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Stereocomplexed PLA nanocomposites: From *in situ* polymerization to materials properties

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ABSTRACT

From the ecofriendly point of view, renewable and biodegradable polylactide (PLA) is considered as one of the best biobased polymers for many applications. However the use of PLA particularly in long-lasting applications like automotive, electronics and food packaging is restricted by its low crystallization ability/degree, impeding its industrial implementation. In this work, we propose to combine two strategies, often used to overcome this drawback, that is, via addition of nanofillers such as nanoclays and PLA stereocomplexation in order to enhance the rigidity, thermal and gas-barrier properties of the polyester matrix. To enhance the dispersion of nanoclays, the “grafting from” approach was thereby employed via *in situ* intercalative and metal-free ring-opening polymerization of L-lactide and D-lactide from the surface of a hydroxyl-functionalized organomodified montmorillonite (i.e., Cloisite 30B). These nanohybrids were subsequently melt-blended with commercial PLA in order to obtain stereocomplexed (or not) PLA-based nanocomposites upon the stereochemistry of the nanohybrids. The morphology and dispersion of the resulting materials were examined by Wide-Angle X-ray Diffraction (WAXD) and Transmission Electron Microscopy (TEM). Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA) were carried out to assess the thermo-mechanical performances of the nanocomposites. Moreover, their oxygen-barrier properties were also evaluated. The stereocomplex directly obtained by melt blending PLA and the bio-PDLA nanohybrid has both enhanced melting temperature (more than 40 °C) and storage modulus (higher than 60%) than those of commercial PLA. Moreover, the nanocomposites obtained show a significant improvement in oxygen-barrier properties. With homo-grafted blend and stereo-grafted blend strategy, the relative oxygen permeability was again reduced by, i.e. 41% and 46% respectively in comparison to PLA matrix.

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1. Introduction

Aliphatic polyesters have been intensively studied over the past years as biodegradable substitutes for the

petroleum-based plastics in the frame of environmental concerns about plastic wastes [1–3]. Some of them can be also derived from renewable sources, making them sustainable when greenhouse gas emission and depletion of petroleum resources are concerned. Polylactide (PLA) thereby represents the most investigated aliphatic polyester for a wide range of applications, due to its biodegradability, renewability and excellent mechanical properties, good processability and low cost [4,5]. High molecular

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weight PLA is obtained by ring-opening polymerization of lactide (LA). Due to the presence of two chiral centers, LA exists as two optically active stereoisomers: D,D-lactide (D-LA) and L,L-lactide (L-LA). The final properties of PLA depend more on the content of optical impurities between both LA enantiomers within PLA chains rather than its molecular weight. For content in D-lactide higher than ca. 7%, the resulting PLA materials are amorphous with a glass transition temperature (T_g) of around 55 °C [6,7]. In contrast, PLA homopolymers prepared from optically pure L-LA or D-LA are semi-crystalline polyesters with a melting temperature (T_m) of about 175 °C and a T_g of ca. 55–60 °C. The mechanical properties of semi-crystalline P(L-LA) are suitable for short-time applications like food-packaging [8–13].

However, the main issue about PLA concerns its low crystallization rate and degree, impeding its industrial implementation for long-lasting applications like automotive and electronics [14,15]. In order to span the range of possible applications, several strategies have been attempted for PLA to enhance its crystallization rate, namely by adding nanosized fillers or via stereocomplexation. PLA stereocomplexes can be readily formed by mixing an equivalent ratio of PLLA and PDLA chains. Due to the strong van der Waals interactions within the stereocomplex crystalline structure [16–18], T_m of stereocomplexes reaches melting temperature around 230 °C, which is approximately 50 °C higher than T_m of either PLLA or PDLA homopolymers [19]. For this reason, stereocomplexation is used to enhance the crystallization rate, the thermal-resistance, and the hydrolysis-resistance of PLA-based materials. Layered silicate/PLA nanocomposites generally obtained via melt-blending are also considered improving thermal, mechanical and transporting properties of PLA matrix [20–26]. Due to the nanosized dimensions of the layered silicate, these improved properties are generally reached at low silicate content (less than 5 wt%). Intercalation of PLA chains into silicate galleries and even clay exfoliation throughout the polyester matrix are obtained using adequately organomodified nanoclay, specifically Cloisite 30B (Cl30B) [27–29].

