Crystallization and microstructure of poly(butylene oxalate)

Pei-Chun Kuo, Chieh-Tsung Lo*, Chuh-Yung Chen

Department of Chemical Engineering, National Cheng Kung University, No. 1, University Road, Tainan City 701, Taiwan

A B S T R A C T

Crystal structure and morphology development of poly(butylene oxalate) (PBOX) during isothermal crystallization were studied with X-ray diffraction, time-resolved simultaneous small-angle X-ray scattering, differential scanning calorimetry, and optical microscopy. Results indicate that the decrease in the long period at low crystallization temperature indicated the occurrence of secondary crystallization in the interlamellar space. Meanwhile, the lamellar thickness slightly increased with crystallization temperatures due to the formation of thicker crystalline layers at high temperatures. The crystal growth rate of PBOX was analyzed by optical microscopy. Using values of the equilibrium melting temperature of 117.4 °C and the fold surface free energy of 32.37 erg/cm^2 obtained by the Gibbs−Thomson theory, the nucleation parameter, K_g, of 97264 K^2 and the lateral surface free energy of 17.68 erg/cm^2 were determined from the Lauritzen and Hoffman equation. These values are comparable to various semicrystalline polymers previous reported and are not available up to now for PBOX in the literature.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

There has been a growing interest in developing biodegradable polymers for a wide variety of applications, including packaging, tissue engineering, and drug delivery. Biodegradable polymers are obtainable from environmentally friendly materials, such as agriculture crops. This makes biodegradable polymers are recyclable and bio-resolvable and they can be obtained in abundance and low cost. Thus, the use of them has significance in the sustainable development and environment protection. On the other hand, most of the conventional non-degradable thermoplastics are originated from the petroleum resource that may cause the depletion of the resource. Although the development of biodegradable polymers is undoubted the immanent task to achieve, the use of agricultural resources to produce biodegradable polymers may also generate numerous issues, such as the limited availability of foodstuff and the competition between food and non-food production in critical geographic areas. Polyoxalates, which are produced mostly from grass, seem more suitable to be used in the biocompatible materials.

A polyoxalate has an ester backbone, which can be hydrolytically cleaved to produce propylene glycol and oxalic acid. Since the pioneering work on polyoxalates investigated by Carothers et al.

[1], both the synthesis and applications of polyoxalates are the subject of research by many groups. The polyoxalates are synthesized from a two-step reaction. The first step lies in the ester interchange reaction of diols with ester of oxalic acid to form a prepolymer [2]. Further postpolymerization under heat and reduced pressure completes the second step to obtain the polymer. The synthesized polyoxalates are characterized to be hydrophobic and have satisfactory mechanical properties. This makes polyoxalates highly appropriate for practical use, including drug delivery [3,4] and the water treatment for the removal of heavy metal ions [5]. Ballistreri et al. [6] investigated the primary thermal decomposition of poly(ethylene oxalate) and found that the intramolecular exchange reactions predominated in the primary thermal fragmentation processes, resulting in the formation of cyclic oligomers up to tetramer. Thibeault et al. [7] further proposed the competing mechanism of thermal decomposition of polyoxalates through depolymerization, fragmentation to polyenes and CO_2, and crosslinking. When poly(ethylene oxalate) was heated to 170–260 °C, polycondensation, depolymerization, and decomposition occurred and the process of decomposition was second order [8]. Finelli et al. investigated the thermal properties of poly(butylene oxalate) and its random copolymer with azelaic acid [9]. The content of the azelaic acid in copolymer mainly caused decreases in both the melting and glass transition temperatures. In addition to the thermal properties and thermal decomposition of polyoxalates, one of the most dominant factors to develop polyoxalates is the crystallization behavior. In the application point of view, specific crystal morphology determines the final properties of the

* Corresponding author. Tel.: +886 6 2757575x62647; fax: +886 6 2344496.
 E-mail addresses: chiehtsung06@yahoo.com.tw, tsunglo@mail.ncku.edu.tw
(C.-T. Lo).

materials. For instance, when drug delivery is considered, crystalline regions do not erode at the same rate as amorphous regions [10]. The hydrolysis of the crystalline polymers is prolonged when compared to their amorphous counterparts [11]. The crystal morphology of polymers also plays a key role on the adhesion formation after peritoneal surgery [11]. Up to date, however, studies on the polyoxalate crystallization are limited.

In this work, we investigate the isothermal crystallization of a member of polyoxalate family, namely poly(butylene oxalate) (PBOX), using X-ray diffraction, *in situ* small angle X-ray scattering, differential scanning calorimetry, and optical microscopy. The structural parameters, including the long period, lamellar thickness, and degree of crystallinity, were obtained to form a comprehensive picture of the crystal morphology. The combination of these techniques provides information not only on the lamellar dimensions but also the crystallization mechanism of PBOX. The knowledge of the microstructure of the PBOX, coupled with its crystallization behavior and thermal properties, will help to guide the rational design of polyoxalates for various applications.

