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Influence of cellulose nanofibrils on soft and hard segments of polyurethane/cellulose nanocomposites and effect of humidity on their mechanical properties



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ABSTRACT

Cellulose nanofibrils (CNFs) were prepared by sulfuric acid hydrolysis from cotton microfibers, and used to prepare polyurethane (PU) nanocomposites by mixing CNFs and PU water suspensions. CNFs as nanofillers improved the tensile strength of PU significantly up to 10 wt% content. With an increase in the CNF content, the glass transition temperature of PU and the temperature onset of the soft segment increased compared with those of neat PU. However, the crystalline phase present in soft domains and its melting temperature decreased. The influences of humidity on the mechanical properties of PU/CNF nanocomposites were also investigated. The tensile strength at different elongations of PU/CNF nanocomposites decreased substantially after being exposed to 60% relative humidity for 24 h; for 10 wt% loading, the tensile strength at 500% dropped from 10.64 to 2.34 MPa. This behavior was attributed to the formation of hydrogen bonds of PU and CNFs with water.

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1. Introduction

The introduction of nanoparticles into polymer matrices has attracted considerable attention because it can significantly improve the thermal and mechanical properties of the polymeric matrix even at very low contents [1–5]. Among the nanofillers used as reinforcements, cellulose nanofibrils have been highlighted owing to their biodegradability, low density, high aspect ratio, easy availability and low cost [1,2,6–38]. Cellulose is a polysaccharide consisting of linear chains composed of β -D-glucopyranose repeating units linked by

(1–4)-glycosidic bonds. Cellulose microfibers consist of ordered regions, commonly referred to as nanofibrils, nano-whiskers or whiskers, linked by amorphous cellulose chains. These nanofibrils can be extracted by controlled acid hydrolysis, which more readily hydrolyses the amorphous regions, leaving crystals with diameters and lengths that directly depend on the hydrolysis conditions and source [21]. When strong sulfuric acid is used, negatively charged sulfate groups are introduced and, consequently, stable aqueous suspensions are obtained. Cellulose nanofibers have abundant hydroxyl groups (OH) on the surface that can form hydrogen bonds with the polymer matrix and between nanofibers, developing a strong reinforcement. Cellulose nanofibers have been incorporated as reinforcing fillers in a wide range of polymer matrixes such as poly(β -hydroxyoctanoate) [7], poly(styrene-

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co-butyl acrylate) [8], poly(vinyl chloride) [9], polypropylene [10], waterborne epoxy [11], poly(vinyl alcohol) [12], poly(-acrylic acid) [13], polyethylene oxide [14], poly(lactic acid) [15], polystyrene [16], polymethylmethacrylate [17] and rubbers [18–19], including polyurethane.

Segmented thermoplastic polyurethanes are very versatile polymers that are typically constructed by alternating soft (SS) and hard (HS) segments that are separated into microphases owing to thermodynamic incompatibility between the segments. Generally, HS can be organized in semi-crystalline or amorphous domains, whereas SS form an amorphous or elastic region in which the HS are dispersed [32]. The ratio between SS and HS present in the polyurethane chain can be easily manipulated to give a wide range of polyurethanes with various properties and applications [31–34].

This study reports the preparation and characterization of nanocomposites of water-based polyurethane with cellulose nanofibrils. The nanofibrils were extracted by acid hydrolysis from cotton microfibrils and introduced into a waterborne polyurethane elastomer to prepare PU/CNF nanocomposites with different loading levels of CNF. The present study focuses on the favored interaction of cellulose nanofibrils with SS and HS of polyurethane, as well as the behavior of the reinforcing properties of nanofibers against humidity. This study shows that although the nanofibrils strongly mechanically reinforce the polyurethane, they largely lose their reinforcing properties when subjected to humidity, even at fractions above the percolation threshold.

2. Materials and methods

2.1. Materials

Cotton fibers with a particle size of 50 μm (SigmaCell Cellulose type 50) were purchased from Sigma-Aldrich. Nanofibrils were dialyzed in Spectra/Por Dialysis Membranes with the following characteristics: membrane tube type RC, MWCO: 12 to 14,000, 75-mm flat width, vol/length = 18 mL/cm, length = 15 mm. Concentrated sulfuric acid (98%) was purchased from Sigma-Aldrich and used as received. Waterborne polyurethane with trade name Witicobond W-320 was kindly supplied by Chemtura Corporation.

