CrossMark

The effect of a secondary process on polymer crystallization kinetics – 3. Co-poly (lactic acid)

Azizan A. Aziz, Sani A. Samsudin[1], James N. Hay[*], Michael J. Jenkins

The School of Metallurgy and Materials, College of Physical Science and Engineering, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

A B S T R A C T

The crystallization kinetics of a copolymer of L-lactic acid with 4% D-lactic acid has been studied using FTIR spectroscopy by measuring the absorbance of the crystalline carbonyl stretching band at 1759 cm^{-1}. Copolymerization greatly reduced the rate of crystallization and the technique directly measured the relative crystallinity over extended periods with sufficient accuracy to test the validity of the Avrami equation. This was modified to account for the simultaneous presence of a secondary process from the onset of crystallization, such that the overall fractional crystallinity, X_t, is related to the lapsed time, t, by.

$$X_t = X_{p,\infty}(1 - \exp{-Z_p t^n})\left(1 + k_s t^{\frac{1}{2}}\right)$$

where $X_{p,\infty}$ is the final fractional crystallinity achieved by the primary process, Z_p is the primary composite rate constant incorporating nucleation and growth, and k_s is the secondary rate constant.

The additional crystallinity produced by the secondary processes is sufficient to account for the observed fractional constant n values on analysis of the total development of crystallinity with time. It was concluded that the analysis using the Avrami equation should be restricted to the time dependence of the crystallinity produced by the primary process alone.

1. Introduction

There is increasing commercial interest in poly (l-lactic acid), PLA, as an environmentally-friendly thermoplastic replacement for oil based polyolefins since it is produced from renewable sources, is biodegradable and biocompatible [1–3]. As a partially crystalline polymer it has thermal and mechanical properties comparable to those of the polyolefins but as an amorphous polymer the glass transition temperature is somewhat low, 55 °C, leading to physical ageing altering the material properties with time at room temperature and in vitro.

The crystallization behaviour of PLA in bulk and from solution has been extensively studied using a wide range of techniques, light microscopy, DSC, X-ray crystallography and FTIR spectroscopy, to control the crystallinity and rate of crystallization [4–10]. In this respect, fruitful areas of research have been in controlling the stereoregularity of PLA by copolymerization with d-lactic acid and d- and meso-lactides [11,12] which greatly reduced the rate of crystallization while the addition of talc [12] and other minerals

[13,14] greatly increase the rate of crystallization by acting as nucleating agents.

However, in analyzing the crystallization kinetics with the Avrami equation [15] most authors, [11–14] obtained constant fractional n values between 2.5 and 3.5. Fractional values have no mechanistic significance in terms of the crystallization mechanisms adopted by Avrami, i.e.,

$$X_t = X_\infty(1-\exp{-Zt^n}) \qquad (1)$$

where X_t is the fractional crystallinity which has developed at time t, X_∞ is the limiting fractional crystallinity finally achieved, Z is a composite rate constant incorporation nucleation rate or density and growth rate; n is an integer constant characteristic of the crystallization mechanism and in terms of the crystallization models of linear growth of crystals in 1, 2 and 3 dimensions and heterogeneous (constant nucleation density) or homogeneous nucleation (constant nucleation rate) adopted by Avrami n should have integral values between 1 and 4.

Similar results have been obtained with many other polymers but recently in a study of the crystallization kinetics of polyesters, in particular poly (ethylene terephthalate) [16–18] and poly (ε-caprolactone) [19,20], the fractional n values have been explained in terms of an overlap between primary and secondary crystallizations; the additional crystallinity due to the secondary process increased the observed n value to above that attributed to the crystallization mechanism in proportion to the value of the secondary rate constant.

In order to extent these kinetic studies and test the generality of these observations the isothermal crystallization of a copolymer of PLLA with 4% d-lactic acid has been studied using FTIR spectroscopy thermal analysis since this technique has the potential to measure the development of crystallinity for extended periods and with sufficient accuracy to separate primary and secondary processes. In this way it is hoped to explain the frequently observed fractional n values in the analysis of the crystallization kinetics of polymers and extend the explanation to another polymer system.

2. Experimental

A random copolymer of l-lactic acid with 4% d-lactic acid, co-PLA, from NatureWorks LLC, USA was used in this study. It was supplied as semi-crystalline moulding pellets with a molecular weight of 194 kg mol^{-1}. Thin films, 10–15 μm thick, were prepared by evaporation of 5% w/v solution in chloroform and solvent removed by storing overnight in a heated vacuum oven at 80 °C.

These films were mounted vertically between two 100 mg KBr discs (approx. 1mm thick) in a Linkam THM 600 hot-stage cell and placed within the sample chamber of a Nicolet FTIR spectrophotometer, model Magna IR 8700 equipped with a DTGS-KBr detector and controlled by Omnic 8.1 software. Spectra of co-PLA were measure in transmission at a resolution of 1–4 cm^{-1} and total of a 100 scans accumulated for each spectrum along with a background spectrum. A blank 200 mg KBr disc was used in measuring the background spectrum. Automatic smooth and baseline corrections were made before analyzing the spectra.

In the crystallization experiments, the samples were heated to the melt at a heating rate of 50 °C min^{-1} and held at 200 °C for 2 min to ensure the sample was completely melted and to erase thermal history. It was then immediately cooled to the isothermal crystallization temperature. A series of spectra were collected at a constant time interval of 2 min over 1000–1500 min.

3. Results and discussion

3.1. Primary crystallization

The IR spectrum of PLA has been well characterized especially the changes which occur on crystallization. It has been reported, [9,21–24] that the most significant change is to the broad intense carbonyl stretching band, centred at 1755 cm^{-1}; it changes in shape on crystallization, see Fig. 1, narrowing by losing intensity between 1740–1750 and 1765–1780 cm^{-1} as well as increasing in intensity with a shift in λ$_{max}$ from 1749 to 1759 cm^{-1}. These changes are reversed on melting. The change in shape of the carbonyl bands is due to the presence of chain conformers which are present in equilibrium in the mobile liquid state but change on crystallization corresponding to the formation of 10:3 helix.

The breadth of the carbonyl band has been attributed to the presence of four overlapping peaks [24] assigned to different conformations of the carbonyl group and in particular the band with λ$_{max}$ at 1759 cm^{-1} has been assigned to the gt conformer. This is adopted by the segments in the crystalline regions but is also present in the amorphous regions in thermal equilibrium with other conformer. In isothermal measurements the change in absorbance at 1759 cm^{-1} is attributed to the increase in crystallinity.

The change in absorbance at 1759 cm^{-1} on crystallization was analyzed as follows; the initial absorbance, A_o, before crystallization had started, was attributed to the amorphous content.

Assuming a two component system for the partially crystalline copolymer, the absorbance at time t, A_t, has amorphous and crystalline components such that,

$$A_t = (1-X_t)A_o + X_tA_c \qquad (2)$$

where A_c is the absorbance of a totally crystalline sample of constant thickness. The fractional crystallinity, X_t, is

$$X_t = \frac{(A_t-A_o)}{(A_c-A_o)} \qquad (3)$$

Since A_c is not normally measured a relative crystallinity, X, relative to that achieved at the end of the measurements was defined