Polymer Degradation and Stability 97 (2012) 1915–1921

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Rheological characterization of a thermally unstable bioplastic in injection molding conditions

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ARTICLE INFO

Article history:
Received 9 December 2011
Received in revised form
27 January 2012
Accepted 15 March 2012
Available online 23 March 2012

Keywords:
Poly(hydroxy-alkanoates)
Bioplastics
Rheology
Thermal degradation
Injection molding
Inline monitoring

ABSTRACT

Poly(hydroxy-alcanoates) bioplastics have an unusually small temperature processing window due to their thermal instability, which affects both molecular weight distribution and rheological behavior. The use of a rheometrical device mounted on an injection molding machine has been shown to allow the study of dynamic viscosity variations for very short residence times in the melt (down to a few tens of seconds). Moreover, dynamic viscosity can be obtained over a wide range of shear rates (up to 50000 s^{-1}) with both Bagley and Rabinowitsch corrections.

The rheological data obtained for a poly(3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV copolymer shows that the reduction in viscosity associated with degradation is very fast and is detectable even at temperatures close to the melting point. Size Exclusion Chromatography analysis of selected samples shows that, except for residence times below 15s, molecular mass distribution is substantially affected, shifting toward lower masses, and with an increase in oligomer compound content. These oligomers may act as plasticizers of the bioplastic.

The results also suggest that important thermomechanical degradation takes place during the plasticization/feeding step of injection molding.

1. Introduction

Poly(hydroxy-alcanoates) bioplastics, while presenting the virtue of being both bio-based and biodegradable, have two main disadvantages currently impeding their large scale application in the polymer processing industry: Their price is still high compared to commodity petroleum-based polymers, and they have a very small melt processing temperature window, making extrusion or injection molding complex [1].

Kunioka and Doi [2] studied the thermal stability of various poly(hydroxy-alcanoates) (poly(3-hydroxybutyrate), PHB, and copolymers such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate, PHBV) by measuring their molecular mass distribution as a function of time and temperature. They showed that all samples were thermally unstable above 170 °C. The main degradation pathway is random chain scission by β-elimination, leading to a drastic reduction in molecular weights.

Since the injection molding grades currently available (from firms like Biomer, Tiannan and Mirel), have melting temperatures ranging from 165 °C (PHBV) to 178 °C (PHB), it is clear that thermal degradation and the associated molecular mass reduction cannot be completely avoided during processing. It can only be minimized by using the so- called reverse temperature profile [1], recommended by all suppliers, with temperatures above the melting point close to the hopper and temperatures below 160 °C close to the injection nozzle.

Rheometrical measurements of the degradation of PHA bioplastics (poly(3-hydroxybutyrate-co-3-hydroxyvalerate, PHBV copolymers) in the melt have been studied by Melik and Schechtman [3] using torque rheometry, and later by Ramkumar and Bhattacharya [4] using shear rheometry. With both techniques, the time needed to melt the biopolymer is relatively short (typically less than 1 min), allowing one to follow the reduction in viscosity over time from an early stage. Nevertheless, the range of accessible shear rates (10–100 s^{-1} for torque rheometry, 10^{-2}–100 s^{-1} for steady shear rheometry) is limited. More recently, Chen et al. [5]

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doi:10.1016/j.polymdegradstab.2012.03.021

studied the evolution of melt viscosity with time over a larger range of shear rates (5–10^3 s^{-1}) using a capillary rheometer. In those circumstances, the rheological measurement can only be done for residence times higher than 8–10 min, since a large volume of polymer has to be completely melted in the barrel of the rheometer before starting its extrusion.

In the present work, we have carried out rheological measurements on a commercial PHBV copolymer up to very high shear rates (typically in the range of 50–50,000 s^{-1}) for short residence times in the melt state (below 3 min) using a rheometrical device mounted on an injection molding machine used in purge mode. With such a device, the average residence time in the melt state before rheological testing can be as short as a few seconds, due to the rapid melting of the polymer due to combined heat and shear.

2. Materials and methods

2.1. Materials

A poly(3-hydroxybutyrate-co-3-hydroxyvalerate) PHBV, produced by Tianan Biologic (China) for injection molding (Grade Y1000P) was used. It has a melting temperature of 165 °C. According to the data provided by the supplier, it contains an antioxidant and a nucleating agent of unknown nature. Before processing, it was dried following the supplier's recommendations (48 h at 95 °C in order to obtain a moisture content below 250 ppm, measured by the Karl Fischer method). An injection grade polypropylene (Total Petrochemical, PPH 418787) was also used for comparison.

2.2. RHEOBUSE device

The rheometrical device used was designed by Bonneau and Terrisse [6] and commercialized by EAHP ("High Polymers Application School", Strasbourg, France) under the trade name "RHEOBUSE". Based on an earlier patent [7] this device can be mounted on an injection molding machine used in purging mode (Fig. 1). The interest of such a device is to allow viscosity measurements on polymer melts in conditions that are close to those of real processing, taking into account the thermomechanical history.