2.2. Extraction of cellulose nanofibrils

A colloidal suspension of CNFs in water was extracted by acid hydrolysis according to the procedure described by Dong et al. [37]. Cotton microcrystalline cellulose microfibrils (MCC) were immersed in a sulfuric acid solution (64% w/v) at 45°C using a MCC:acid solution ratio of 1:7.1 g/mL. The mixture was stirred vigorously for 90 min and then diluted 5-fold with cold deionized water (5°C) to quench the reaction. The resulting dispersion was centrifuged at 10,000 rpm for 10 min at 10°C to separate nanofibrils from the acidic solution. The sediment containing the nanocrystals was dispersed in water and centrifuged again. This operation was performed three times, and the final sediment was dispersed in 150 mL deionized water, followed by dialysis against water until its pH became ~5.

2.3. Nanocomposite preparation

PU/CNF nanocomposites were obtained by mixing the CNF dispersion with PU water suspension in the desired amount. The mixtures were magnetically stirred for 4 h and then cast onto glass slides (75 \times 25 \times 1.2 mm), which were allowed to dry in a conventional oven at 60°C for 3 h. A series of nanocomposite films containing 5, 10, 15, and 20 wt% of CNFs with a thickness of 0.3–0.4 mm were prepared and designated as PU_5% CNF, PU_10% CNF, PU_15% CNF, and PU_20% CNF, respectively.

2.4. Characterization

The CNF morphology was characterized by a Supra 35 Zeiss field-emission scanning electron microscope (FESEM). 5 μL of CNF aqueous suspension (4.3 g/100 mL) was diluted in 1 mL of isopropyl alcohol, and 3 μL of the resultant suspension was cast onto silicon substrates, dried in dynamic vacuum for 1 h at room temperature and coated with carbon by sputtering prior to FESEM analysis. The morphology of the cryogenically fractured surfaces of PU/CNF nanocomposites was analyzed using an EVO LS15 Zeiss scanning electron microscope (SEM). The test samples were attached to an aluminum stub and sputtered with gold prior to analysis. XRD patterns of the films were obtained by using a Shimadzu XDR-6000 diffractometer with Cu $K\alpha$ radiation (wavelength: \sim 1.5418 Å). Scans were carried out from $2\theta = 5^\circ$ to 60° at a scan rate of $1^\circ/\text{min}$. DSC analysis of the film scans was performed using a TA Instruments MDSC 2920 calorimeter. Two temperature and heating rate ranges were used to evaluate the thermal behavior of the composites and pure polymer. In the first run, the samples were scanned from -20 to 200°C at $10^\circ\text{C}/\text{min}$ to verify the melting temperature (T_m) and enthalpy (ΔH). In the second run, to verify the glass transition temperature (T_g), the samples were scanned from -100 to 150°C at $20^\circ\text{C}/\text{min}$. In both cases, the measurement was conducted in nitrogen atmosphere with a flux flow rate of 65 mL/min. TGA of the films was conducted in the temperature range 25 – 680°C at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere with a flow rate of 100 mL/min using a TA Instruments model Q600. The mechanical behavior of the nanocomposites was studied at room temperature using an Instron model 3639 universal testing machine in accordance with ISO 37:2011 using a load cell of 100 N and crosshead speed of 13 mm/min. The samples were cut according to ISO 1286:2006, and the results were averaged from five test specimen data. To analyze the influence of absorbed water on the mechanical properties of the nanocomposites, the samples were kept in dynamic vacuum for 24 h, weighed and then left for 24 h in a chamber with humidity controlled at 30% or 60% relative humidity. Then, the samples were weighed again and immediately subjected to a tensile test. The absorbed water (WA) was calculated using the following equation:

$$\text{WA} (\%) = \left(\frac{W_t - W_0}{W_0} \right) \times 100 \quad (1)$$

where W_0 is the sample mass after vacuum and W_t , that after humidity exposure.

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