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The role of cellulose nanocrystals in the improvement of the shape-memory properties of castor oil-based segmented thermoplastic polyurethanes

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ABSTRACT

The effect of the addition of cellulose nanocrystals on segmented thermoplastic polyurethane shape-memory properties was investigated. To this end, polyurethane bionanocomposites were synthesized by *in situ* polymerization, adding cellulose nanocrystals in the first step of polymerization and using components from renewable resources in polyurethane formulation. Thereby, microphase separated polyurethane/cellulose nanocrystal bionanocomposites were obtained, presenting two main transitions, soft and hard phase melting temperatures. Furthermore, it was observed that due to the addition of cellulose nanocrystals, hard phase crystallinity increased. Regarding thermally-activated shape-memory properties, a significant improvement was observed in the shape recovery values with the addition of cellulose nanocrystals, being these bionanocomposites good candidates to use in applications where shape-memory properties are required.

1. Introduction

Segmented polyurethanes are an important class of polymers that have found many applications as biomaterials due to their excellent physical properties and relatively good biocompatibility [1–3]. Technically, segmented thermoplastic polyurethanes (STPU) are block copolymers with alternating amorphous or crystalline hard and soft segments, denoted as HS and SS, respectively, that separate into microphases or domains, due to the thermodynamic incompatibility between both segments [4–7]. Therefore, manipulating their composition and choosing properly the chemical structure of the components, a wide variety of polyurethanes can be synthesized with different types of molecular architectures, specifically designed for each application [8,9]. In the last decades, the use of components from renewable resources have received steadily growing attention in polyurethane synthesis, owing to the dominant consumption patterns, the limited fossil resources and their increasing cost, as well as the public concern about climate change. Polyols derived from vegetable oils [10–14] are a good example of materials that can be used to synthesize segmented polyurethanes with a high percentage of components derived from renewable sources. Moreover, the use of nanoreinforcements also from renewable resources, such as cellulose nanocrystals, chitin nanocrystals and bacterial cellulose [15–18], are gaining increasing interest, because they are used to improve the final properties of the synthesized nanocomposites, as well as to increase the amount of carbon from renewable resources in nanocomposites formulation.

The use of segmented polyurethanes as shape-memory polymers, mainly as thermally-activated shape-memory (TASM) polymers, has received increasing attention in the last few years because of their applications in microelectromechanical systems, actuators, for self healing and health monitoring purposes, and in biomedical devices [19–21]. TASM polymers consist of two components on the molecular level: first, molecular switches, which are segments having a thermal transition at a determined temperature (T_{trans}) and responsible for shape fixity by forming physical cross-links; and second, network points that link these segments and determine the permanent shape [22–25]. Regarding segmented polyurethanes, in almost all cases, SS acts as the switching segment, and HS determines the permanent shape.

The main objective of this work was the synthesis of polyurethane/cellulose nanocrystal bionanocomposites with high contents of carbon from renewable resources by *in situ* polymerization, and the posterior TASM characterization of the synthesized bionanocomposites, in order to study the role of cellulose nanocrystals

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(CNC) in shape-memory properties. To this end, thermal and mechanical properties of the synthesized bionanocomposites were determined, as well as their TASM properties by cyclic thermo-mechanical tests.

2. Materials and methods

2.1. Materials

Concentrated sulphuric acid (H_2SO_4, >98%) was purchased from Sigma–Aldrich Corporation (Missouri, United States), as well as tetrahydrofuran (THF, >99.9%) and microcrystalline cellulose (MCC) with a particle size between 100 and 150 μm. For polyurethane synthesis, 1,6-hexamethylene diisocyanate (HDI) supplied by Bayer (Leverkusen, Germany) under the trade name Desmodur H and corn-sugar based 1,3-propanediol (PD) supplied by Quimidroga SA (Barcelona, Spain) were used as hard segment. Poly(butylene sebacate) diol was used as soft segment, a difunctional semicrystalline polyester derived from castor oil ($T_g = -54$ °C, $T_m = 67$ °C and $\Delta H_m = 138.26$ J g^{-1}), denoted as CO2, with a molecular weight of 1900 g mol^{-1}, which has been already used and characterized in previous works [6,26]. Moreover, the quantity of carbon from renewable resources of CO2 was determined by ASTM D 6855, resulting in a value of 70%.

2.2. Isolation of cellulose nanocrystals

Cellulose nanocrystals were prepared by acid hydrolysis of MCC using the following method: 20 g of MCC were dispersed in 500 mL of 64% (w/w) aqueous H_2SO_4 and stirred constantly for 30 min at 45 °C. The resultant suspension was subsequently diluted and washed by continuous centrifugation with deionized water. For removal of the remaining acid, nanocrystals were dialyzed against deionized water until the pH of the dialysis water stayed constant. Finally, a loose powder was obtained by freeze-drying the CNC suspension at a concentration of 0.05 mg mL^{-1}. Therefore, CNC with a rod-like morphology were isolated with an average diameter of 8.3 ± 0.9 nm and an average length of 152 ± 21 nm, resulting in an aspect ratio of 18.3 ± 2.7.

