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Physical and mechanical properties of a vegetable oil based nanocomposite

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ABSTRACT

Nanocomposites films were prepared from a bio-based waterborne polyurethane and cellulose nanocrystals (CNCs) obtained from the sulfuric acid hydrolysis of cellulose nanofibers. The polyurethane used as matrix of the nanocomposite film was synthesized from a biobased macrodiol derived from castor oil, 2,2-bis(hydroxymethyl) propionic acid, 1,6-hexamethylene diisocyanate and triethylamine. The concentration of CNC in the films was varied from 0 to 10 wt.%, and the films obtained by casting were characterized by DSC, DMA, tensile tests and TGA. Due to the hydrophilic nature of the PU, the nanocrystals were well dispersed, obtaining homogenous and transparent films which displayed improved thermal and mechanical properties compared to the neat PU. The impact of the CNCs on the crystallization of the polymer was analyzed. Finally, the mechanical properties were fitted to well known theoretical models, allowing a better understanding of the interactions between polymer and filler in the composites.

1. Introduction

Over the last decades, the interest on developing environmentally friendly materials has grown exponentially, as the consciousness for a sustainable development has become more and more widespread [1–5]. In particular, there is also an increasing interest in the replacement of synthetic reinforcements in composites by natural fibers/particles, due to their renewability and low environmental impact [4,6].

One of the main objectives is the replacement of non-renewable resources for renewable ones, such as the cellulose, which is a structural component of the cell wall of plants [7–9]. Usually, cellulose is processed in different ways to obtain technically better materials, particularly, cellulose nanocrystals (CNCs). They are rod-like particles with width in the range of 2–20 nm and lengths that can reach several hundreds of nanometers, and can be isolated from microfibrillated or microcrystalline cellulose among other numerous sources using mechanical or chemical (enzymatic or acid hydrolysis) methods or a mixture of both [8]. CNCs are ideal candidates as nanotechnologic materials because of their rod-like nanostructure, abundance, biodegradability, renewability and multi-functionality, with the result that for some applications they can replace high-cost, non-biodegradable synthetic fibres, for example, carbon nanotubes [10].

The most important properties of CNC are its mechanical properties, such as very high modulus, theoretically 124–172 GPa, while experimentally 12–150 GPa with a high dispersity of results [11–16], a very low density, resulting in a specific tensile modulus (tensile modulus/density) higher than steel's (85 vs 25 $\mathrm{kJ\,kg^{-1}}$) [17]. Because of this, CNC are very good candidates as reinforcement for polymeric nanocomposites. Nevertheless, cellulose is a carbohydrate, and as such, it has many hydroxyl groups in the surface, making it more attractive in combination with polar matrices. Also, when using non-polar polymers, the CNC can be superficially modified, however it must be considered that surface modification also reduces the interaction among the CNC, reducing the reinforcing effect, thus a balance between dispersion and cellulose interaction must be found in such cases [18].

On the other hand, polyurethanes (PUs) are a family of polymers that has been used for several applications in a wide range of products such as biomedical, coatings, foams, adhesives and composites [19]. In particular, segmented PUs are copolymers with a structure of alternated soft and hard segments, the first ones consisting mainly of the long chains of polyol/macrodiol, and the latter being formed by the isocyanate and the chain extender usually added to these formulations. The large variety of available polyols and isocyanates leads to the high versatility of the PUs [20,21]. Conventional PUs are synthesized using organic solvents, but with the increasing interest in using eco-friendly materials, the development of waterborne polyurethanes (WBPUs) has

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been promoted [22,23]. In this case, the use of WBPUs as polymer matrix, restricts the available fillers to those with hydrophilic nature, and once again, CNCs are ideal candidates [24].

In this study, a WBPU was synthesized using a natural macrodiol derived from castor oil and 1,6-hexamethylene diisocyanate (HDI) and it was used as the matrix for cellulose nanocomposites. The CNCs used in this study were prepared from cellulose nanofibers derived from Kraft pulp by acid hydrolysis. The composites obtained were characterized by their thermal and mechanical properties.

2. Materials and methods

2.1. Materials

Microfibrillated cellulose (MFC) was provided by University of Maine and was hydrolyzed using sulfuric acid (96%, Aldrich) [25]. For the synthesis of the WBPU, 2,2-bis(hidroxymethyl)propionic acid (DMPA, 96%, Aldrich), 1,6-hexamethylene diisocyanate (HDI, 98%, Aldrich), triethylamine (TEA, 99%, Aldrich), dibutyltin dilaurate (DBTDL, 95%, Aldrich) and acetone (technical grade, Aldrich) were used. The macrodiol used was derived from castor oil, with the chemical structure showed in Fig. 1 and M_n of 1320 g mol^{-1} [21,26].

2.2. Methods

2.2.1. Acid hydrolysis

To obtain the CNCs, an acid hydrolysis was performed. 103.9 g of MFC with a solid content of 3.85 wt.% (4 g of dried MFC) where mixed with 414.3 g of distilled water, cooled in an ice bath and strongly stirred. Once the temperature was stable around 2 °C, 514.5 g of H_2SO_4 96% were slowly added (1 h). Then the temperature was risen to 44 °C and kept at that value for 1 h. To finish the reaction, the mixture was diluted to a final volume of 1 L. Then, it was dialyzed against distilled water for one week until reaching a pH around 5 and stored at 4 °C [9,27,28]. Once the suspension was obtained, the solid content was determined by drying a small amount of the suspension at 50 °C overnight, and weighing the dried solids. The procedure was performed by quadruplicate.

