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From elastomeric to rigid polyurethane/cellulose nanocrystal bionanocomposites

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ABSTRACT

Bionanocomposites with high content of carbon coming from renewable resources were synthesized. Different cellulose nanocrystal (CNC) contents were added by solvent casting procedure to highly crystalline bio-based polyurethanes with different soft/hard segment ratios. Properties of the resulting bionanocomposites were evaluated in order to study the effect of both CNC content and polyurethane soft/hard segment ratio on the structure/properties relationships. Thereby, from elastomeric to rigid polyurethane/CNC bionanocomposites containing 1, 3, 5 and 10 wt% of CNC and bio-based polyurethanes with 17 and 46 wt% of hard segment content were prepared. CNC were isolated by sulphuric acid hydrolysis, obtaining rod-like crystalline structures. A good dispersion of CNC was obtained for all the bionanocomposites, which interact with the polyurethane segment that was not associated in ordered domains. Thermomechanical and tensile tests revealed that those bionanocomposites presented good mechanical properties, competing with petrochemical based nanocomposites.

1. Introduction

Polymer nanocomposites have attracted great interest during recent years due to their unique and fascinating properties that potentially compete with the most advanced materials in nature [1–4]. Furthermore, owing to more environmentally aware consumers, increased price of crude oil and global warming, renewable biodegradable raw materials have raised great interest in the last years. Cellulose is one of the most abundant and renewable biopolymers in nature produced by plants, trees, bacteria and sessile sea creatures called tunicates [5]. It is used as reinforcing material in composite synthesis in the form of fibers or derivatives [6]. Nevertheless, in relatively recent years, cellulose nanocrystals (CNC), highly crystalline rod-like nanomaterials isolated from cellulose fibers by acid hydrolysis, have received increasing attention [7–12]. The combination of CNC high surface area, high aspect ratio, environment benefits and low cost, as well as the exceptional mechanical properties, have made them attractive to use in bionanocomposite synthesis [13–15]. Moreover, the characteristics of CNC depend on the origin of the fibers and the exact hydrolysis conditions (acid concentration, temperature and reaction time), which must be adjusted depending on the substrate to be hydrolyzed [9,16,17].

CNCs have been incorporated as reinforcing fillers into a wide range of polymer matrixes [13,14,18–21], including segmented polyurethanes [22–26], due to their before mentioned appealing intrinsic properties. Moreover, other cellulose reinforcement forms, such as bacterial cellulose [27,28] and cellulose nanofibers [29,30] have also been incorporated into polyurethane matrixes. Segmented thermoplastic polyurethanes (STPU) are very versatile polymers, mainly due to the way they are synthesized and the wide range of different components that can be used, giving from elastomeric to rigid materials. Moreover, owing to the relative ease of fabrication into devices, biocompatibility, biostability and flexibility of STPUs, they are the material of choice for many biomedical applications [31,32]. Technically, STPUs are block copolymers with alternating amorphous or crystalline hard segments (HS) and soft segments (SS) that separate into microphases or domains, due to the incompatibility between both segments [33]. Thereby, taking into account the ability of polyurethanes to have different types of molecular architectures specifically designed for each application and thanks to the addition of CNCs as the loading-bearing constituent, new polyurethane nanocomposites could be synthesized to use in a wide variety of applications. The use of components from renewable resources such as vegetable oils and sugars for the synthesis of polyurethanes, and cellulose nanocrystals as reinforcements, leads to the synthesis of bionanocomposites with high contents of carbon coming from renewable resources.

In previous work, nanocomposites were prepared by solvent casting, using STPUs with low hard segment content and based

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on a petrochemical amorphous soft segment [26,34]. In the work reported in the present article, components derived from renewable resources, such as castor oil based highly crystalline polyol and corn-sugar based chain extender, were used to prepare from elastomeric to rigid bio-based STPUs, varying soft/hard segment ratio. Furthermore, cellulose nanocrystals were used as renewable reinforcements in order to prepare bio-based STPU bionanocomposites, with the aim to enhance their mechanical behaviour in the elastic region (modulus and yield strength), and being in that way candidates for replacing petrochemical-based nanocomposites in traditional applications. The evaluation of thermal and mechanical properties of bionanocomposites and also the morphological characterization were performed.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose (MCC) was supplied by Sigma Aldrich, as well as dymethylformamide (DMF, >99.8%) and sulphuric acid (>98%). For the synthesis of polyurethanes, 1,6-hexamethylene diisocyanate (HDI, Bayer) and 1,3-propanediol (PD, Quimidroga SA) were used as hard segment and a castor oil derived difunctional polyester (poly(butylene sebacate) diol) was used as soft segment [35].

