Ingeo 2002D is a clear extrusion sheet grade and is easily processed on conventional extrusion and thermoforming equipment. On the other hand, Ingeo 4032D can be easily converted into highly transparent films using temperatures up to 150 °C. These properties make it suitable for laminating and other packaging applications.

It is well known that PLA crystallinity can induce significant improvements in stiffness, strength, heat deflection temperature and chemical resistance [6]. In this respect, different researchers have studied the complex PLA crystallization process and the selection of suitable nucleating agents to improve the crystallization rates [7,8]. Related to this, the nucleating ability of a commercial

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polycaprolactone (PCL) (Capa™ FB100 from Perstorp, Sweden), a crystalline and biodegradable petroleum-based polyester, is also evaluated in this work.

PLA, PCL and their blends have been widely investigated because of their compelling commercial applications [9–12]. Further to these studies, this paper intends to gain deeper knowledge of the effect that previous thermal history may exert on the polymer microstructure and, therefore, on its thermo-rheological response at temperatures below its melting point. To accomplish this goal, comprehensive material characterization has been carried out by means of simultaneous thermogravimetry/differential thermal analysis (TG/DTA), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), frequency sweep tests and polarized light microscopy.

2. Experimental

Two commercial polylactic acids (PLAs), with the trade names Ingeo 2002D and Ingeo 4032D (produced by NatureWorks LLC, United States), and a commercial polycaprolactone, Capa™ FB100 (manufactured by Perstorp, Sweden), were used. These polymers will hereinafter be referred to as "fresh" PLA 2002, PLA 4032 and PCL samples. Prior to use, the polymers were dried overnight at 90 and 50 °C for PLAs and PCL samples, respectively.

In addition, a blend 70/30 (wt.%) of PLA 4032/PCL (abbreviated PLA/PCL) was also studied. This blend was prepared with a Rheomix 3000p mixer from Thermo Haake (Germany), equipped with two counter-rotating rollers. PLA 4032 and PCL were mixed for 20 min at 180 °C, and a rotation speed of 50 rpm. This sample will be referred to as "fresh" PLA/PCL blend.

Simultaneous TG/DTA measurements were conducted using a Seiko TG/DTA 6200 (Japan). Temperature ramps at 10 °C/min, from 40 to 600 °C, under N_2 atmosphere, were carried out on 5–10 mg of "fresh" samples.

In order to conduct DMTA/frequency sweep tests, different specimens were prepared by compression-moulding in a hot press. Firstly, the samples were subjected to 50 bar of pressure for 20 min, at 180 °C for the PLA 4032 and PLA/PCL samples, and 80 °C for the PCL sample. Subsequently, the specimens were allowed to cool down to room temperature over a time interval of 5 hours inside the press. This represents a cooling rate of 0.5 °C/min in the PLA 4032 and PLA/PCL blend samples and of 0.17 °C/min in the PCL sample. The resulting material will be referred to as "moulded", in contrast to the as-received material (referred to as "fresh"). "Moulded" samples were also characterized by DSC and Polarized Light Microscopy.

Differential scanning calorimetry (DSC) tests were performed with a TA Q-100 (TA Instruments, USA). Samples of 5–10 mg were subjected to three different testing protocols, composed of two heating steps (20–200 °C) at a rate of 10 °C/min, with an intermediate cooling step conducted at rates of −70, −10 and −3 °C/min, for protocols I, II and III, respectively. All the tests were performed with a N_2 gas flow rate of 50 mL/min. From these different protocols, the polymers crystalline fractions were determined.

Dynamic Mechanical Thermal Analysis (DMTA) and frequency sweep tests were performed on rectangular samples of 50 mm length, 10 mm width and 3 mm thickness, with a Seiko DMS 6100 (Seiko Instruments Inc., Japan) in double cantilever (bending) mode. With respect to the DMTA measurements, these were conducted on PLAs and PLA/PCL samples at a constant frequency of 1 Hz and strain within the LVE interval, with the application of a heating rate of 1 °C/min, from 40 °C up to the material cold crystallization temperature. Isothermal frequency sweep tests from 0.02 to 100 Hz were carried out on PLA 4032 samples, also within the linear viscoelasticity (LVE) region, at 30, 60 and 80 °C.

The microstructure of the materials was examined with an optical microscope, Olympus (Japan) BX51, equipped with a pair of crossed polarisers. For this analyses, 0.1 mm-thick films (prepared in hot-plate press) were placed on a LTS 350 hot stage (Linkam Scientific Instruments Ltd., UK), and subjected to different temperature programmes controlled by a Linkam TP 94.

3. Results and discussion

3.1. Thermal characterization

The thermal characterization of "fresh" neat polymers and the PLA/PCL blend was carried out by simultaneous thermogravimetric/differential thermal analysis (TG/DTA) and by calorimetric (DSC) tests. First of all, the thermal degradation temperatures (T_d) shown by the peak maximum in the DTG curves were evaluated by TG/DTA tests. This technique allows sample mass loss and phase transitions to be determined simultaneously in an open system (Fig. 1A and B). However, glass transition temperatures (T_g) and melting points (T_m) can be better visualised by the DSC results shown in Fig. 2.

Fig. 1A shows the DTG curves for the "fresh" neat polymers and the PLA/PCL blend. Very similar values of the thermal degradation temperatures can be observed for both PLAs, which are much lower than that showed by PCL (see values in Table 1). As expected, the thermal degradation of the PLA/PCL blend occurs in two overlapped steps, with peaks located at the values for its single components.

The thermal events observed in these materials before decomposition seem to be more complex, as revealed by DSC results. Fig. 2 shows the heat flow thermograms for the first and second heating ramps for "fresh" PLAs and PCL samples. A cooling rate of 10 °C/min, corresponding to protocol II, was applied between them. It can be observed that, for PLAs samples, both first and second heating ramps present a thermal event at around 60 °C, which corresponds to the glass transition of their amorphous fraction. In contrast, only the first ramp shows, at about 150 °C, the melting peak of the PLA crystalline fraction. The absence of the melting peak for the second ramp indicates that recrystallization upon cooling from the melt does not occur at the cooling rate applied (too fast for the polymer chains to reorganise into crystalline regions). Instead, a more pronounced glass transition is observed, as chain mobility is not constrained by PLA crystals. On the contrary, both first and second ramps for the PCL display a melting peak around 60 °C, which indicates that PCL recrystallizes faster than PLA. The glass transition temperature for the PCL, located at