



## Dynamic and structural correlations in nanocomposites of silica with modified surface and carboxylated nitrile rubber



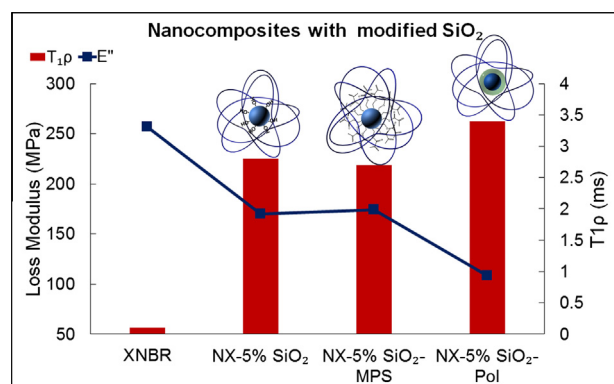
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### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 28 September 2015

Revised 12 December 2015

Accepted 17 December 2015

Available online 17 December 2015

#### Keywords:

Polymer–matrix composites  
Thermomechanical properties  
Solid state NMR

### ABSTRACT

Distinct affinities between the organic and inorganic phases were observed in nanocomposites prepared through a colloidal route with carboxylated nitrile rubber and modified silica nanoparticles, which resulted in variable mechanical properties and improved thermal stability. Nanoparticles with modified surface affected the macromolecular arrangements of the elastomeric matrix, changing the final mechanical behavior of the nanocomposite, which could be predicted by the spin–lattice relaxation time measured by solid-state NMR. It was also possible to identify how each different nanoparticle affected the molecular dynamic of nanocomposite, correlating the dynamic–mechanical analysis with the NMR data of the saturated carbons of the elastomer.

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<http://dx.doi.org/10.1016/j.jcis.2015.12.028>

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### 1. Introduction

Among the organic/inorganic hybrid materials, polymeric nanocomposites with silica have attracted a great attention due their improved and versatile properties. The pioneer and largest application of SiO<sub>2</sub> nanoparticles was as fillers in tires aiming to increase their wet grip, rolling and mechanical resistance [1].

During the last few years, silica showed to be very versatile, becoming essential for many applications, such as coatings [2], flame retardants [3], optical devices [4], electronic matrices [5], sensors [6] and drug delivery [7]. Silane agents, on the other hand, have been widely used to modify the surface of nanoparticles and have gained prominence promoting interfacial adhesive strength between particles and macromolecules due to changes in the chemical reactivity and hydrophobicity of nanoparticles [8–10]. Specifically, the carboxylated nitrile rubber (XNBR) latex exhibits several advantages since the presence of colloids in the aqueous suspension of nanoparticles facilitates their incorporation by the polymeric matrix. Additionally, XNBR contains carboxyl groups that interact strongly with fillers resulting in better mechanical properties [11–14].

To investigate the role played by SiO<sub>2</sub> nanoparticles in the XNBR matrix, we synthesized modified nanoparticles with silane coupling agents followed by the formation of a hydrophobic shell with controlled thickness. Solid-state NMR was used to investigate how these modified nanoparticles affected the interface between organic and inorganic phases [15,16]. Using the technique of cross polarization (CP) in NMR, it was possible not only to overcome the difficulty to acquire spectra of dilute nuclei, such as <sup>13</sup>C and <sup>29</sup>Si, but also to get important information about the dynamics of the nanocomposite structure. The dynamics can be evaluated by CP approach through the measurement of the spin–lattice relaxation time in the rotating frame ( $T_{1\rho}$ ) and the contact time between both nuclei involved in the process ( $T_{IS}$ ) [17]. The magnitude of these parameters is dependent on the magnetization transfer of an abundant spin nucleus (I), such as hydrogen, to another less abundant spin (S), as <sup>13</sup>C. When this technique is used in combination with Magic Angle Spinning (MAS) and high-power decoupling, it provides high-resolution spectra for solids, being possible to study a very specific site of the polymer structure and its environment. Complementally, thermogravimetric (TGA) and dynamic mechanical analyzes (DMA) were performed to evaluate the aspects of the hybrid materials structures that interfere in the final materials performance and applications [18].

## 2. Experimental section

### 2.1. Synthesis of the nanoparticles and nanocomposites

The nanoparticles and nanocomposites were synthesized as previously described [19,20]. Colloidal silica nanoparticles (SiO<sub>2</sub>) were prepared at room temperature through the hydrolysis and controlled condensation of 26.4 mmol of tetraethyl orthosilicate (TEOS, 98%, Aldrich, USA) in a mixture of 25 mL of distilled water, 70 mL of absolute ethanol and 0.51 mol of NH<sub>3</sub> from an aqueous solution (30%, analytical grade, Synth, Brazil) under stirring for 24 h. The modified nanoparticles were synthesized by adding the 3-(trimethoxysilyl)propyl methacrylate (MPS) coupling agent (98%, Aldrich, USA) into the suspension of unmodified silica (SiO<sub>2</sub>-MPS). The core/shell systems (SiO<sub>2</sub>-Pol) were prepared by applying the precipitation co-polymerization of styrene (St, >99%, Aldrich, EUA) and divinylbenzene (DVB, 80%, Aldrich, EUA) in the presence of azobisisobutyronitrile (AIBN, DuPont, Brazil), polyvinylpyrrolidone (Aldrich, EUA) and anhydrous ethanol under stirring for 5 h at 60 °C.