2.2. Isolation of cellulose nanocrystals

CNCs were isolated from microcrystalline cellulose through an acid treatment with sulphuric acid, which removes the disordered or paracrystalline regions of cellulose and leaves crystalline regions intact. Hydrolysis was carried out with 64% (w/w) sulphuric acid at 45 °C for 30 min with constant stirring. The resulting suspension was subsequently diluted with water and washed with successive centrifugations. Then, dialysis against distilled water was performed to remove any free acid molecules from the dispersion and finally, samples were freeze-dried at a concentration of 0.05 mg/mL. The hydrolysis protocol employed introduces a small amount of sulphate groups on the surface of the CNCs, which cause electrostatic repulsion between the nanocrystals and lead to their good dispersability in many polar solvents such as DMF [36] for the subsequent preparation of bionanocomposites.

2.3. Synthesis of STPUs

STPUs were synthesized following a previous route [35]. Briefly, in the first step, the isocyanate-terminated prepolymer was synthesized by the reaction between polyol and an excess of HDI at 90 °C for 5 h, and once obtained the prepolymer, the chain extender was added in stoichiometric ratio. The resulting viscous liquid was quickly poured between two Teflon-coated metal plates and left to cure under pressure for 10 h at 100 °C. Thereby, polyurethanes with 17 (STPU17) and 46 (STPU46) wt% of hard segment content were synthesized.

2.4. Preparation of bio-based STPU bionanocomposites

Polyurethane bionanocomposites with different percentages of CNC were synthesized by solvent casting procedure. Polyurethanes were dissolved in DMF (25 mg/mL) and different quantities of CNC were added. Then, the mixtures were sonicated in Vibracell 75043 for 1 h at 0 °C and finally, they were solution cast onto Teflon petri dishes and subjected to a pressure–temperature cycle at 80 °C using a vacuum pumping unit, in order to remove the solvent [34,37,38]. Transparent polyurethane bionanocomposite films containing 1, 3, 5 and 10 wt% of CNCs were successfully prepared, and they were designated as STPU17-1, STPU17-3, STPU17-5 and STPU17-10 (for the bionanocomposites based on the polyurethane with 17 wt% of HS content), and STPU46-1, STPU46-3, STPU46-5 and STPU46-10 (for the bionanocomposites based on the polyurethane with 46 wt% of HS content).

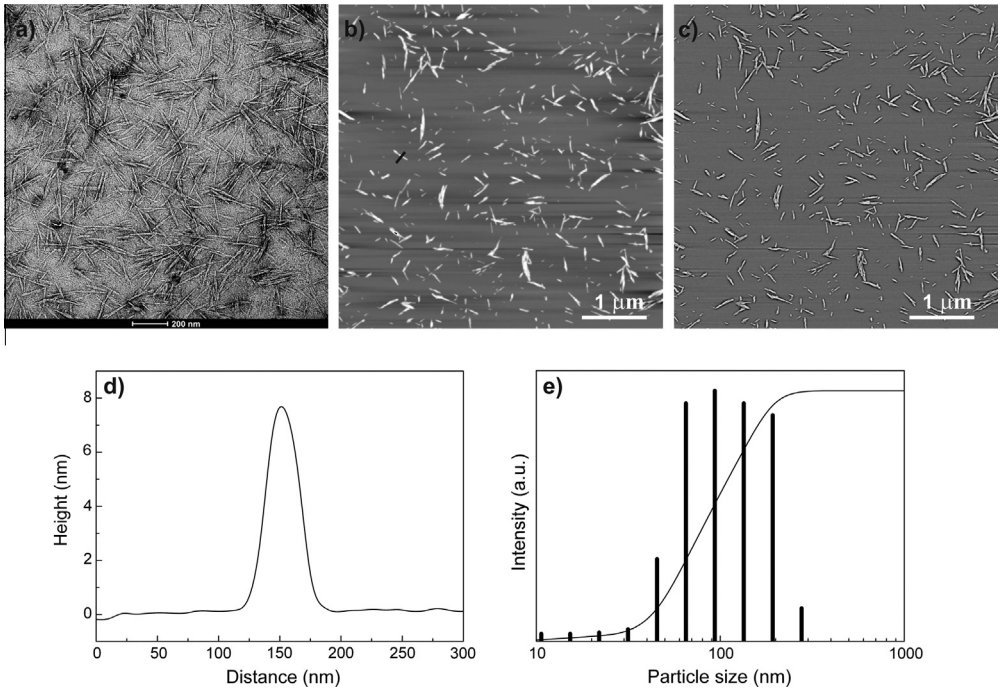

Fig. 1. TEM (a) and AFM height (b) and phase (c) images of rod-like cellulose nanocrystals. Height profile of cellulose nanocrystals (d) and size distribution of cellulose nanocrystals measured by dynamic light scattering (e).