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Influence of block composition on structural, thermal and mechanical properties of novel aliphatic polyester based triblock copolymers

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A series of ABA type triblock copolymers [Poly(lactide)-*block*-poly(hexamethylene 2,3-*O*-isopropylidene tartarate)-*block*-poly(lactide)] PLA-*b*-PHIT-*b*-PLA based on renewable monomers L-tartaric acid and L-lactide have been synthesized and the effect of the PLA chain length on the properties of the triblock copolymers has been systematically investigated. The block nature of the copolymers was established by differential scanning calorimetry (DSC) which showed two glass transition temperatures (T_g) corresponding to PHIT and PLA blocks. Solution cast films of these triblock copolymers turned out to be brittle in nature and to overcome this, ε-caprolactone was copolymerized with L-lactide to generate a separate series of triblock copolymers [PLA-*ran*-PCL]-*b*-PHIT-*b*-[PLA-*ran*-PCL]. Our study systematically demonstrates that the PLA-to-PCL ratio in the outer block composition influences the mechanical properties via a delayed post-yield stress drop phenomenon. The study further elaborates the time-synchronized strain-field analysis of the novel triblocks to be a convincing approach for the characterization of micro-deformation modes.

1. Introduction

Biodegradable polymers have attracted a great deal of interest in the past two decades, since they have the potential to provide a solution in better managing plastic waste and also show promise in biomedical and pharmaceutical applications [1–3]. The diverse applications of biodegradable polymers have given new impetus for the development of a wide range of tailored polymeric biomaterials. Aliphatic polyesters such as poly(lactide) (PLA), poly(glycolide) (PGA), and poly(ε-caprolactone) (PCL) are well established as biodegradable polymers and widely used as bioadsorbable surgical sutures, absorbable bone plates, surgical fixation devices, drug carriers, and cell scaffolds in tissue engineering [3–6].

PLA is a useful biomaterial produced by the ring opening polymerization of lactide, the precursor for which is derived from natural resources such as corn or wheat. Its biodegradability and good mechanical and physical properties make it suitable for biomedical as well as packaging applications [7–11]. Copolymerization with different comonomers and modulation of their ratio in the copolymer can be an effective method to alter and/or broaden the properties of PLA based materials. Random and block copolymers based on glycolide, lactide and caprolactone such as poly(lactide-*co*-glycolide) (PLGA), poly(lactide-*co*-caprolactone) (PLC) and poly(glycolide-*co*-caprolactone) (PGC) have been developed for various applications and are well documented [12–20].

Tartaric acid is an inexpensive natural resource and has received significant attention for the synthesis of functional polymers and a variety of polymers are derived from it such as polyesters [21–27], polyamides [28,29], poly(ester amide)s [30,31] and polycarbonates [32–35], etc. The tartaric acid based polyesters can be used as drug carriers and controlled release agents in controlled drug delivery. Huang et al. [26] have reported the ability of poly(alkylene tartarates) and its copolyesters as controlled release agents and showed the effects of different chemical modifications of poly(alkylene tartarates) on the release of two model compounds, methylene blue and bovine pancreatic insulin. Similarly, Ahlers et al. [27] demonstrated the good biocompatibility and biodegradability of polytartarates and suitability for controlled release applications.

Recently, we reported on the synthesis of tartaric acid based polyesters and copolyesters followed by their facile post-polymerization modification to generate hydroxyl functionalized polyesters and copolyesters [21,22]. In general, tartaric acid based polyesters are synthesized by the step-growth polymerization method where synthesis of high molecular weight polyesters are difficult. In the present study, a series of PLA-*b*-PHIT-*b*-PLA triblock copolymers based on the renewable monomers L-tartaric acid and L-lactide have been synthesized and characterized. The resultant triblock copolymers were synthesized by combining two different polymerization techniques, step-growth and ring opening

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polymerization to achieve high molecular weight polyesters. In the first step, hydroxyl terminated PHIT was prepared by step-growth polymerization and in the second step it was used as a macroinitiator for the ring opening polymerization of L-lactide and ε-caprolactone to synthesize ABA type triblock copolymers.

2. Experimental section

2.1. Materials

L-Tartaric acid (99%), *p*-toluenesulfonic acid (98%), 2,2-dimethoxypropane (98%) and 1,6-hexanediol (97%) were purchased from Spectrochem Chemicals. 1,6-Hexanediol was distilled under reduced pressure and stored under a nitrogen atmosphere. L-Lactide (98%), tin(II) 2-ethylhexanoate (95%), titanium tetraisopropoxide (97%), and dry toluene (99.8%) were purchased from Aldrich and used as received. Solvents were dried and purified, when necessary, by appropriate standard procedures.

2.2. Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 spectrometer at 25 °C operating at 300 and 75.5 MHz, respectively. Tetramethylsilane (TMS) and deuterated chloroform were used as an internal reference and solvent, respectively. IR spectra were recorded on a Thermo Nicolet IR 200 spectrometer using KBr disks. Molecular weights were determined by gel permeation chromatography (GPC) using monodisperse polystyrene standards. Tetrahydrofuran (THF) was used as the mobile phase and the flow rate was set at 1.0 mL/min at 35 °C using a Waters high-pressure liquid chromatograph equipped with Waters (styragel HR 4 THF) columns and a VE 3580 RI detector. The thermal behaviour of the polyesters was examined by differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) under nitrogen atmosphere. DSC data were obtained from samples of 4–6 mg at heating/cooling rate of 10 °C min^{-1} using a DSC Q200 calibrated with indium.

Thermogravimetric analysis (TGA) was carried out at a heating rate of 10 °C min^{-1} on a Perkin–Elmer Pyris-6 TGA thermobalance under a nitrogen atmosphere.

