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European Polymer Journal 41 (2005) 2335–2342
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Influence of melting conditions on the thermal behaviour of poly(L-lactic acid)

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Received 19 January 2005; received in revised form 17 April 2005; accepted 18 April 2005
Available online 24 June 2005

Abstract

The influence of melting temperature and time on the thermal behaviour of poly(L-lactic acid) (PLLA) was studied with differential scanning calorimetry (DSC). Different melting conditions were investigated at temperature ranging from 200 to 210 °C, and for time from 2 to 20 min. For lower-molecular-weight PLLA, a single exothermic peak could be observed at cooling rate of 2 °C/min, after melted at different conditions. The obtained peak temperature and degrees of crystallinity dramatically increased with an increase of melting temperature or time. During subsequent heating scans, double melting peaks could be observed, which were significantly affected by prior melting conditions. The degradation of this material in the melt and the melt/re-crystallization mechanism might be responsible for the observations above. Apart from double melting, double cold crystallization peaks were observed during heating traces for this material after fast cooling (20 °C/min) from the melt. Prior melting conditions could significantly influence the cold crystallization behaviour. The competition between the crystallization from the nuclei remained after cooling, and that from spontaneous nucleation might be responsible for the appearance of double peaks. Additionally, the influence of melting conditions on the thermal behaviour of PLLA was dependent on the initial molecular weight.

Keywords: Poly(L-lactic acid) (PLLA); Thermal degradation; Melt crystallization; Double cold crystallization; Double melting

1. Introduction

Poly(L-lactic acid) (PLLA) is a biodegradable synthetic polymer of increasing interest, widely used in the biomedical field [1–3]. Thermal behaviour is an important aspect characterizing the physical properties of semi-crystalline polymers, and publications concerning the crystallization behaviour of PLLA have been well documented. For example, Miyata et al. reported the influence of molecular weights on the isothermal crystallization and non-isothermal melt crystallization behaviour of PLLA [4]. Iannace et al. studied the isothermal and non-isothermal crystallization kinetics to analyse the effect of crystalline and amorphous morphology on hydrolytic degradation [5]. Mijovic et al. investigated the molecular dynamics of PLLA before, during and after crystallization [6]. Based on the Hoffman–Lauritzen theory [7], crystallization regimes were investigated for PLLA, and regime II to regime III transition was

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0014-3057/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.eurpolymj.2005.04.030

detected at 115 °C by Iannace et al. [8] and at 120 °C by Di Lorenzo [9]. Apart from melt crystallization, the non-isothermal cold crystallization of PLLA from glassy state was also addressed in the literature [10,11]. Especially, double cold crystallization behaviour was observed for approximately amorphous PLLA samples [11], as reported for several other semi-crystalline polymers [12–18].

In parallel with crystallization investigations, several studies on the melting behaviour of PLLA have been reported. As observed for many semi-crystalline polymers, copolymers and blends [19–21], double melting peaks appeared at DSC curves during heating process for bulk PLLA samples isothermally crystallized [8,22], or prepared with slow cooling rates [23].

Biodegradable and biocompatible PLLA devices can be produced using melt-based standard methods of polymer processing. At temperatures above 180 °C, PLLA undergoes thermal degradation [24–30] by hydrolysis, leading to lactide reformation, oxidative main chain scission, and inter- or intramolecular transesterification. That sensitivity to temperature may be reflected, for example, in the influence of the processing conditions on the final product properties, including a series of physical and mechanical properties, degradation profile and biological response. Migliaresi et al. [28] presented the influence of compression moulding conditions on the molecular weight of PLLA and the crystallization capability of the materials after different thermal treatment. Gogolewski et al. [29] reported some DSC data about the effect of the injection moulding process on the thermal properties of PLLA, but the authors were more interested in the influence on the molecular weight and molecular weight distribution of PLLA, as well as on a comparative study of PLLA and several other biodegradable polyesters. Ikarashi et al. [30] investigated the effect of heat extrusion of PLLA on the biological response to cells. However, a more detailed research on this subject is needed as the non-specific information generated will contribute to an overall understanding of the thermal behaviour of the material and its relation with its properties.

As it will be seen later in this paper, some published work has reported already the effect of temperature and time on the change of molecular weight of PLLA. Therefore, this study will focus on the influence of melting conditions (melting temperature and time) on the non-isothermal melt crystallization, cold crystallization and subsequently melting behaviour of PLLA using differential scanning calorimetry (DSC).

2. Experimental

The materials were kindly supplied by Purac Biochem with two inherent viscosities: 1.75 dl/g (PLLA1) and 5.87 dl/g (PLLA2). The molecular weight M_n and M_w of the polymers were evaluated from gel permeation chromatography [10]. For PLLA1, the molecular weights, M_n and M_w, were 86,000 and 151,000, respectively, and for PLLA2, M_n and M_w, were 269,000 and 301,000, respectively.

A Perkin–Elmer DSC 7 was used to study the crystallization and melting behaviour of PLLA under a nitrogen flow of 20 $cm^3 min^{-1}$. To well control the influence of melting condition on the thermal behaviour of PLLA, small pieces of raw PLLA granules were directly used. The weight of the samples was about 10 mg. Each PLLA sample was only tested once. Two groups of experiments were performed. For the first group, the samples were heated to 200 °C or 210 °C at 20 °C/min, kept for 2, 5, 10, or 20 min, then the DSC traces were recorded during a cooling ramp at 2 °C/min, and during a subsequent heating process at 20 °C/min. For the second group, the samples were heated to 200 or 210 °C at 20 °C/min, kept for 2, 5, or 20 min, then the DSC traces were recorded at cooling rate of 20 °C/min, and subsequent heating processes at 2, 5, 10, or 20 °C/min. Separate calibrations for baseline were made for all heating and cooling rates. Calibration for the temperature and energy scale was carried out using a pure indium standard. Separate calibrations were made for all heating rates. Particular precautions were taken for temperature calibration on cooling. 4-Cyano-4′-octyloxy-biphenyl (M24), which was kindly supplied by Prof. Schick (University of Rostock, Germany), was used for the calibration on cooling, and the procedure followed that suggested in the literature [31].

3. Results and discussion

3.1. Melt crystallization and subsequent melting behaviour

The crystallization process of PLLA1, after melted at different conditions, was monitored during cooling at 2 °C/min. Fig. 1(a) shows that a single exothermic peak appears in each curve. The values of the peak temperatures, T_p, crystallization enthalpies, ΔH_c, and the degrees of crystallinity are collected in Table 1. The degrees of crystallinity are obtained by comparing the enthalpy of melt crystallization with the value of an infinitely large crystal, taken as 81.3 J/g [32]. The degrees of crystallinity dramatically increase from 0.196 to 0.570 and exothermic peak temperature shifts from 103.1 to 109.4 °C, with increasing of melting temperature or time.

The differences observed in Fig. 1(a) may be attributed to the degradation of PLLA1. It was well documented that the extent of degradation of PLLA increased with increasing melting temperature or time [24–30]. For example, Xu et al. [27] reported that, after