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An alternative approach for the incorporation of cellulose nanocrystals in flexible polyurethane foams based on renewably sourced polyols

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ABSTRACT

This work analyzes not only the effect of cellulose nanocrystals on final properties of castor oil and corn based flexible polyurethane foam nanocomposites but also a deep analysis about the changes on micro/nanostructure and morphology is carried out. Cellulose nanocrystals were isolated from microcrystalline cellulose by acid hydrolysis and incorporated in aqueous suspension to renewably sourced polyols for foam synthesis. The effect of cellulose nanocrystals percentage on cell morphology, nano/microstructure and properties of the foam nanocomposites was analyzed by scanning electron microscopy, atomic force microscopy, Fourier transform infrared spectroscopy, compressive mechanical properties, hysteresis and resilience tests and dynamic mechanical analysis. To verify the presence of cellulose nanocrystals in the foam cell walls, infrared near-field microscopy and nanospectroscopy were employed. Results suggested that interactions between cellulose nanocrystals and polyurethane hard segments occurred and foam cell walls were reinforced. The overall reinforcing effect showed to be dependent on the cellular structure of the foam, which was in turn influenced by the presence of cellulose nanocrystals.

1. Introduction

The increase of global environmental awareness and the depletion of fossil resources have promoted the use of renewably sourced polymers and raw materials for polymer synthesis (Williams and Hillmyer, 2016). For example, vegetable oils such as castor oil or soybean oil have shown great potential to be used as polyols in polyurethane synthesis (Petrovic, 2008; Zhang et al., 2015) and this way reduce the amount of petrochemical precursors in the final material. In the nanocomposites field, cellulose, the most common biopolymer on earth, (Klemm et al., 2005) has become an interesting source of nanoreinforcements in the form of cellulose nanofibers (CNF) or cellulose nanocrystals (CNCs) which are characterized by their low density, high modulus and tensile strength, biodegradability, renewability and availability (Mariano et al., 2014). Apart from their renewable nature, nanoreinforcements are known to enhance mechanical properties of the matrix at low levels of filler content, (Mittal, 2010) resulting in lower environmental impact. Although wood is the main cellulosic source, annual plants as well as agroforestry or industrial residues have great potential as sources of cellulosic nanomaterials (Jonoobi et al., 2015). CNCs have been widely used in polyurethane nanocomposites due to the aforementioned superior mechanical properties and environmental advantages. The common methods for the synthesis of polyurethane nanocomposites include solvent casting (De Oliveira Patricio et al., 2013; Rueda et al., 2013b), melt blending (Ramôa et al., 2013; Valentini et al., 2015) and in-situ polymerization (Rueda et al., 2013a; Saralegi et al., 2014). In the case of polyurethane foams, which present a crosslinked structure, the solvent casting and melt blending procedures are not suitable and hence the in-situ polymerization technique is used adding the nanoreinforcement to the polyurethane precursors at the begin-

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ning of the polymerization (Alavi Nikje et al., 2014; Bernal et al., 2011). One of the main challenges in the incorporation of the nanoreinforcements is to obtain a good dispersion of nanoentities so that a close interaction is created between the matrix and the nanoreinforcement and mechanical properties are enhanced (Hussain et al., 2006). In works concerning flexible polyurethane foam/CNC nanocomposites, the nanoentities were incorporated to the polyol component in solid state. Mosiewicki et al. (2015) incorporated commercial micro/nano cellulose directly to the polyol and mixed by mechanical stirring. Cordero et al. (2015) dehydrated a CNC suspension obtained by acid hydrolysis and mixed with the polyol by sonication. It is accepted that the sulfate groups at the CNC surface introduced by sulfuric acid hydrolysis cause electrostatic repulsion between particles resulting in stable aqueous suspensions (Beck et al., 2012). However, when CNCs are dried, agglomerates could be formed depending on the drying technique and their redispersibility even in water is compromised due to strong hydrogen bonding generated in the cellulose backbone (Dong and Gray, 1997; Khoshkava and Kamal, 2014). One alternative of redispersion consists on the use of polar organic solvents and its subsequent removal, but the redispersion seems not to be complete even this way (Viet et al., 2007).

In this work the effect of CNCs not only on the final properties of the foam nanocomposites but also on the morphology and micro/nanostructure of the nanocomposites was analyzed since the effect on final properties is a consequence of the changes in morphology and micro/nanostructure caused by the incorporation of nanoentities. CNCs were isolated by acid hydrolysis from microcrystalline cellulose (MCC) and their sulfur content and morphology were characterized by elemental analysis, conductometric titration and atomic force microscopy (AFM). The aqueous CNCs dispersion obtained after CNCs isolation procedure was directly incorporated in a renewably sourced polyol mixture. This way, CNCs drying and redispersion steps or the use of pollutant organic solvents were avoided. After removing the water from the polyol-CNCs mixture, foams were synthesized in a one shot method in open molds. To analyze the effect of different CNC percentages on the morphology, microstructure and final properties of the foam nanocomposites scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, compressive mechanical tests, resilience test, dynamical mechanic analysis (DMA), AFM and infrared near-field microscopy (IR s-SNOM) and nanospectroscopy (nano-FTIR) were used.

