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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

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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

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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 τ_{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 ΔR (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_{KOH}/g and 250 mg_{KOH}/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

mixed, then mechanically stirred and subsequently sonicated. Afterwards, the solvent was completely evaporated at 70 °C, until achieving constant weight. Finally, an excess of pMDI was added, to reach a NCO/OH ratio equal to 1.3, and the system was carefully hand-mixed. Then, the cellulose-polymer mixture was cast into a mold and cured for 1 h at 70 °C under light pressure (10 MPa). The films (thickness ~ 200 μm), were removed from the mold and postcured at 70 °C for 12 h in a convection oven.

2.4. Microscopy

The cellulose nanocrystals were characterized by atomic force microscopy (AFM Nanoscope III Digital Instruments) in tapping mode, and the results processed in amplitude mode.

2.5. Rheologic and dynamic-mechanical tests

The unreacted liquid mixtures were characterized using a rheometer (Rheometrics ARES) with a 200 g cm transducer, working in cone and plate geometry (25 mm fixtures) under nitrogen flux. The strain amplitudes used for the frequency sweeps were in the range of 0.01% to 5%, depending on the sample, in order to ensure that the measurements were performed in the linear viscoelastic range.

Dynamic-mechanical tests were performed on the cured elastomeric samples in a Perkin Elmer dynamic mechanical analyzer, DMA 7e, using tensile fixtures under nitrogen atmosphere. The specimens were cut to 20 mm × 4 mm × film thickness, measured with a precision of 0.01 mm. The dynamic and static stresses were kept at 200 and 240 kPa, respectively. The frequency of the forced oscillations was fixed at 1 Hz and the heating rate was of 10 °C/min. At least two replicate determinations were made for each sample to ensure the reproducibility of results. The main relaxation temperature associated with T_g of the polyurethane (PU) matrix was determined from the temperature position of the maximum in $\tan \delta$.

2.6. Positron annihilation lifetime spectroscopy measurements

For PALS measurements the fast-fast timing coincidence system described elsewhere [25] was used. A time resolution (FWHM) of 255 ps was obtained using the RESOLUTION.code [26]. Positron lifetime spectra were recorded at room temperature with a total number of $2\text{--}3 \times 10^6$ coincidence counts using a 0.2 MBq sealed source of $^{22}\text{NaCl}$ deposited on a thin Kapton foil (1.08 mg/cm²). The source was sandwiched by two “identical pieces” of sample material. Since the thickness of a single film was not enough to absorb, and then annihilate, all positrons injected there (a detailed discussion about the implantation, slowing-down and thermalization of positrons in condensed matter is given in Ref. [27]), the two “pieces” of the reinforced polyurethane were prepared following the same procedure used by G. Consolati et al. for similar samples [28]; i.e., by stacking several layers of the film in order to stop all the injected positrons (~ 170 mg/cm²) and, then, by compressing the pieces to eliminate the air gaps between two subsequent layers.

According to the common interpretation for PALS measurements in polymers, spectra were deconvoluted into three discrete lifetime components using the LT program [29], with adequate source correction. Positron lifetime spectra were also analyzed using the POSITRONFIT program [26]; results showing very good agreement with those obtained from the decomposition of the PALS spectra using LT.

In agreement with the common interpretation for PALS measurements in polymers, we ascribed the longest component to ortho-Ps decay in the nanoholes forming the free volume. The intermediate component (0.35–0.50 ns) is attributed to positrons annihilated in low electron density regions of the structure. The shortest component (0.1–0.2 ns) is due to positrons annihilated in the bulk and to para-Ps annihilations.

3. Results and discussion

3.1. Atomic force microscopy of the cellulose nanocrystals

An aliquot of the cellulose DMF suspension was further diluted; then AFM was performed on the evaporated preparation (Fig. 1). The individual cellulose crystals visible in the image have diameters in the range of 20 nm and lengths up to about 300 nm, which are in agreement with values usually reported for wood derived cellulose nanofibers [30]. Some aggregates could be seen at lower magnification (not shown), which may have formed during the DMF evaporation or been present in the original suspension.

