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Phase separation in poly(butylene terephthalate)-based materials prepared by solid-state modification

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ABSTRACT

The morphology of a series of poly(butylene terephthalate) (PBT)/fatty acid dimer diol (FADD)-based copolyesters prepared by solid-state modification (SSM) was studied. It was shown that in copolyesters containing less than 10 wt% FADD two different phases, i.e. a PBT crystalline phase and a PBT-rich amorphous phase, are present. The FADD residues were more or less homogeneously distributed throughout the interlamellar regions. For copolymers containing more than 10 wt% of FADD, a three-phase morphological model has to be used due to phase separation of a FADD-rich amorphous phase from the PBT-rich matrix, as confirmed by solid-state nuclear magnetic resonance spectroscopy and transmission electron microscopy. The final morphology was dependent on the morphology of the PBT/FADD-based physical mixtures prior to SSM. In addition, it was shown that FADD diffusion during SSM influences the final morphology.

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1. Introduction

Poly(butylene terephthalate) (PBT) is a semi-crystalline polyester, showing a high crystallization rate, good dimensional stability and excellent chemical resistance [1]. Nevertheless, PBT is often copolymerized with various comonomers to make the material suitable for more demanding applications. Melt copolymerization (M-PC) or reactive blending of PBT with various comonomers or polymers have been performed in order to ascertain the desired properties. For example, sugar-based diols or polyarylates were used to obtain PBT-based copolyesters with an increased T_g [2–4]. Moreover, PBT-based materials with increased ductility have received significant attention from the scientific and

industrial community. Commonly, this is achieved by preparing PBT-based thermoplastic elastomers.

Thermoplastic elastomers (TPEs) consist of “hard” and “soft” segments, where the latter provides the flexibility and the former the stiffness within a certain temperature range. In the case of PBT-based TPEs, PBT acts as the hard segment, while the soft segment is often poly(tetramethylene oxide) (PTMO). However, there is a strong desire to replace PTMO by renewable alternatives. Natural oil-based comonomers are good candidates to fulfill this role, especially dimerized fatty acids or their derivatives. Hitherto, El Fray et al. [5,6] and Gaymans et al. [7,8] successfully used bio-based dimerized fatty acids as building blocks for the preparation of PBT-based TPEs.

Typically, PBT-based TPEs or copolymers are prepared by conventional M-PC or reactive blending. These methods have the advantage that they are easily applicable on large scale. Nevertheless, copolyesters with a random chemical microstructure are usually obtained when these methods are used. The random

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chemical microstructure of these copolymers negatively influences the melting and crystallization behavior. In order to prepare PBT-based copolymer materials with retained crystalline features and crystallization rate, solid-state modification (SSM) by transesterification can be used [9,10]. Jansen et al. [10,11] have pioneered the use of SSM as a method to prepare PBT-based copolyesters. They proved that the comonomer was exclusively incorporated into the mobile amorphous fraction (MAF) of the copolyesters. Due to mobility limitations, the rigid amorphous fraction (RAF) and the crystalline fraction were excluded from the modification process. This incorporation yielded copolyesters with a non-random overall chemical microstructure and, indeed, retained melting temperatures and crystallinities. However, the MAF of these copolyesters did show a practically random chemical microstructure [12].

The chemical microstructure and morphology of a copolymer are of great importance and determine the final thermal and mechanical behavior of the material. In SSM, the miscibility between the amorphous PBT matrix and the comonomer is of paramount importance and considerably influences the thermal and mechanical properties [13]. It is well known that many polymer blends are not molecularly miscible for thermodynamic reasons. The entropy increase of mixing two polymers is very small and commonly phase separation in polymer blends is observed. This behavior was extensively studied in PBT-based mixtures such as PBT/polyarylate (PAR) [14–16], PBT/PC [4,17–20], and PBT/PTMO [21,22]. Most of these systems show some form of phase separation in a certain composition window. The presence of such a phase-separated morphology can greatly enhance the properties of the material. It is known that for TPEs phase mixing between the hard and soft phase is not desired because this deteriorates the properties of both phases. Moreover, if trans-reactions can take place between the phases a random copolymer would be obtained, which also show deteriorated properties. Such behavior has been widely investigated for mixtures of polyesters where the morphology and properties were studied during transesterification [23–25]. Therefore, the presence of a phase-separated morphology can be of great importance for the material properties, which have so far been studied extensively by using techniques such as transmission electron microscopy or small-angle X-ray scattering.

In our recent study [26], we incorporated a fatty acid dimer diol (FADD) into PBT by using SSM. It was shown that the incorporation was successful and that there was a strong influence of the chemical overall composition of the copolyesters on the chemical microstructure and morphology. In this manuscript, the final morphology as a function of chemical overall composition of these materials is described. In addition, the morphology before the SSM reaction and the morphology development during the SSM reaction are evaluated. Solid-state nuclear magnetic resonance spectroscopy, small-angle X-ray scattering and transmission electron microscopy are used as a complementary approach to fully elucidate the morphology of the series of investigated copolyesters.

