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Analysis method

Solution crystallization analysis of poly(lactic acid) by Scalls: A facile approach for thermal analysis of polymers in solution

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ABSTRACT

Non-isothermal solution crystallization and dissolution behaviour of both enantiomers (D and L) of poly(lactic acid) (PLA) and their blends were studied by the unique Solution Crystallization Analysis by Laser Light Scattering (Scalls) method. For the first time, we have investigated the crystallization of this biopolymer in solution, as well as the subsequent dissolution or "solution melting". It was found that addition of the D-enantiomer (PDLA) to the L-enantiomer (PLLA) in solution resulted in the formation of stereocomplex crystals (SC), and the nucleation-effect of the crystals was intensified with increase in PDLA content, leading to an earlier onset of crystallization and increased crystallization peak area. Differential Scanning Calorimetry (DSC) analysis confirmed the formation of SC during solution crystallization. Large re-crystallization events were seen for the pristine polymers, indicative of their low crystallization rates. Overall, results obtained by Scalls provided promising information regarding PLA crystallization kinetics, which significantly influences practical applications of this biopolymer.

1. Introduction

Solution crystallization techniques can provide promising results to understand microstructural behaviour in polymers and to construct much needed structure-property relationships in polymer systems. The most common, conventional techniques used for these studies thus far, are crystallization analysis fractionation (CRYSTAF), temperature rising elution fractionation (TREF) and crystallization elution fractionation ((CEF) [1,2]). Both these techniques require complex instrumentation and long analysis times. A turbidity fractionation analyser, also known as Solution Crystallization by Laser Light Scattering (Scalls), was developed in our group at University of Stellenbosch [3] following the original paper by Shan et al. [4] The Scalls system has advantages over the conventional TREF and CRYSTAF techniques when analysing the crystallization behaviour of polymers. Advantages include short analysis times, fairly inexpensive instrumentation, the ability to observe both the solution crystallization and solution melting of polymers, the small amounts of solvent required, and that the setup allows for a wide selection of solvents to be used. The use of Scalls for crystallization and dissolution studies of polyolefins has previously been reported by van Reenen et al. [3,5]. To date, only polyolefins have been studied by Scalls [6]. In recent years, biopolymers have attracted great attention in both academia and industry. Among the biopolymers, poly(lactic acid) (PLA) has been used most extensively, not only because it is biocompatible and biodegradable but also because it can be obtained from renewable resources. PLA is a linear aliphatic thermoplastic polyester, generally produced by the ring-

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opening polymerization of the lactide monomer. Lactide is a cyclic dimer prepared by the controlled polymerization of lactic acid, which in turn is obtained by the fermentation of corn, sugar cane, sugar beet, etc. [7] It has three isomeric systems namely poly(L-lactic acid) (PLLA), poly(D-lactic acid) (PDLA) and poly(DL-lactic acid) (PDLLA), which is a racemic mixture of L-and D-lactic acid. PLA can exhibit a variety of different properties depending on the isomeric forms present. Its ease of processing, stiffness and good strength makes this polymer a promising material and suitable to replace non-degradable commodity plastics. The major drawback is the polymer's low crystallization rate and crystallinity compared to other commonly used thermoplastics [8]. Ikada et al. [9] was the first to report formation of a stereocomplex when blending PLLA and PDLA in a 1:1 ratio. The stereocomplex displayed a different crystal structure to those of the homopolymers. Since Ikada's findings, extensive work has been done to increase the crystallization rate and to enhance the crystallization, especially of PLLA, and to study the crystal structure of these systems. These include the investigation of asymmetric blends of PLLA and PDLA [8], effect of blend ratios [10,11], the nucleation effect of stereocomplex crystals [12,13], cold-crystallization studies and blending of PLLA with inorganic nucleating agents [7,14,15] These studies were all done by calorimetric measurements from the melt using DSC. To the best of our knowledge, the crystallization and melting of PLLA and PDLA homopolymers and PLLA/PDLA blends from dilute solutions have not been reported. No research has been carried out on solution crystallization and solution melting behaviour of PLA, not even with conventional solution crystallization techniques. The Scalls method was found to be an effective tool to investigate this unexplored area of PLA research. In this study, PLLA and PDLA homopolymers and PLLA/PDLA blends with varying blend ratios were examined by Scalls, using 1,2,4-trichlorobenzene (TCB) as solvent. Promising results were obtained and compared to those reported in literature when analysed from the melt.