3.2. Unreacted liquid suspensions

3.2.1. Rheological characterization

The viscoelastic behavior of these materials was discussed in a previous work [9], so just a brief presentation

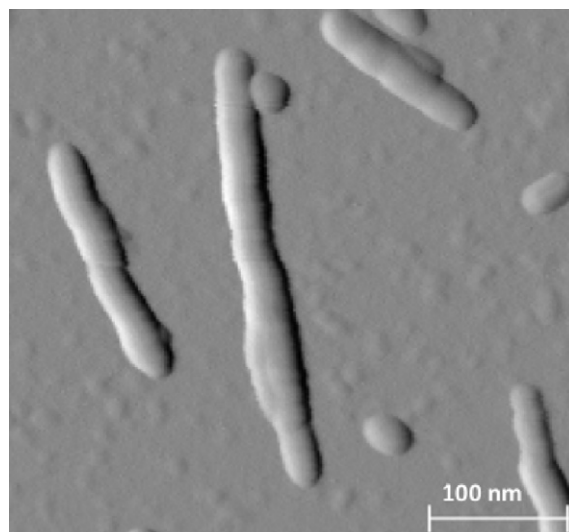


Fig. 1. Atomic force microscopy (amplitude mode) of hydrolyzed cellulose crystals.

will be included here for completeness and to support further discussions of PALS results.

The linear viscoelastic response to sinusoidal oscillations of the polyols-pMDI mixture with and without cellulose nanocrystals is shown in Fig. 2. The unreacted liquid mixture with no added nanocrystals behaves as a Newtonian liquid, with zero storage modulus. Thus, the plot shows only G'' ; its constant slope (in the whole range of frequencies) has an exponent equal to 1.0, as expected from a viscous liquid with no elasticity. The corresponding constant viscosity ($\eta' = G''/\text{freq}$), indicates that no reaction takes place during testing at room temperature [9].

By adding cellulose nanocrystals the material behavior changes to that of a viscoelastic liquid. There is a clearly non-zero elastic component and the value of the viscous component (loss modulus G'') is higher than that of the elastic component (storage modulus G') in the whole range of frequencies observed for the 0.5 wt.% suspension. At 1 wt.%, there is a crossover of the elastic and viscous components. At low frequencies, G' is higher than G'' and there is a low frequency-plateau (equilibrium modulus), which indicates that this is a structured material with a solid-like behavior. At all frequencies, the 5 wt.% suspension shows higher elastic component than the viscous one ($G' > G''$). Previous analysis of these data suggested that percolation occurs at around 1 wt.% [9] in this system. Above that concentration, well-dispersed nanocrystals can touch each other and form large percolating structures of H-bonded “rods”, which can be easily destroyed by shearing the sample outside the analyzed linear viscoelastic range.

3.3. Cured materials

3.3.1. Dynamic mechanical characterization

The cured films containing different concentrations of cellulose nanocrystals were examined using dynamic mechanical testing in tensile geometry.

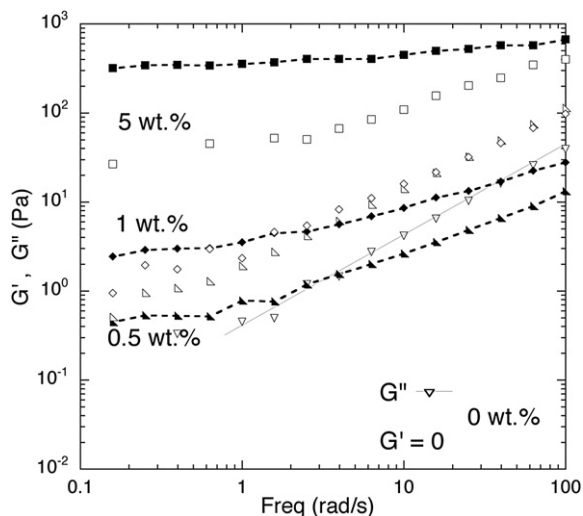


Fig. 2. Storage modulus (G' , filled symbols) and loss modulus (G'' , open symbols) of the liquid unreacted mixture of polyol-MDI with different concentrations of cellulose nanofiber as a function of frequency.

While preparing the films, the polymer cross-linking is carried out in the presence of the cellulose; consequently, a chemical reaction between the OH groups of the cellulose and the isocyanate groups of the polymer also occurs. This reaction is not unexpected since isocyanate or polyurethane formulations have been used for long time as adhesives, varnishes and coatings in different wood applications. Thus, a strong interaction matrix-reinforcement is developed during the preparation of the nano-composite films. The characteristics of this interaction have been discussed in detail in a previous publication [9].