2.3. Synthesis of polyurethane bionanocomposites

Polyurethane bionanocomposites were synthesized by *in situ* polymerization with different CNC contents and 17 wt% of HS content (with a molar ratio of 1:2:1 among components, polyol:diisocyanate:chain extender + CNC), using a two step procedure in THF solution [15]. As sketched in Fig. 1, prepolymers with different chemical structures can be formed. Although not shown in the scheme, prepolymers with isocyanate and hydroxyl ending groups from cellulose nanocrystals could form longer prepolymer structures. In the second step of polymerization, the chain extender was added, enabling the coupling of these prepolymers and forming different hard segment structures.

To avoid the agglomeration of cellulose nanocrystals, the freeze-dried CNCs were redispersed in THF at a solid content of 0.5 wt%, without additives or any surface modification. First of all, the prepolymer was synthesized at 100 °C for 6 h by reacting HDI with CO2 in the presence of CNCs, previously dispersed in THF. The concentration of the resulting prepolymer was 75 mg mL^{-1} and a condenser was used to avoid THF evaporation. Afterwards, the chain extender, 1,3-propanediol, was added in stoichiometric amount to the prepolymer, and the mixture was stirred at 100 °C for 2 h before casting and curing on a Teflon dish at 60 °C for 48 h under vacuum, in order to obtain a film. The amount of reactive hydroxyl group on cellulose nanocrystals was measured by titration of excessive isocyanate groups, resulting in a value of 2.1 ± 0.2 mmol g^{-1}. This polymerization method allows obtaining bionanocomposites with cellulose nanocrystals covalently linked to the polyurethane chains. Furthermore, the neat polyurethane was also synthesized following the procedure used for bionanocomposites synthesis, but without adding CNCs. Thereby, a neat polyurethane, denoted as STPU17, and bionanocomposites with different CNC contents ranging from 0.25 to 2 wt% were successfully synthesized and denoted as STPU17/CNC-X, being X the amount of CNC added (wt%).

2.4. Characterization techniques

The thermal behavior of the neat polyurethane and the bionanocomposites was analyzed by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). On one hand, DSC scans were recorded on a Mettler Toledo 822^e instrument (Ohio, United States), equipped with a robotic arm and with an electric intracooler as refrigeration unit. Samples were scanned from −60 to 220 °C at a scanning rate of 20 °C min^{-1}, operating under dry nitrogen atmosphere. Moreover, the crystallization process was followed by cooling the samples from 220 to −60 °C at a scanning rate of 10 °C min^{-1}. A second heating run was also performed, but as it did not add any extra information, it was not included in this work. On the other hand, DMA measurements of the neat polyurethane and the bionanocomposites were performed in tension mode on a DMA Q-800 (TA Instruments, Delaware, United States). A constant frequency of 1 Hz was used, and samples were scanned from −100 to 150 °C at a rate of 2 °C min^{-1}.

Thermally-activated shape-memory properties of the synthesized neat polyurethane and the bionanocomposites were also characterized in tension mode on a DMA Q-800, performing cyclic tests at 60 °C. Samples were first conditioned at 60 °C for 15 min and subsequently elongated to 50% applying a force ramp of 0.1 N min^{-1}. Then, samples were cooled to 15 °C at a rate of 5 °C min^{-1} and the stress was released maintaining the temperature at 15 °C. Finally, samples underwent the recovery process by being heated at a rate of 5 °C min^{-1} to the recovery temperature, 60 °C. This temperature was selected as the transition temperature because above 60 °C SS crystallites melt, acting as switching segments, whereas HS crystallites restricted molecular motion, being responsible for shape recovery. Shape fixity (R_f) and shape recovery (R_r) values were determined for each thermo-mechanical cycle, according to the equations presented in literature [19,22].

The mechanical properties of the synthesized films were measured on a MTS Insight 10 instrument (MTS Systems Corporation, Minnesota, United States), equipped with a 250 N load cell. Dog-bone shape specimens (22.25 mm in length, 5 mm in width and 0.7 mm in thickness) were used for tensile tests, according to ASTM D 1708-93 standard. Five replicates of each material were used to measure Young's modulus (E), yield strength (σ_y), tensile strength at maximum elongation (σ_{max}) and strain at break (ε_b) values, calculated from the load–displacement data, where the deformation was measured by the crosshead displacement. Moreover, the work-of-fracture in the elastic region (8% strain) and the total work-of-fracture were also measured integrating the area under stress–strain curves obtained by tensile tests.

Finally, atomic force microscopy images (AFM) were obtained in tapping mode on a Nanoscope IIIa scanning probe microscope Multimode™ Digital Instrument (Bruker Corporation, Massachusetts, United States), equipped with an integrated silicon tip/cantilever having a resonance frequency of 300 kHz. Samples cross sections were prepared using a Leica EM FC6 cryo-ultramicrotome (Leica Microsystems, Wetzlar, Germany) equipped with a diamond knife and operating at −120 °C, in order to observe the dispersion of CNCs in the neat polyurethane. The measurements were performed