2. Experimental section

2.1. Materials

Poly(butylene terephthalate) (PBT) granulate ($M_n = 18$ kg/mol, $M_w = 47$ kg/mol) was provided by DSM (Geleen, the Netherlands) and the fatty acid dimer diol (FADD) was a gift from CRODA (Gouda, the Netherlands). Potassium nitrate (KNO_3), sodium nitrate (NaNO_3) and sodium nitrite (NaNO_2) were all obtained from Sigma–Aldrich. 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, 99%) was obtained from Biosolve (Valkenswaard, the Netherlands). All chemicals were used as received, unless denoted otherwise.

2.2. Solid-state modification (SSM)

The preparations of the PBT/FADD-based physical mixtures and copolyesters were described in our previous paper [26].

2.3. Measurements

Small-angle X-ray scattering (SAXS) was performed at the Dutch-Belgian Beamline (DUBBLE) BM26B of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France [27–29]. The sample-to-detector distance was approx. 2 m and the sample was irradiated with X-rays with a wavelength of 1.033 Å. A Dectris-Pilatus 1M detector with a resolution of 981×1043 pixels and a pixel size of $172 \times 172 \mu\text{m}$ was employed to record the 2D-SAXS scattering patterns. Standard corrections for sample absorption and background subtraction were performed. The data were normalized with respect to the incident beam intensity in order to correct for primary beam intensity fluctuations. The scattering pattern from silver behenate was used for the calibration of the wavevector scale of the scattering curve. The SAXS patterns were acquired at room temperature. The scattering vector q was defined as $q = 4\pi \sin \theta / \lambda$ with 2θ being the scattering angle.

Differential scanning calorimetry (DSC) was performed by using a DSC Q100 from TA Instruments. The measurements were carried out from -50 to 260 °C with heating and cooling rates of 10 °C/min under a nitrogen flow of 50 mL/min. The T_g s were obtained from the inflection point of the thermogram recorded during the first heating run.

Wide-angle X-ray diffraction (WAXD) measurements were performed on a Rigaku Geigerflex Bragg-Brentano Powder Diffractometer using $\text{CuK}\alpha$ radiation, wavelength 1.54056 Å, at 40 kV and 30 mA. The scans were performed with a 0.02° step in 2θ and a dwell time of 3 s in the 2θ range from 10 till 35° . The analyses were performed on the copolyester powder samples, directly after SSM.

Variable-temperature (VT) solid-state $^{13}\text{C}\{^1\text{H}\}$ Cross-Polarization/Magic-Angle Spinning (CP/MAS) NMR and $^{13}\text{C}\{^1\text{H}\}$ Insensitive Nuclei Enhanced by Polarization Transfer (INEPT) MAS NMR experiments were carried out on a Bruker AVANCE-III 500 spectrometer employing a double-resonance probe for rotors with 4.0 mm outside diameter. These experiments utilized a MAS frequency of 10.0 kHz, a $5.0 \mu\text{s}$ $\pi/2$ pulse for ^1H and ^{13}C , a CP contact time of 3.0 ms, and TPPM decoupling during acquisition [30]. The CP conditions were pre-optimized using *L*-alanine. The $^{13}\text{C}\{^1\text{H}\}$ INEPT MAS NMR spectra were recorded using the refocused-INEPT sequence with a J-evolution period of either $1/3J_{\text{CH}}$ or $1/6J_{\text{CH}}$ and assuming a $^1J_{\text{CH}}$ of 150 Hz, i.e. for a J-evolution time of $1/3J_{\text{CH}}$ the signals from CH and CH_3 groups are positive, while those of CH_2 are negative [31,32]. The temperature was controlled using a Bruker temperature control unit in the range from 30 to 180 °C. The VT $^{13}\text{C}\{^1\text{H}\}$ CP/MAS and $^{13}\text{C}\{^1\text{H}\}$ INEPT MAS NMR spectra were recorded under isothermal conditions at selected temperatures. A heating rate of 2 °C/min was employed between the isothermal measuring temperatures. The reported temperatures are corrected for friction-induced heating due to spinning using ^{207}Pb MAS NMR of $\text{Pb}(\text{NO}_3)_2$ as a NMR thermometer [33].

Transmission electron microscopy measurements were performed on a Tecnai 20 microscope, operated at 200 kV. Ultrathin sections were obtained at -45 °C using a Leica Ultracut S/FCS microtome. The sections were stained using RuO_4 -vapor for 30 min. The ruthenium tetroxide (RuO_4)-solution was prepared in accordance with the method described by Montezinos et al. [34].

3. Results and discussion

The modification of poly(butylene terephthalate) (PBT) with a bio-based fatty acid dimer diol (FADD) was accomplished using

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