2. Experimental section

2.1. Materials

PBOX was synthesized, according to a literature method, by a two step reaction [6,8]. Briefly, 1 mol diethyl oxalate (Acros Organics) and 1.2 mol 1,4-butanediol (Alfa Aesar) were mixed in a reactor. Tetrabutyl titanate (Ti(OBu)$_4$, Sigma–Aldrich) was used as a catalyst and the mixture was kept at 140–160 °C for 4 h. After solidification and removal of alcohol, the transesterification was carried out at 180 °C for 4 h under a pressure of 1–3 torr to synthesize PBOX. The prepared PBOX has the molecular weight of about 10,000 g/mol and the glass transition temperature of −20 °C.

2.2. X-ray diffraction (XRD)

X-ray diffraction analysis of the examined materials was performed at room temperature using a Rigaku RINT-2000 diffractometer coupled to a source of filtered CuK$_\alpha$ radiation. Data were collected in the angle scan from 10° to 80° with a scan rate of 5°/min.

2.3. Small angle X-ray scattering (SAXS)

Samples for SAXS measurement were prepared via the melting of PBOX into DSC aluminum sample pans (Perkin Elmer). The sample thickness was 1 mm. The sample pans made ideal sample holders because the aluminum was fairly transparent to the high-brilliance X-rays, and the rigid pans maintained the sample thickness when the polymer was melted in the vertically mounted SAXS sample chamber [10]. The SAXS measurements were conducted in Sector 23A1 at the National Synchrotron Radiation Research Center in Taiwan. The incident beam energy was 8 keV. A two-dimensional CCD detector, at a distance of 2 m from the sample, was used to measure the intensity of scattering. During SAXS measurement, the samples were initially equilibrated at 120 °C, which is above the melting temperature of PBOX, for at least 20 min. Samples were rapidly quenched to a crystallization temperature to allow for crystallization. Data were collected at 10-sec intervals during isothermal crystallization over the range of the scattering vector (q) from 0.006 to 0.27 Å^{-1}, where $q = 4\pi\sin(\theta/2)/\lambda$, θ is the scattering angle, and λ is the incident radiation wavelength. The scattering data were appropriately corrected for incident flux, absorption, detector sensitivity variation, and dark current, and the scattering

intensity was azimuthally averaged to obtain the one-dimensional intensity data [$I(q)$] as a function of q.

2.4. Differential scanning calorimetry (DSC)

The thermal properties of PBOX were measured using a scanning differential calorimeter (DSC 7, Perkin Elmer). Samples of ∼5 mg were heated from 25 °C to 120 °C with a heating rate of 10 °C/min and the melting temperature of PBOX crystallized at different temperatures was analyzed. Melting temperatures were calibrated with indium and tin standards and were reported as the peak in the melting endotherm.

2.5. Optical microscopy

Optical microscopy was carried out with a Nikon H550L Eclipse 50i LV-UEPI microscope in conjunction with a hot stage. Samples were prepared by dropping polymer solution on a glass slide to form a specimen with a thickness of ∼20 μm. The specimen was heated to 120 °C for 20 min to remove the residual crystals and was rapidly quenched to the desired crystallization temperatures to allow for PBOX crystallization. The growth of spherulites was recorded using a Sony color video camera (SSC-DC80 Super Exwave) and the radii of the spherulites as a function of time were measured from time-lapsed frames of spherulitic front. Reported spherulitic growth rates (G) were determined as the mean of the rates from at least 20 spherulites, monitored on from several samples.

2.6. SAXS analysis

Before the extraction of the morphological parameters of interest from the SAXS measurements, the data have to be extrapolated to both the high and low q regions [12]. Extrapolation to $q = $ zero in the region of the beam stop was accomplished by the extrapolation of the intensity using Debye–Bueche approximation [13]

$$I(q) = \frac{I(0)}{\left(1 + q^2\xi^2\right)^2} \tag{1}$$

where ξ is the correlation length. On the other hand, the extrapolation in the high q region was performed with the aid of the Porod law [14]

$$I(q) = \frac{K_p}{q^4}\exp\left(-\sigma_I^2 q^2\right) + I_b \tag{2}$$

here, I_b is the contribution to scattering from local electron density fluctuations in the amorphous phase, K_p is a Porod law constant, and σ_I is the transition thickness between crystalline and amorphous phases.

The one-dimensional correlation function, $\gamma(r)$, which offers more details of the microstructure, is the Fourier transform of the corrected SAXS data, given by Ref. [15].

$$\gamma(r) = \frac{1}{Q}\int_0^\infty q^2 I(q)\cos(qr)dq \tag{3}$$

where Q is the invariant. The invariant is computed for each file as the area under the Lorentz-corrected intensity profile [15].