2.2.2. Synthesis of WBPU

For the synthesis of the WBPU, a one-step procedure was used [21,29]. The macrodiol was dried in rotary evaporator for one day prior to use, then 18 g were weighed and taken to 80 °C under strong stirring. Then 1.15 g of DMPA (acting as internal emulsifier), 4 drops of DBTDL (catalyst) and 4.47 g of HDI were added in that order (slow addition in the case of HDI). The reaction was performed for 4 h, but during the last 2 h the temperature was reduced to 60 °C and 100 mL of acetone were added in aliquots of 10 mL, to diminish the viscosity of the reaction medium. Finally, to neutralize the ionic groups, TEA was added and heating was turned off. When the system reached room temperature, 100 mL of water were added and the system was gently stirred overnight. Rotary evaporation was used to eliminate any trace of acetone from the suspension.

2.2.3. Preparation CNC/WBPU films

The nanocomposites were prepared adding different percentages of CNC (0, 1, 3, 5 and 10 wt.%, dry basis) to the polymer. The needed amount of the CNCs suspension (originally 1.108 wt.%) was mixed with water (when required) and stirred overnight, as well as the WBPU suspension. The addition of water to the cellulose suspension was performed to keep the total liquid weight equal for all the nanocomposites prepared and thus reducing differences in drying times. The CNCs suspension was sonicated during 30 min and then mixed with the already prepared (fully reacted) WBPU dispersion, stirred for 5 min and sonicated for 30 min more. The films were obtained by solvent casting in a Petri dish with PTFE/Teflon coating for 24 h at 50 °C [30].

2.2.4. Characterization

Atomic force microscopy was performed using an AFM Multimode Bruker, using tapping mode at a scan rate of 0.996 Hz, 512 samples per line, amplitude set point between 350 and 400 mV and drive amplitude between 100 and 150 mV.

The crystalline index (CI) of the CNCs was evaluated by X-ray diffraction, using a PHILIPS X'PERT PRO automatic diffractometer equipped with a Cu(Kα) radiation source (λ = 0.1546 nm). Data was collected from 2θ = 5 to 80° at a scanning rate of 0.026°/s. Crystalline peaks 1–10, 110, 102, 200 and 004 appear at 2θ: 14.6°, 16.8°, 20.2°, 22.7° and 34.7°, respectively [31–33]. The CI was calculated, after performing the deconvolution of the crystalline peaks and the amorphous contribution, as the ratio of the area under the crystalline peaks to the total area in the range 10–36° [34].

Dynamic light scattering (DLS) was used to measure the size of WBPU particles in the dispersion. Using a Malvern Zetasizer Nano S-90 with a laser of 632 nm (Malvern Instruments Co. Ltd., Worcestershire, UK), at 25 °C on the samples highly diluted in deionized water.

The color of the films was determined using a LOVIBOND Reflectance Tintometer RT Series. The data obtained from the equipment is expressed as L, a and b (lightness, red-green and yellow-blue indexes, respectively). The total color difference (ΔE) and whiteness index were calculated by Eqs. (1) and (2) respectively, considering the neat WBPU as Ref. [35].

$$\Delta\ E= \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (1)$$

$$WI = 100-\sqrt{(100-L)^2 + a^2 + b^2} \quad (2)$$

WBPU, CNC and nanocomposites characteristic functional groups were analyzed by Fourier transform infrared spectroscopy (FTIR) using a Nexus Nicolet spectrophotometer, by attenuated total reflection (ATR) technique with a ZnSe crystal. 64 scans with a resolution of 8 cm^{-1} were averaged to obtain each spectrum. The spectra were normalized using the peak at 2930 cm^{-1} for easier comparison.

A Jeol JSM-6460LV scanning electron microscope operating at 15 kV was used to observe the fragile fracture surface of the composites obtained under liquid nitrogen. Previously, the samples were sputter-coated with a thin layer of a mixture of gold and palladium.

Differential scanning calorimetry (DSC) thermograms were obtained using a DSC Mettler Toledo 822 under N_2 atmosphere, and performing scans in three steps: from −75 °C to 200 °C at 20 °C min^{-1}, then to −75 °C at −5°C min^{-1} and finally to 180 °C at 20 °C min^{-1}. The glass transition temperature was determined as the midpoint of the heat capacity change. ΔH is calculated based on the weight of the polymer in the composite.

Dynamic mechanical analysis (DMA) was performed using a Gabo Eplexor 100 N, performing temperature scans from −100 °C to 100 °C

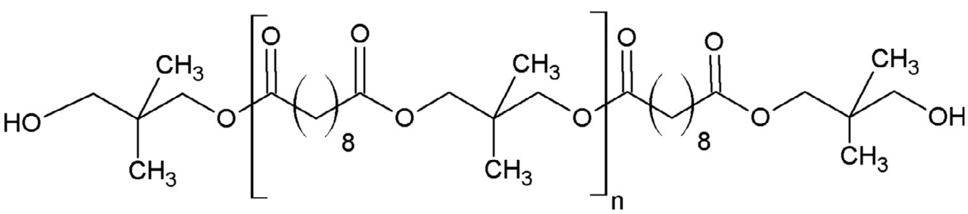

Fig. 1. Chemical structure of the macrodiol used.