In the present work, both strategies, i.e. the addition of layered silicate nanofillers and stereocomplexation were hence investigated to cooperatively enhance the rigidity, barrier and thermal properties, and the crystallinity extent of PLA-based nanocomposites. In addition, we investigated Cl30B as nanofillers to carry out a “grafting from” approach for the enhancement of affinity between nanofillers and the matrix [27,30,31]. It consisted to promote ring-opening polymerization (ROP) of L and D-lactide from the two hydroxyl moieties of the quaternary ammonium available at the surface of the organomodified clay for the synthesis of Cl30B-grafted nanohybrids. To promote ROP [32,33] of L(D)-lactide monomers, 1,8-diazabicyclo [5,4,0] undec-7-ene (DBU) was employed as metal-free catalyst, affording a sustainable solution rather than using current organometallic catalysts like tin(II) octoate [34–36]. These resulting nanohybrids were subsequently melt-blended with PLA upon stereocomplexation or not in order to assess their thermal, mechanical and barrier properties by DSC, TGA, DMTA and gas permeation analyses.

2. Experimental part

2.1. Materials

Poly(lactide (PLA) was kindly provided by Futerro S.A., Belgium (0.4% mol in D-lactide content, number-average molecular weight of ca. 100,000 g/mol). L-lactide and D-lactide were supplied from Purac, respectively, recrystallized from dried toluene and stored in a glove box. 1,8-Diazabicyclo [5,4,0] undec-7-ene (DBU) (Fluka) was dried over BaO, distilled and stored in a glove box. Cloisite®30B (Cl30B), a montmorillonite organomodified by 23.4 wt% of methyl bis(2-hydroxyethyl)tallowalkyl ammonium cations was supplied by Southern Clay Products (USA). Amberlyst® 15, ion-exchange resin, in hydrogen form, was supplied by Fluka, and used oven dried overnight at 60 °C.

2.2. Characterization

Gel Permeation Chromatography (GPC) was performed in CHCl₃ at 35 °C using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 1 ml/min) refractive index (ERMA 7517), an automatic injector (Polymer Laboratories GPC-RI/UV) and three columns: a PL gel 10 µm guard column and two PL gel Mixed-B 10 µm columns. PS standards were used for calibration.

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were recorded on polymer samples, using a BIO-RAD Excalibur spectrometer equipped with an Attenuated Total Reflectance (ATR) Harrick Split PeaTM. Unless specified, the other analyses were carried out on the injection-molded samples. The morphology of the nanocomposites was analyzed by Wide-Angle X-ray Diffraction (WAXD) and transmission electronic microscopy (TEM). WAXD patterns were recorded between 1.65° and 30° (by steps of 0.04°) with a Siemens D5000 diffractometer (Germany) operating with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). For TEM analyses, the samples were cryomicrotomed at –100 °C with an Ultracut FC4E microtome from Reichert–Jung. A truncated pyramid was cut in the sample and ultrathin sections of the pyramid were removed for TEM analyses. The TEM images were recorded with a Philips CM100.

DSC Q2000 from TA instrument was used for Differential Scanning Calorimetry (DSC) analysis. Samples (weighing ~ 10 mg) were sealed in aluminum DSC pans (T_{zero}) and placed into the DSC cell. The DSC analyzer was calibrated with indium. Samples were heated from –20 °C to 230 °C at a heating rate of 10 °C/min. Thermogravimetric analyses (TGA) were carried out with a TGAQ5000 apparatus from T.A. Instruments under nitrogen or air flow (heating rate: 20 °C/min).

For Dynamic Mechanical Thermal Analyses (DMTA) injection-molded (35 × 12 × 2 mm) specimens of either unfilled PLA or PLA-Cl30B based nanocomposites were prepared accordingly (specimens collected after extrusion were injection-molded into rectangular bars for 3 min at 190 °C – at 220 °C for stereocomplexes), under a pressure of 900 MPa and then rapidly cooled to room temperature.

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