2. Experimental

2.1. Materials

PLLA (Purasorb® PL) and PDLA (Purasorb® PD) were supplied by Purac Co. (Netherlands). The polymers were used as obtained from the supplier. 1,2,4-Trichlorobenzene (TCB, spectrophotometric grade, (Sigma-Aldrich, > 99% purity)) was used as purchased.

2.2. Sample preparation

Sample concentrations were kept constant at 1 mg/ml. The solutions were made up by dissolving 20 mg of polymer in 20 ml TCB. For PDLA/PLLA specimens, homopolymers were transferred to a quartz tube containing the TCB. Samples were thus solution mixed within the tube during the dissolution process before crystallization studies started. The labelling was as follows: DL10/90 refers to a blend containing 10 wt% PDLA and 90 wt% PLLA.

2.3. Solution crystallization analysis by laser light scattering (Scalls)

A general schematic representation of the Scalls setup is shown in Fig. 1. The development, along with detailed information regarding the layout, has been discussed in previous literature [3,5,6]. The technique is based on the measurement of laser light intensity. A quartz tube containing the polymer solution is placed in a special opening within an aluminium block, mounted on a magnetic heater stirrer. Openings in the block allow the laser beam to pass through the solution and the changes in intensity are picked up by photodiode detectors. On cooling, polymer crystals are formed which scatters the laser beam and results in a decrease in laser intensity. Likewise, during heating, the increase in laser intensity is measured due to dissolution of the polymer. The first derivative of the raw voltage data allows for the analysis of peaks associated with crystallization and dissolution events. Three lasers with wavelengths of 405 nm (denoted blue), 532 nm (green) and 635 nm (red) were used. Crystallization studies were done by cooling polymer solutions in a controlled manner from 100 °C to 30 °C at various rates between 0.2 °C/min and 3 °C/min. Heating rates were kept constant at 1 °C/min and solutions were heated from 30 °C to 130 °C during dissolution analyses. Stirring speed was set to 500 rpm. Each experiment was repeated a minimum of three times to check the reproducibility of the results obtained.

2.4. Differential scanning calorimetry (DSC)

Thermal analysis studies were done by DSC under N_2 atmosphere. The instrument used was a TA Instruments Q100 calorimeter calibrated with an indium standard according to standard procedures. Cooling and heating rates were fixed at 10 °C/min.

3. Results and discussion

We will first discuss the results obtained for PLLA and PDLA individually, and then the PLLA and PDLA blends. It has to be mentioned that only results for the blue laser (405 nm) are shown in this paper, and curves were normalized for improved comparison of data.

3.1. PLLA and PDLA homopolymers

The crystallization profiles, as obtained from Scalls for PLLA and PDLA polymers are shown in Fig. 2 where Fig. 2a and 2b represents the raw voltage data for the blue laser signal response during cooling at different controlled rates (0.2 to 3.0 °C/min). The decrease in voltage correlates to a decrease in laser intensity so, as soon as crystals are formed in solution, the laser beam is scattered and a decrease in laser intensity was detected. From the first derivative plots (Fig. 2c and 2d), it is clear that both PLLA and PDLA crystallization phenomena can be tracked in solution due to the presence of well-defined and distinct peaks. This is advantageous due to the fact that biocompatible and biodegradable polymers such as PLA will, in the near future, become suitable alternatives to traditional petroleum-