The temperature position of the main relaxation process of the polymeric matrix is denoted T_α and is related to the glass transition temperature T_g of the matrix and to the drop in storage modulus G' (in a temperature scan), because of a mechanical coupling effect [31]. As can be seen from the plot $\tan \delta$ versus temperature (Fig. 3), the transition of the PU sample is wide, which can be traced to the use of a mixture of two polyols with different molecular weights and functionalities for the production of the films. The addition of cellulose up to about 1 wt.% does not produce important shifts in the position of T_α , although the onset of the relaxation is not the same for all the samples. Additionally, the sample with 5 wt.% of nanocrystals clearly leads to a large T_α increase, from ~ 35 – 50 °C for the neat PU film to 90 – 135 °C for the filled sample, a substantial shift that has not been reported in other cellulose-filled systems. Moreover, in studies in which nanofillers/nanoreinforcements with high surface/volume ratio have been utilized, the shifts in T_g or in T_α were much smaller or non-existent [32,33]. In the present case, the reaction at the interface is largely responsible for the change in T_g .

The cellulose crystals act as multifunctional crosslinking agents, reducing the mobility of the polymer, in addition to the strong physical interactions that can also be developed between the NCO or the C–O–C groups in the polyether-polyurethane polymer with the OH groups on the nanocellulose.

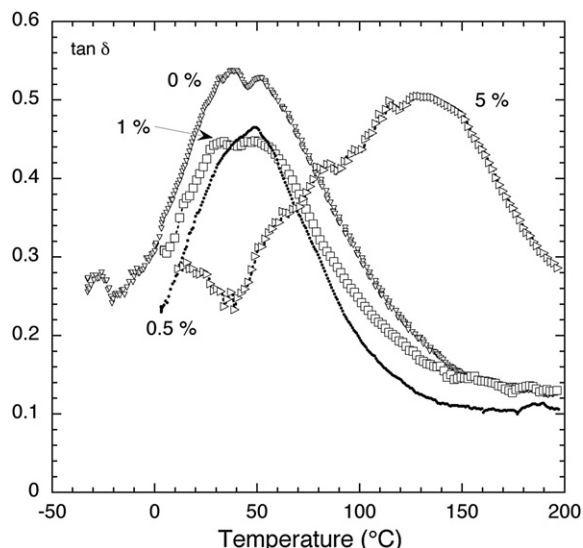


Fig. 3. Damping function ($\tan \delta$) of the cured elastomers filled with different concentrations of cellulose nanocrystals.

There is a large effect of the nanocrystals addition on the height of the $\tan \delta$ peak, related to the fraction of polymer chains taking part in the relaxation. The addition of just 0.5 wt.% of nanocellulose is enough to reduce the height of the peak by as much as 15% with respect to the maximum observed for the neat PU. This reduction is maintained for the 1 wt.% sample, indicating that fewer polymer chains are relaxing. Additional considerations must be made to account for the behavior of the 5 wt.% sample, such as lower flexibility of the chains due to the interactions with a large amount of nanocrystals.

Further discussion of these results follows after the presentation of PALS data.

3.3.2. Positron lifetime results

In all cases, from the decomposition of PALS spectra the longest-lived lifetime associated with the pick-off annihilation of o-Ps ($\tau_{o-Ps} = 1670 \pm 40$ ps) and the second lifetime component resulting from positron annihilations without forming Ps ($\tau_2 = 310 \pm 15$ ps) were constant, within the experimental scatter. As mentioned in the Introduction Section, the average volume of the nanohole v_h can be estimated from $v_h = 4/3\pi R^3$ in which R can be determined from Eq. (1). The free nanohole volume in all the samples studied was $68.5 \pm 1.5 \text{ \AA}^3$. Similar values of v_h were reported when studying different glassy polymers such as polystyrene and polycarbonate (Ref. [34] and references therein), polymethyl methacrylate [35] and epoxy composites [19]. On the other hand, v_h values reported for styrene butadiene rubber, natural rubber and NR/SBR blends [23] and for polyethylene are higher (between 2 and 5 times) than those reported in this work.

