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## Material properties

# Effect of the nano-cellulose content on the properties of reinforced polyurethanes. A study using mechanical tests and positron annihilation spectroscopy

Mirta I. Aranguren<sup>a,\*</sup>, Norma E. Marcovich<sup>a</sup>, Walter Salgueiro<sup>b,c</sup>, Alberto Somoza<sup>b,c</sup><sup>a</sup> INTEMA and Chemical Eng. Department (CONICET and Universidad Nacional de Mar del Plata), Juan B. Justo 4302, 7600 Mar del Plata, Argentina<sup>b</sup> IFIMAT-UNICEN, Pinto 399, 7000 Tandil, Argentina<sup>c</sup> CICPBA, Calle 526 entre 10 y 11, 1900 La Plata, Argentina

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## ABSTRACT

A study of the effect of the addition of cellulose nanocrystals on the properties of a polyurethane matrix was carried out. To this aim, mechanical and dynamic mechanical tests together with positron annihilation lifetime spectroscopy (PALS) were used. The rheological response of the unreacted liquid suspensions indicates strong interactions between nanocrystals and polymer, showing a viscoelastic solid-like behavior at low cellulose concentration. The study of the cured elastomers revealed a strong dependence of their properties on cellulose content, with a peculiar behavior appearing below the percolation threshold (~0.8 wt.%). PALS studies revealed that, for the neat polyurethane and nanocomposites, the free nanohole volume value remains unchanged. Conversely, the fractional free volume is strongly dependent on nanocellulose concentration. This parameter shows very good correlation with mechanical ones (Young's and storage moduli) related to the elastomer rigidity. Results are analyzed in terms of the interaction between the polyurethane chains that become attached to the cellulose nanocrystals through strong physical H-bonding and covalent linkages.

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## 1. Introduction

Polyurethane elastomers are a class of polymers that offer great versatility and an ample range of properties, depending on the precursors selected in the formulation [1]. On the other hand, the use of fillers or reinforcements in polymer materials is a common practice that allows further tailoring of mechanical behavior. The composite properties are determined by those of the main components as well as the interactions developed at the interface that can generate an interphase region with different properties than those of the bulk polymer matrix [2–4]. The influence of this region on the material properties becomes

particularly important when dealing with nanocomposites, where the fillers/reinforcements have nanometric dimensions and the surface/volume ratio is high. For this reason, at a given concentration a nanosized reinforcement offers a much larger interfacial surface for contact and interaction with the polymer matrix than macro or micro particles/fibers, and a large fraction of the polymer becomes part of this interphase region influenced by the presence of the reinforcement. Consequently, variation of the glass transition temperature  $T_g$  of the polymer could be expected, depending on the nature of the two main components and the interfacial interactions.

During the last few decades, considerable academic and industrial research efforts have been devoted to developing cellulose nanocrystals and nanofibers [5,6]. There are strong reasons for this: cellulose is the most abundant polymeric material in nature, is available everywhere, can

\* Corresponding author. Tel.: +54 2234816600; fax: +54 2234810046.  
E-mail address: [marangur@fi.mdp.edu.ar](mailto:marangur@fi.mdp.edu.ar) (M.I. Aranguren).

be obtained from different resources, is biodegradable and can be modified to generate whiskers of high aspect ratio, high modulus and low density. To obtain these nanofibers, cellulose must be separated from other components of the plant and exposed to different (sometimes, cooperative) treatments that decompose its hierarchical structure down to nanometric “rods”. One frequently reported method is the acidic hydrolysis of cellulose, which produces cellulose nanocrystals with diameter of 5–20 nm [7,8] and length ranging from 100 nm to a few microns, depending on the cellulose source and the process variables. Although the high OH concentration on the surface of the crystals suggests high attraction between them, the use of sulfuric acid during hydrolysis is known to leave sulfate groups on the crystal surface, which produce repulsion and help to produce stable suspensions in aqueous media and highly polar solvents [9].

The surface hydroxyl groups on the cellulose can be reacted to produce modified cellulose crystals [8]. Co-reaction with a polymerizable mixture has also been reported, so that the nanofibers became covalently attached to the polymer [9]. This specific type of interaction at the interface nanofiber-polymer produces radical changes in the glass transition of the material, which can be investigated by different techniques, including dynamic mechanical analysis and positron annihilation spectroscopy, through measurement of the material free volume.