Nanocomposites (thereafter referred to as NX) films were prepared by the colloidal route, which involves the mixture of commercial polymer latex of XNBR (43.7% of solids containing 25% of acrylonitrile, Nitriflex, Brazil) with the colloidal silica nanoparticles. Aqueous dispersions of pure SiO<sub>2</sub>, SiO<sub>2</sub>-MPS and SiO<sub>2</sub>-Pol nanoparticles were prepared in the presence of 0.1 mol L<sup>-1</sup> of sodium dodecyl sulfate (SDS) to improve the nanoparticle

dispersion in the XNBR latex, which was homogenized for 1 h and dried in Petri dishes at 50 °C.

### 2.2. Methods of characterization

The morphology and size of the SiO<sub>2</sub>-MPS nanoparticles were characterized by scanning electron microscopy (SEM) in a JEOL JSM-5600LV operating at 20 kV, and the SiO<sub>2</sub>-Pol images were collected using a TECNAI F20 field emission HRTEM operating at 200 kV. Solid-state NMR spectra were recorded in a Bruker Avance III spectrometer operating at a magnetic field of 9.4 T Oxford, which has a related frequency of 400 MHz for the hydrogen-1 nucleus. Analyzes were performed using techniques of cross polarization with rotation under the magic angle and total sideband suppression (CPTOSS) at room temperature (23 °C). Values of  $T_{1\rho}$  were estimated by running the CP with variable contact time pulse sequence by using the recycle delay of 7 s, variable contact time (10 μs to 50 ms) and the spinning speed on magic angle of 5 kHz. The data processing to determine the  $T_{1\rho}$  was done by using the treatment proposed by Kolodziejewski and Klinowski [17] for heterogeneous samples, adjusting the data points according to Eq. (1), where  $I_0$  is the absolute amplitude,  $T_{IS}$  is a CP time constant related to the dipolar interaction between the I (<sup>1</sup>H) and S (<sup>13</sup>C) spins of specific functional groups, and  $1/T_{IS}$  is the CP rate constant that depends on the number and mobility of the protons. Dynamic mechanical properties of the nanocomposites were measured in a DMA 2980 equipment, TA instruments Q800. An oscillatory shear deformation at the constant frequency of 1 Hz with the conditions of 25 μm of amplitude, heating rate of 3 °C/min in the range of –60 °C to 30 °C was applied to analyze the samples with length of 50 mm and width of 10 mm. The thermal degradation of nanocomposites was evaluated by the thermoanalyzer (TGA), TG 209 F1 from Netzsch. The samples were examined under an O<sub>2</sub> flow rate of 10 mL min<sup>-1</sup>, at a heating rate of 10 °C min<sup>-1</sup> and in the range of 25–900 °C.

$$I(\tau) = I_0(1 - T_{IS}/T_{1\rho}(I))^{-1}[\exp(-\tau/T_{1\rho}(I)) - \exp(\tau/T_{IS})] \quad (1)$$

## 3. Results and discussion

Unmodified SiO<sub>2</sub> nanoparticles were synthesized hydrolyzing TEOS with a basic catalyst in a defined amount of H<sub>2</sub>O/ethanol [19,20], while the MPS coupling agent was grafted on the nanoparticles to react with the silanol groups of SiO<sub>2</sub>, resulting in spherical nanoparticles (SiO<sub>2</sub>-MPS) of 250 nm with sharp size distribution (Fig. 1a). The MPS added polymerizable vinyl groups on the surface of nanoparticles, which acted as seeds for the co-polymerization between the DVB crosslinker and styrene in the presence of a stabilizer. This optimized procedure allowed the synthesis of monodisperse hybrid nanoparticles of SiO<sub>2</sub>-Pol with polymeric shells of 50 nm (Fig. 1b) [21].

The absence of any <sup>13</sup>C solid state NMR signal from the methoxy carbon around 50 ppm in the SiO<sub>2</sub>-MPS spectrum of Fig. 1 indicates that the MPS was bonded to the surface of nanoparticles [2,22]. The signals at 8, 17 and 22 ppm are related to methylene carbons from MPS, as well as the signals at 124.2, 136.8 and 168.3 ppm are attributed to the methacrylate group (see Table 1). The spectrum of the SiO<sub>2</sub>-Pol shows signals of the methyl (17 ppm) and methylene (30 ppm) carbons of commercial DVB and a peak of the polymer shell backbone at 41 ppm. Moreover, the polymerization of styrene with DVB in the polymeric shell around the nanoparticles resulted in linear and branched macromolecules, remaining some residual vinyl groups of the DVB, as indicated by the peaks at 138 and 113 ppm [23,24]. The signals of less shielded carbons at

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