Regarding the value of τ_2 , this lifetime may be arising from free positrons confined in some kind of very small cavities, comparable to a cluster of few vacancies, with sizes of about 2–2.5 Å. A similar interpretation was given for the second lifetime component measured in amorphous silicon and vitreous silica samples [36,37]. These cavities do not necessarily have spherical geometry and, for this reason, typical cavity dimensions were given. However, assuming a spherical approximation, an effective radius of the cavities is estimated varying between 1 Å and 1.25 Å, with the volume associated with the cavities ranging from $\sim 4 \text{ \AA}^3$ and $\sim 8 \text{ \AA}^3$. These volume values are approximately one order of magnitude smaller than that of the free nanohole volume given above.

In Fig. 4, the evolution of the intensities associated with these two lifetimes is shown. As mentioned above, spectra were decomposed into three discrete lifetime components. Thus, τ_2 is the intermediate lifetime and its associated intensity is I_2 and the intensity associated with the longest-lived lifetime $\tau_3 \equiv \tau_{o-Ps}$ is I_{o-Ps} . In our case, I_2 is proportional to the concentration of cavities characterized by the positron lifetime τ_2 .

As can be seen in the figure, the data points labeled **a** (neat PU), **b** (1 wt.% cellulose) and **c** (5 wt.% cellulose) show a systematic decrease of the intensities with increasing cellulose concentration; the highest value corresponds to the neat PU. Conversely, the sample with 0.5 wt.% reinforcement shows the lowest I_{o-Ps} and I_2 values. Similarly, an anomaly in the behavior of the sample

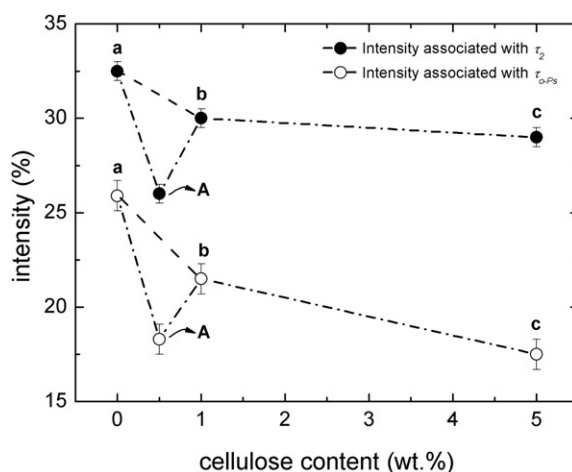


Fig. 4. Intensity I_i associated with the second (τ_2) and the long-lived (τ_{o-Ps}) lifetime components as a function of the cellulose content (see text). Dashed lines are visual guides.

containing 0.5 wt.% of cellulose was also found when measuring the modulus of the sample (see discussion in following sections) and in the plot of $\tan \delta$ against temperature (see Fig. 3), where that sample shows a narrower relaxation process. These results could be attributed to the fact that the 0.5 wt.% sample is below the percolation threshold of the nanocrystals in this system, as already pointed out in the *Rheological characterization* Section (a detailed discussion is given in Ref. [9]).

On the other hand, there is an interesting issue that deserves to be pointed out: as can be seen in the plot I_2 vs. I_{o-Ps} (Fig. 5), there is good linear correlation between both intensities. This behavior would indicate that both intensities obey the same structural process (see discussion below).

Various approaches were used to get the fractional free volume from positron data [38–41]. In the present work, we have used the simplest one in which the number of the nanoholes forming the free volume in polymers is

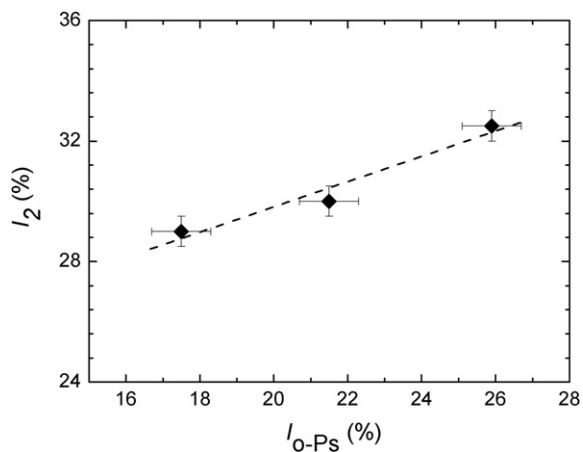


Fig. 5. Intensity associated with the second lifetime component I_2 as a function of the intensity associated with the o-Ps lifetime component I_{o-Ps} . Dashed line represents a linear fit to the data points ($R = 0.98$).