2.3. Measurements of mechanical properties

Mechanical performance of all the samples was evaluated from solution cast films with a total length of 70 mm, width of 20 mm and ~1 mm thickness with a Zwick universal tensile testing machine (model-Z250) at room temperature with a test speed of 1 mm/min. The samples were cut from the circular solution cast film having diameter of 80 mm. Three specimens were tested for each composition.

2.4. Strain field evaluation methodology

The images for the strain field evaluation were acquired during the tensile testing on a Zwick universal tensile testing machine (model-Z250), by an online video monitoring system at 1 s regular intervals using a CCD (charge-coupled device) camera with resolution of 1280 × 1024 pixel (1280 pixel in tensile direction). The specimens were spray-coated with solvent dispersed acrylic black dye by air brush to generate an optically active random structure (in the grey scale) prior the testing. The surface displacement of the points of a normally 10 × 10 pixels mesh were estimated with a grating technique where each point will be identified by image processing within a cell of 15 × 13 pixels. The strain-field images were obtained by the integral computation of the various deformation stages obtained from surface displacement measurements of the structured grey contrast images by a grating technique by using GOM-ARAMIS software which calculates essentially the strain-statistics and displays the strain distribution on the specimen via surface displacement contours/train contours along the direction of tension. The derivatives of the displacement field give rise to the strain field. The time-dependent strain field evolution characteristics were obtained by image-synchronisation with time. The evolution of the strain field which is time dependent, corresponding to a defined extent of deformation may be characterised by using digital image correlation principles via the transformation of the pixels (coordinates) of the deformed image with respect to the reference image.

2.5. Synthesis

2.5.1. Synthesis of poly(hexamethylene 2,3-O-isopropylidene tartarate) (PHIT) [21]

Dimethyl 2,3-*O*-isopropylidene-L-tartarate (6 g, 27.52 mmol) and 10% molar excess of 1,6-hexanediol (3.54 g 29.97 mmol) were placed in a Schlenk tube equipped with a Dean Stark apparatus and condenser, under nitrogen atmosphere. The reactants were stirred to a homogeneous mixture and 0.5 mol% of titanium tetraisopropoxide (42 μL) was added as the catalyst. In the first step (esterification), the reaction mixture was heated at 110 °C for 6 h when almost the theoretical amount of methanol was collected. In the second step (polycondensation), a vacuum (0.5–1 mm Hg) was applied and the reaction mixture was heated at 160 °C for 12 h when the stirring completely ceased. The cooled reaction mixture was then dissolved in a minimum amount of chloroform and poured into ten-fold excess of methanol to precipitate the polymer. (87% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.76 (s, 2H), 4.21 (m, 4H), 1.69 (m, 4H), 1.48 (s, 6H), 1.40 (s, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.8, 113.6, 77.2, 65.7, 28.4, 26.4, 25.3; FT-IR (KBr disk, cm^{-1}) 2928 ($\bar{\upsilon}_{C-H}$), 1741 ($\bar{\upsilon}_{C=O}$), 1218 and 1162 ($\bar{\upsilon}_{C-O-C}$).

2.5.2. Synthesis of triblock copolymers poly(lactide)-block-poly(hexamethylene 2,3-O-isopropylidene tartarate)-block-poly(lactide) (PLA-b-PHIT-b-PLA)

Block copolymers were synthesized by ring opening polymerization of L-lactide where hydroxyl terminated poly(hexamethylene 2,3-*O*-isopropylidene tartarate) (PHIT) was used as the middle block as well as the macroinitiator. PHIT and L-lactide were taken in different weight ratios, for example the weight ratio of PHIT and L-lactide was 1:2 in the case of PLA_2-*b*-$PHIT_1$-*b*-PLA_2 and so on. Overall, five different triblock copolymers of the type PLA-*b*-PHIT-*b*-PLA were prepared.

General procedure: In a dry and nitrogen purged Schlenk tube PHIT, tin(II) 2-ethylhexanoate and dry toluene were taken and stirred to a homogeneous mixture at 135 °C for 0.5 h. The reaction mixture was cooled and L-lactide was added under nitrogen atmosphere and was heated at 135 °C for 30 h. The cooled reaction mixture was then diluted with chloroform and precipitated into ten-fold excess of methanol.

2.5.3. PLA_2-b-$PHIT_1$-b-PLA_2

92% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.21–5.14 (q, J = 7.2 Hz, 7H), 4.79 (s, 2H), 4.22–4.14 (m, 4H), 1.68–1.58 (m, 25H) 1.51 (s, 6H), 1.39 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.6, 169.0, 113.3, 76.7, 68.5, 66.2, 27.8, 25.9, 24.8, 16.1; FT-IR (KBr disk, cm^{-1}) 2946 ($\bar{\upsilon}_{C-H}$), 1756 ($\bar{\upsilon}_{C=O}$), 1194 and 1094 ($\bar{\upsilon}_{C-O-C}$).

2.5.4. PLA_4-b-$PHIT_1$-b-PLA_4

96% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.19–5.12 (q, J = 6.6 Hz, 14H), 4.77 (s, 2H), 4.20–4.12 (m, 4H), 1.77–1.56 (m, 46H) 1.48 (s, 6H), 1.37 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.5, 169.1, 113.3, 76.8, 68.6, 66.5, 27.8, 25.9, 24.8, 16.2; FT-IR (KBr disk, cm^{-1}) 2947 ($\bar{\upsilon}_{C-H}$), 1760 ($\bar{\upsilon}_{C=O}$), 1192 and 1094 ($\bar{\upsilon}_{C-O-C}$).