Because s-SNOM and nanoFTIR are relatively new techniques, in the following their basic working principles are briefly described.

IR s-SNOM and nano-FTIR spectroscopy (Huth et al., 2012, 2011; Keilmann and Hillenbrand, 2009) allow for infrared imaging and spectroscopy with nanoscale spatial resolution. s-SNOM is based on an AFM employing a metalized tip, which is illuminated with monochromatic infrared laser radiation. The tip acts as an antenna and concentrates the infrared field at the tip apex. Due to near-field interaction of this strongly localized field with the sample surface, the tip-scattered field contains information about the infrared sample properties. Interferometric detection of the tip-scattered light – simultaneously to the AFM topography – yields nanoscale resolved infrared amplitude and phase infrared images, providing maps of the chemical properties of the sample surface. Nano-FTIR is based on s-SNOM. The tip is illuminated with a broadband infrared radiation. At a fixed sample position, the tip-scattered light is recorded with an asymmetric Fourier transform spectrometer, yielding amplitude- and phase-resolved infrared spectra.

The spatial resolution of s-SNOM and nano-FTIR only depends on the tip diameter, which is typically in the order of a few ten nanometers for commonly used commercial tips. It is thus improved by more than a factor of 100 compared to standard FTIR spectroscopy.

Table 1
Designation and formulation of polyurethane neat foams and foam nanocomposites.

Sample	P1 (pphp)	P2 (pphp)	TDI (g)	CNC (wt%)
PF100	100	–	49.3	–
PF100-0.5	100	–	49.3	0.5
PF100-0.75	100	–	49.3	0.75
PF100-1.5	100	–	49.3	1.5
PF80	80	20	50.6	–
PF80-0.75	80	20	50.6	0.75
PF80-1.5	80	20	50.6	1.5

In this work s-SNOM phase images and nano-FTIR phase spectra are shown, revealing information about the infrared absorption and thus chemical composition of the sample (Govyadinov et al., 2014, 2013; Huth et al., 2012; Mastel et al., 2015).

2. Experimental

2.1. Raw materials

Castor oil based Lupranol Balance 50® (P1) (BASF, 49.7 mg KOH/g, 1129 g/eq) and corn sugar based polytrimethylene ether glycol (P2) (79.4 mg KOH/g, 706 g/eq) were used as polyol components. Amine catalyst Tegoamin® B75, tin catalyst Kosmos® 29 and surfactant Tegostab® B-4900 were supplied by Evonik. Toluene diisocyanate (TDI), generously supplied by Bayer was used with a constant isocyanate index of 120. Distilled water was used as blowing agent. Microcrystalline cellulose (MCC) and sulfuric acid (H_2SO_4) (96%) were supplied from Aldrich.

2.2. Isolation of cellulose nanocrystals

MCC was subjected to sulfuric acid hydrolysis to remove the amorphous regions (Rueda et al., 2013a; Saralegi et al., 2014). MCC was mixed with H_2SO_4 (64%) at 45 °C for 30 min. Deionized water was added to stop the hydrolysis process. The diluted suspensions were centrifuged at 4000 rpm for 20 min and the CNC rich sediment was collected. Finally, pH was stabilized at 5–6 value by a dialysis process against deionized water. An aqueous suspension of 0.5 wt% CNC was obtained.

2.3. Synthesis of foam nanocomposites

Foams were synthesized in a one shot method as previously reported (Ugarte et al., 2014). Prior to the foaming process, the CNC suspension was incorporated to the polyol component as follows. The CNC suspension was first sonicated in an ultrasonic bath for 30 min and thereafter incorporated to the polyol. Water was removed by vacuum while the mixture was continuously stirred. Water elimination was checked by weight difference and thermogravimetric analysis (TGA). The resulting polyol-CNC dry mixture was first sonicated for 30 min and then mixed at high speed for 10 min with a high shear stirrer. For foaming, water, catalysts and surfactant were incorporated and mixed with the polyol-CNC dry mixture for 90 s at 2000 rpm. Water, catalysts and surfactant quantities were maintained constant at 3.5, 0.7 and 1.1 parts per hundred polyol (pphp), respectively. Finally, TDI was incorporated and mixed for 10 s. The resulting foam nanocomposites were left to rise freely and cured for 24 h before demolding. The designation and formulation of foam nanocomposites are summarized in Table 1. For comparative purposes, polyurethane foam matrixes were also synthesized.