represented by the intensity associated with the o-Ps lifetime [42,43]. Under this frame, the fractional free volume f_v can be assumed to be proportional to the number of nanoholes and to the average volume of each nanohole. Then, the following semi-empirical equation can be used:

$$f_v = Av_h I_{o-Ps} \quad (2)$$

where A is an empirical scaling constant and I_{o-Ps} is given in percentage. A value for the factor $A = 0.0018$ was empirically determined by Y.C. Jean [38].

As a consequence of the constancy of τ_{o-Ps} for all the samples studied, the free nanohole volume of the neat PU and the reinforced samples remains constant. Then, f_v is directly proportional to the ortho-positronium intensity. Therefore, the qualitative behavior of f_v as a function of the cellulose content is the same than that presented in Fig. 4 for I_{o-Ps} .

From measurements on polyisoprene, polyvinylacetate, polystyrene and polycarbonates, Srithawatpong et al. [44] reported the existence of a simple relationship between the average nanohole volume determined from τ_{o-Ps} and the glass transition temperature determined by DSC; i.e. $v_h = \alpha T_g$, where $\alpha = 3.27 \times 10^{-4} \text{ nm}^3/\text{K}$. These authors concluded that in these polymers T_g was not an iso-free-volume state and, therefore, the fractional free volume f_v at T_g increases with an increasing T_g . Conversely, for a good number of polymers the variation in the o-Ps intensity with temperature is more complex than that of the o-Ps lifetime; i.e., at T_g the I_{o-Ps} values are different.

From our PALS results, the outcome is that, for all samples, the bulk polymer and the cellulose-filled ones, the volume of the nanoholes remains constant. This result indicates that the addition of cellulose nanocrystals to the neat PU does not change v_h and that the free nanohole volumes in the composites are only formed in the polyurethane matrix.

3.4. General discussion

To further discuss the reported results, Fig. 6 shows the fractional free volume f_v , as well as the Young's and the rubbery storage moduli (on a reverse scale), as a function of the cellulose nanocrystals content. As known, the rubbery modulus correlates to the cross-link density of a sample, the chain rigidity and the filler concentration; the Young's modulus E was reported in a previous publication [9]. As can be seen, f_v follows (qualitatively) similar behavior to the inverse of the modulus. For the neat polyurethane, the maximum value of f_v and the minimum value of E are reached. Then, with the addition of cellulose, the fractional free volume gradually decreases, while the rigidity (storage and Young's moduli) progressively increases. Again, the anomalous behavior of the 0.5 wt.% sample appears clearly in the figure, but the same observation as for the rest of the samples can be made: a low f_v corresponds to high rigidity.

For further discussion on the tendency of the parameters plotted in Fig. 6 we only consider the data points for: i) the neat PU sample; and ii) the samples containing 1 wt.% and 5 wt.% of cellulose nanocrystals. As mentioned before, the 0.5 wt.% sample (labeled **A** in the figure) has apparently

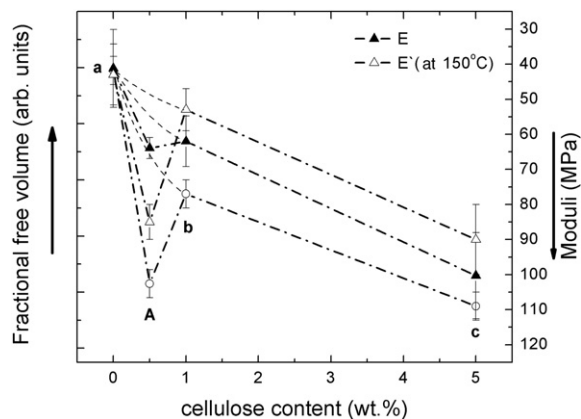


Fig. 6. (○) Fractional free nanohole volume and (▲) Young (E) and (△) rubbery storage (E') moduli (to plot both moduli a reversed scale was used) as a function of the cellulose content. Lines only represent visual guides.

anomalous behavior, which was explained as the result of being below the percolation threshold, while the other samples were above this critical value.

