Evaluation of modified silica nanoparticles in carboxylated nitrile rubber nanocomposites

Renata L. Sala [a], Tatiane M. Arantes [a], Elson Longo [a], Edson R. Leite [a],
Caio M. Paranhos [b], Emerson R. Camargo [a],*

[a] LIEC – Interdisciplinary Laboratory of Electrochemistry and Ceramics, Department of Chemistry, UFSCar-Federal University of São Carlos, Rod. Washington Luis km 235, CP 676, 13565-9905 São Carlos, SP, Brazil
[b] Department of Chemistry, UFSCar – Federal University of São Carlos, Rod. Washington Luis km 235, CP 676, São Carlos, SP 13565-9905, Brazil

HIGHLIGHTS

- We modified silica nanoparticles with a silane agent and with a polymeric shell.
- SiO_2 nanoparticles induced arrangements in XNBR nanocomposites.
- The SDS induced the polymeric macromolecules organization in the nanocomposites.
- The silica nanoparticles dispersed in the polymer forming a mass fractal system.
- The silica nanoparticles and XNBR chains formed three-dimensional network.

GRAPHICAL ABSTRACT
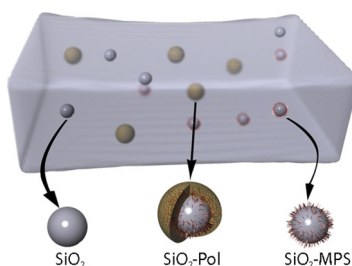
SiO_2 SiO_2-Pol SiO_2-MPS

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ABSTRACT

Surface-modified silica nanoparticles have a plenty of applications, such as coatings, dyes or biomarkers, catalysts and encapsulated products. When modified with 3-(trimethoxysilyl)propyl methacrylate (SiO_2-MPS) or covered with a polymeric shell obtained from a reaction between divinylbenzene and styrene (SiO_2-Pol), these SiO_2 nanoparticles induced distinct arrangements in polymer nanocomposites (PNC) prepared with commercial carboxylated nitrile rubber (XNBR). The hydrophilicity character of the modified SiO_2 nanoparticles was also altered, improving their interaction with the XNBR macromolecules. Consequently, choosing the PNC properties for different conditions and applications became possible due to the adjustment of the nanoparticle surface characteristics. Although the final characteristics of the nanocomposites films varied according to the nanoparticle used, the PNC prepared with SiO_2-Pol presented better homogeneity than those with SiO_2-MPS.

1. Introduction

Numerous efforts have been focused on the search for new materials involving lower cost, greater durability and, especially, lower environmental impact. In this sense, polymer nanocomposites (PNC) become the focus of many research groups owing to their superior mechanical and thermal properties. The field of PNC is of growing interest due to the remarkable properties that result from the effect of nanofillers in the polymer on macro and micro scales

[1–8]. It has been shown that a system of well-dispersed nanoparticles usually improve composite properties, since agglomerates of particles can generate voids that act as preferential sites for failure, reducing its general performance [9].

Silica nanoparticles with different morphologies, such as spherical [2,10], core/shell [11,12], network [13] and mesoporous [14], have been studied for many applications such as adhesives, industrial coatings, electronic matrices and encapsulated pesticides and drugs [11,15,16]. As fillers in PNC, spherical SiO_2 can improve the interaction between the polymer and the inorganic phase [15]. However, their agglomeration, due to the dominant Van der Waals interactions, has been an obstacle to its wide application [9].

Silica nanoparticles with the surface modified were found to steadily disperse nano-SiO_2 in many organic media [12,17,18]. Furthermore, the silica-core/organic-shell also improves the interaction at the organic/inorganic interface and has been applied in different technological fields [17]. The synthesis of silica/polymer hybrid particles usually is reached via physical or physicochemical interaction between silica particles and the polymer or directly through the polymerization on the surface of nanoparticles. In the meantime, the morphology of hybrid particles that results from the shell polymerization are hard to control and significantly low encapsulation efficiency has been observed [11,12]. Von Werne et al. [19] obtained well-defined polymer-nanoparticle hybrids modifying the surface of silica nanoparticles with initiators for atom transfer radical polymerization (ATRP). They used these initiator-modified nanoparticles as macro initiators, but only small nanoparticles exhibited good control of the polymer molecular weight. On the other hand, McDonald et al. [20] reported a different approach to prepare hollow polymeric microspheres by a process that initially involved the polymerization of chains with low molecular weight, such as styrene, containing a small amount of carboxylic acid [12,20–22].

The purpose of this study was to improve the dispersion of three different kind of silica nanoparticles (unmodified SiO_2, silica with its surface modified with silane groups and silica covered with a polymeric shell obtained from a polymerization reaction) in a matrix of carboxylated nitrile rubber (XNBR), as well as to understand the organic/inorganic interface between the polymer and the nanoparticles with modified hydrophobic and hydrophilic characteristics. Furthermore, we investigated how nanocomposites structures changed when different interfacial groups were used between the nanoparticles and the polymeric matrix.