As seen in Fig. 2, the RHEOBUSE is made up of two parts: a fixed cylindrical part with a channel that has a diameter of 8 mm (a, Fig. 2) equipped with a pressure sensor (b, Fig. 2) and a melt temperature sensor, located in front of the pressure sensor (the thermocouple is embedded in a 1/2 UNF flush-mounted body, in contact with the steel membrane, which is in contact with the melt.)

The second part of the device consists of a rotating barrel (c, Fig. 2) with 7 channels (d, Fig. 2) that have different profiles (detailed on Fig. 3 and Table 1) and can be positioned in succession in front of the channel of the fixed part to provide a series of 7 purge mode injections.

For each channel, the pressure drop $\Delta P = P - P_{atm}$(Fig. 1) and the screw position x (Fig. 1) are recorded as a function of time during injection. The system is optimized in order to reach a steady value of ΔP (plateau on Fig. 4). At the beginning of injection, the pressure signal typically shows an overshoot (and sometimes some instabilities, as in the example given in Fig. 4), before stabilizing to a steady value. This kind of transient phenomenon is related to the material's compressibility, the flow rate and the geometrical characteristics. It has recently been modeled by Mistoulis et al. [8].

In the meantime, the derivative of the screw position allows the calculation of the volume flow rate Q (Fig. 4). In practice, the value of Q should be roughly the same for all the channels, a constant injection velocity is used. A set of 7 couples of experimental values (ΔP_i; Q_i) is thus obtained (one for each channel), and is then used for rheological calculations.

Fig. 3 gives a schematic view of channel #1 on the barrel, which has a constant diameter of 8 mm (equal to that of the channel on the fixed part); and of one of the successive pairs of channels (#2-3, #4-5 and #6-7). While channel #1 has the same diameter $D_1 = 8$ mm over the entire length of the barrel (L_1), the other 6 channels have the same diameter $D_i = D_1$ only over a certain length $L'_i < L_1$ and a smaller diameter d_i over the rest of the barrel (L_i). These sections of a different diameter are separated by a conical transition section (90°). For each pair of channels (#2-3, #4-5 and #6-7), the smaller diameters are the same ($d_i = d_j$), likewise for the conical section, but the lengths of the sections are different ($L_i \neq L_j$ and $L'_i = L'_j$). All the numerical values are given in Table 1.

In all the calculations the steady pressure drops in channel #1: ΔP_0 is taken as a reference. The steady pressure drops in all the other channels can be expressed as a function of ΔP_0. For example for the pair of channels #2 and #3, we have:

$$\Delta P_2 = \Delta P_{L_2} + \Delta P_{\text{cone}} + \Delta P_{L'_2} = \Delta p_{L_2} + \Delta P_{\text{cone}} + \frac{L'_2}{L_0}\Delta P_0 \qquad (1)$$

$$\Delta P_3 = \Delta P_{L_3} + \Delta P_{\text{cone}} + \Delta P_{L'_3} = \Delta p_{L_3} + \Delta P_{\text{cone}} + \frac{L'_3}{L_0}\Delta P_0 \qquad (2)$$

This allows the calculation of the pressure drops in the smaller diameter sections L_2 and L_3:

$$\Delta P_{L_2} = \Delta P_2 - \Delta P_{\text{cone}} + \frac{L'_2}{L_0}\Delta P_0 \qquad (3)$$

$$\Delta P_{L_3} = \Delta P_3 - \Delta P_{\text{cone}} + \frac{L'_3}{L_0}\Delta P_0 \qquad (4)$$

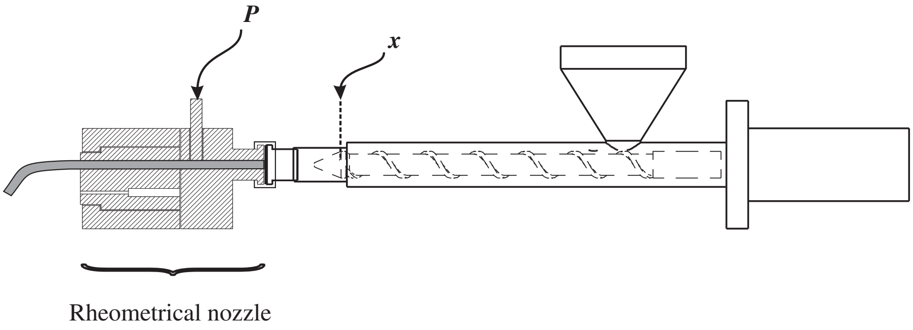

Fig. 1. Rheometrical nozzle mounted on an injection molding machine in purging mode.