PALS results indicate that the average size of the free nanohole volumes for the reinforced samples remains unchanged with respect to that of the neat PU; this means that free volumes and small cavities, also revealed with this nuclear technique, are formed inside the bulk polymer. Therefore, the addition of nanocrystals to the polyurethane does not influence the size of the free nanohole volumes. However, it produces a systematic diminution of the fractional free volume (i.e. the density of these nanoholes in the sample), which correlates well with the increase of the Young's and storage moduli for the 1 wt.% and 5 wt.% samples, as presented in Fig. 6.

A previous publication reported an interfacial covalent reaction between the cellulose and the polyurethane [9]. Therefore, it is reasonably to assume that, because of this reaction and the physical interactions at the interface, the chains attached to the cellulose surface are not able to relax as easily as in the bulk polymer.

Analyzing the results for the sample with 1 wt.% of nanocrystals (a relatively low cellulose concentration), a reduction of the number of relaxing chains can be inferred from the lower $\tan \delta$ peak and the decrease in f_v with respect to those of the neat polyurethane. Furthermore, the cellulose content of this sample is above the percolation threshold (~ 0.8 wt.% [9]), when particle-particle contact is established throughout the sample. Considering the difficulty in the dispersion of nanoparticles/nanofibers, agglomeration must be almost inevitable above percolation. However, the presence of cellulose is still enough to inhibit the movement of attached chains and to cause a decrease in the relative fractional free volumes.

At 5 wt.%, the concentration of cellulose is so large that, even considering agglomeration, there is a large percentage of chains in the interfacial area, while the remaining bulk polymer chains, although maintaining a similar structure to that of the neat polymer, have restricted mobility due to the presence of the rigid nanocrystals. PALS indicates that the

free nanohole volumes remain unchanged, but their relative fraction is still lower than that of the sample containing 1 wt.% of nanocellulose. On the other hand, because of the overall reduced flexibility of the chains, the DMA study does not show a relaxation at the same temperature than the other samples. A higher temperature is needed for the chain to regain flexibility for relaxing, and this is shown in the measurements as a high T_{α} relaxation in the $\tan \delta$ curve.

It is also interesting to jointly analyze the values of the moduli (as a measure of the material rigidity) and positron lifetime data of the samples labeled **a**, **b** and **c**. The rigidity could be precisely related to the lower amount of nanoholes inside the matrix as the amount of cellulose increases.

It is suggested that the polyurethane chains attached to the cellulose nanocrystals through strong physical H-bonding and covalent linkages become less flexible, and thus the bonds formed with the active OH groups on the cellulose surface lead to the observed reduction of nanoholes in the polymer.

On the other hand, PALS results allow concluding that, despite the high sensitivity of this technique to detect open volumes defects with atomic or nanometer sizes, interface effects could not be detected.

4. Conclusions

The incorporation of cellulose nanocrystals in a polyurethane elastomer greatly affects the properties of these materials, as assessed through the analysis of the rheology of the uncured filled mixture of the prepolymers and the mechanical and dynamic mechanical response of the filled cured elastomers, as well as the results related to free nanohole volumes directly obtained using positron annihilation lifetime spectroscopy in these cross-linked samples.

PALS results indicate that, for all samples, free nanohole volumes remain constant ($v_h = 68.5 \pm 1.5 \text{ \AA}^3$); i.e. the addition of nanoreinforcements does not change the values of free volumes, indicating that nanoholes are formed in the neat PU. Additionally, small cavities of essentially constant size (between ~ 4 and $\sim 8 \text{ \AA}^3$) were also detected. Positron data indicate that the fractional free volume is strongly dependent on the nanocellulose concentration; specifically, the amount of nanoholes systematically decreases with respect to that of the neat PU as the concentration of cellulose nanocrystals increases. On the other hand, values of the Young's and storage moduli systematically increase with the nanofiller content. As a result, good qualitative correlation between the decreasing fractional free volume and the increasing rigidity (storage and Young moduli) of the samples as a function of the cellulose concentration was observed.

A particular analysis was made on the results obtained for the 0.5 wt.% sample, which showed an apparently anomalous behavior: low value of the fractional free volume and high values of the mechanical parameters. These results were related to the below-percolation concentration of cellulose in the sample.

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