2. Experimental

2.1. Synthesis

Silica nanoparticles were synthesized through the hydrolysis and controlled condensation of tetraethyl orthosilicate (TEOS 98%, Aldrich, USA). A solution of 25 mL of distilled water, 35 mL of absolute ethanol, and 0.51 mol of NH_3 from an aqueous solution (30%, analytical grade, Synth, Brazil) was prepared and immediately added to a second solution prepared with 35 mL of ethanol and 26.4 mmol of TEOS under vigorous stirring, resulting in a colloidal dispersion of SiO_2 nanoparticles. After 4 h, the surface of the SiO_2 particles was modified by adding 200 μL of 3-(trimethoxysilyl)propyl methacrylate (MPS) coupling agent (98%, Aldrich, USA) directly into the silica dispersion, which was maintained under continuous stirring for 24 h at room temperature. The functionalized SiO_2-MPS nanoparticles were purified by repeated centrifugation and washed with ethanol to separate the nanoparticles by their size, as well as to remove any excess of NH_3 and MPS.

To cover the silica surface with the polymer shell, 50 mL of SiO_2-MPS nanoparticles were dispersed in ethanol (4 mg mL^{-1}) and mixed with 2 mL of a solution prepared with 120 mg of polyvinylpyrrolidone (Aldrich, EUA) and 2 mL of anhydrous ethanol, followed by the addition of 3 mL from a solution prepared with 1980 μL of styrene (>99%, Aldrich, EUA), 2463 μL of divinylbenzene (DVB) (80%, Aldrich, EUA), 360 mg of azobisisobutyronitrile (AIBN) (DuPont, Brazil) and 3 mL of anhydrous ethanol. The reaction was heated to 60 °C using a silicone oil bath under constant stirring for 5 h. After polymerization, the coated nanospheres (SiO_2-Pol) were separated from the suspension by centrifugation and washed with ethanol. The monomers were firstly washed with an aqueous solution of NaOH (5%, Synth, Brazil), distilled water and dried with $MgSO_4$ (PA, Vetec, Brazil) to remove the inhibitor prior to use.

The PNC films were prepared by a colloidal synthesis route mixing commercial polymer lattices of XNBR (43.7% of solids and 25% of acrylonitrile, Nitriflex, Brazil) with the colloidal dispersions of silica nanoparticles. Aqueous colloidal dispersions of pure SiO_2, SiO_2-MPS and SiO_2-Pol nanoparticles (5% in mass) were prepared in the presence of 0.1 mol L^{-1} of sodium dodecyl sulfate (SDS) to improve the nanoparticle dispersion. After that, they were added to the XNBR lattice, gently homogenized for 1 h, dried in Petri dishes in an air circulation oven at 50 °C and then deployed as self-sustained PNC films. One film of XNBR with only SDS was prepared to understand the surfactant influence in the inorganic/organic interface.

2.2. Characterization

The morphology, size, and size distribution of SiO_2, SiO_2-MPS and SiO_2-Pol nanoparticles were analyzed by FTIR, HRTEM and SEM. The infrared spectra were collected at room temperature in the range of 400–4000 cm^{-1} with 32 scans and 4 cm^{-1} of resolution in a FTIR infrared spectrometer (Bruker Equinox 55) with a diffuse reflectance accessory. Diluted nanoparticle dispersions of SiO_2-Pol were dripped on copper grids covered with a thin amorphous carbon film to collect images in a TECNAI F20 field emission HRTEM operating at 200 kV. Scanning electron microscopy images of the SiO_2-MPS nanoparticles were recorded with a JEOL JSM-5600LV operated at 20 kV. Transmittance infrared spectra of nanocomposites films and of pure MPS were collected at room temperature in the range from 650 to 4000 cm^{-1} with 32 scans and 4 cm^{-1} of resolution in a FTIR infrared spectrometer (Bruker Equinox 55) with an attenuated total reflectance accessory (ZnSe monocrystal). DSC curves were taken with a Netzsch Phoenix 204 calorimeter in the range from −100 to +100 °C at a heating rate of 20 °C min^{-1}. X-ray diffraction (XRD) patterns were recorded at room temperature using a LabX XRD-6000 Shimadzu diffractometer operating with Cu K$_\alpha$ radiation, in the 2θ range of 3–30°, in step scan mode with a width of 0.02° and a step time of 2 s. Experiments of SAXS, which provided valuable information about their structural features at a nanometer-level, providing statistical and overall information averaged in a volume in the order of 1 mm^3, were performed in a Bruker AXS 2D Nanostar (EUA) with CuK$_\alpha$ radiation, operating at 40 kV/35 mA in a range of 0.01–0.23 Å^{-1}. The sample-to-detector distance was fixed at 107 cm, and the time-resolved spectra of nanocomposites were collected every 1200 s, with a minimum resolution in $q = 0.00628$ Å^{-1}.

3. Results and discussion

Monodispersed SiO_2 nanoparticles were prepared by the method originally proposed by Stöber et al. [23] and recently optimized by Arantes et al. [24]. To improve and understand the inorganic/organic interface between the nanoparticle and the