The free volume theory allows describing qualitatively and quantitatively the polymeric behavior under different processes such as physical aging, sorption and transport, plasticization and miscibility of blends [10,11]. Despite the different experimental techniques that have been used to get information on the free volume, positron annihilation lifetime spectroscopy (PALS) [12] has become the most popular one due to the capability of ortho-Positronium (o-Ps), the positron-electron bound system in triplet spin state, to localize into the free nanohole volumes. Indeed, o-Ps is repelled from the ionic cores of atoms and molecules due to exchange interactions and it tends to be pushed into low electron density sites of the host matrix, such as cavities forming the free volume. A correlation can be expected between its lifetime  $\tau_{o-Ps}$  and the size of the hole (in spherical approximation of nanoholes of radii  $R$ ), as expressed using simple quantum mechanical models [13–15]

$$\tau_{o-Ps} = 0.5 \left[ \frac{\Delta R}{R + \Delta R} + \frac{1}{2\pi} \sin \left( 2\pi \frac{R}{R + \Delta R} \right) \right]^{-1} \quad (1)$$

The empirical parameter  $\Delta R$  (0.166 nm [16]) takes into account the annihilation of o-Ps with the electrons belonging to the walls of the hole (‘pickoff’ process).

Changes of the average volume of holes ( $v_h$ ) induced by variations of external parameters, such as temperature or mechanical stresses, can be directly monitored by studying the o-Ps lifetime in a positron annihilation spectrum. Specifically,  $v_h = 4/3\pi R^3$  in which  $R$  values are obtained from Eq. (1). Thus, PALS enables the study of free volumes in polymers on a time scale for molecular motions slower than one nanosecond and a nanohole dimension larger than about 2 Å.

Taking advantage of the high specificity of PALS, some of the authors of the present work have studied the effect of

inclusion of different types of microparticles in an epoxy resin matrix. More specifically, using PALS and dynamic mechanical spectroscopy, differential scanning calorimetry and/or electron microscopy, the influence of the thermal residual stresses and the role of the filler content on the free nanohole volumes in those composites was analyzed [17–20]. Furthermore, as a consequence of the change of different external parameters various aspects related to free volume and the physical phenomena involving free nanohole volume in natural and styrene butadiene rubbers, NR and SBR respectively, and NR-SBR blends were studied [21–23]. In these works, PALS was complemented by other experimental techniques usually utilized in the characterization and study of elastomers.

Based on the above, the present work was addressed to analyze the effect of the addition of cellulose nanocrystals into a reactive polymer precursor mixture to produce polyurethane nanocomposites. The changes of the  $T_g$  of the cross-linked elastomers with varying nanocellulose concentrations, below and above the percolation threshold, were investigated and related to the PALS results.

## 2. Experimental

### 2.1. Materials

Cellulose crystals were obtained from microcrystalline cellulose powder, MCC (Avicel PH-101 MCC, FMC BioPolymer, Philadelphia, U.S.A.).

The polyurethane matrix was obtained by reaction of a mixture of a polyether diol (Alkuran, Alkanos, Argentina) and a multifunctional polyol (Daltolac R251, Huntsman Polyurethanes, USA). The hydroxyl values of both reactants were determined according to a standard method [24], being equal to 178 mg<sub>KOH</sub>/g and 250 mg<sub>KOH</sub>/g, respectively. The polyols were cross-linked with multifunctional prepolymer based on 4,4'-diphenylmethane diisocyanate (pMDI) (Rubinate 5005, Huntsman Polyurethanes, USA) with a measured equivalent weight of 131 g/eq (catalog nominal value: 133 g/eq), which corresponds to a value of 32.08 NCO % content.

### 2.2. Cellulose nanocrystals

The MCC was subjected to acid hydrolysis by immersion in concentrated sulfuric acid solution (64 wt.% sulfuric acid in water) at 45 °C under strong continuous stirring, using a ratio of MCC to acid solution of 1 to 8.75 g/ml [7,9].

The hydrolyzed cellulose was repeatedly washed, and the solids were separated from the solution by centrifugation (12,000 rpm, 10 min) after each washing. Finally, the aqueous suspension was freeze-dried to avoid re-agglomeration of the cellulose crystals. Dimethylformamide (DMF) was the polar organic solvent used to re-disperse the nanocrystals by repeated ultrasonic-stirring.

### 2.3. Crosslinked polyurethane films

A mixture of the polyether diol and the polyol in a weight ratio of 60 to 40 was prepared. The polyol mixture and the DMF suspension of the cellulose nanocrystals were

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