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Material Properties

On the key role of SiO_2@POSS hybrid filler in tailoring networking and interfaces in rubber nanocomposites

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ABSTRACT

The present study provides a comprehensive investigation at the micro and nanoscale of the interface between hybrid SiO_2@POSS nanofiller, where silica nanoparticles (NPs) and POSS nanocages are intimately interconnected, and Styrene Butadiene Rubber (SBR). SEM and AFM inspection and, more in depth, solid state ^1H NMR revealed a remarkable fraction of rigid rubber close to the SiO_2@POSS surfaces, which increases with the curing temperature. Instead, a reduced amount of immobilized rubber was detected for SBR/SiO_2 + POSS nanocomposites, obtained by simply mixing SBR, SiO_2 and POSS.

The results allowed us to propose a model for the network formation in C-SBR/SiO_2@POSS.

This is based on the progressive activation by dicumylperoxide (DCP) of the methacryl functionalities of POSS nanounits which, being closely connected to SiO_2 NPs in SiO_2@POSS, promote crosslinking in proximity of the filler surfaces, and lead to the generation of a tight network strongly bonded to the rubber chains.

1. Introduction

Rubber nanocomposites are important technological materials that received increasing interest in recent decades owing to their tunable mechanical properties and broad applications [1–3]. In particular, rubber nanocomposites are the dominating materials in tires due to their excellent mechanical features, dimensional stability, flame retardancy, improved scratch and mar resistance, superior thermal and processing properties, reduced warpage of components and enhanced impact resistance [1–8]. The extent of these properties depends on the viscoelastic properties of the rubber composites, which are related to filler type and amount, filler particle size and shape (aspect ratio), particle aggregation in the matrix (filler-filler interaction) and interfacial adhesion between filler and polymer chains (filler-rubber interaction). These characteristics determine the formation of a percolative filler network in the rubber matrix, which is essential for providing effective reinforcement [9–11].

In this respect, we have recently reported [12] on the promising properties of polyhedral oligomeric silsesquioxanes (POSS) [13–15] used as molecular nanofillers together with SiO_2 nanoparticles (NPs). They were able to enhance simultaneously the filler networking and the filler-rubber interaction in rubber composites for tires.

The hybrid NPs were then used to prepare, by ex-situ blending, styrene butadiene rubber (SBR) nanocomposites which, after DCP curing, display outstanding mechanical strength and reduced hysteresis, becoming very suitable for application in tires. Moreover, comparing the performance of SBR/SiO_2@POSS to that of composites prepared by mixtures of SiO_2 and OctaMethacrylPOSS in the polymer matrix (SBR/SiO_2 + POSS), showed that the functionalization of silica surface with POSS determines a more positive effect on the modulus and reduces the hysteresis. These properties have been associated so far with the peculiar hybrid structure of SiO_2@POSS filler, in which silica NPs aggregates are partially interconnected and surrounded by a thin shell of POSS nanounits which, thanks to their high number of reactive functionalities, seem to promote the formation of “sticky regions” among the silica aggregates and, consequently, a tight filler network wherein rubber is immobilized [12].

Nevertheless, further morphological and physico-chemical evidence should be provided in order to explain, at the molecular level, the filler-rubber interactions occurring in the presence of SiO_2@POSS hybrid NPs

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and their role in modulating network formation and composite mechanical properties.

With this aim, the present study provides a comprehensive investigation at the micro and nanoscale of the interface between SiO_2@POSS and polymer chains, checking the filler adhesion in cured SBR/SiO_2@POSS composites by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) [16–19], and monitoring the changes in the rubber segmental dynamics by both low-field and high-field solid state Nuclear Magnetic Resonance spectroscopy (^{1}H-NMR) [11,20–27], as well as in comparison to the SBR/SiO_2 + POSS system. In this regard, solid state NMR spectroscopy provides clear information about the changes in polymer chain structure and dynamics, and its application in the study of rubber nanocomposites can afford in depth information on the nature and strength of the interfacial interaction between the elastomer blocks and filler nanounits in the final materials.

As both the filler distribution and networking are clearly influenced by the curing with DCP, which activates the POSS functionalities, the interfacial properties of the composites have also been evaluated after curing at increasing temperatures, i.e. starting when the peroxide is in principle less reactive and the curing process is at the early stages, toward the optimum conditions at which it is surely active and the curing is nearly complete [28].

Finally, the macroscopic properties of the composites have been assessed by determining their curing profiles and their mechanical behavior by Dynamic Mechanical Thermal Analysis (DMTA) and tensile stress–strain tests, which allowed us to evaluate their performance under a range of deformations [29,30].

2. Experimental

2.1. Materials

SiO_2@POSS synthesis: Silica Rhodia Zeosil MP1165; OctaMethacrylPOSS (POSS) from Hybrid Plastics; 3-(Trimethoxysilyl) propylmethacrylate 98% (TMMS), DCP from Alpha Aesar.

Compounding: SBR SLR 4630 from Styron Europe GmbH had 25 wt. % of styrene, 63 wt. % of vinyl groups and 37.5 phr of aliphatic extension oil; antioxidant *N*-(1,3-dimethylbutyl)-*N′*-phenyl-*p*-phenylendiamine (6PPD) Santoflex-6PPD was purchased from Flexsys; zinc oxide from Zincol Ossidi; stearic acid Stearina TP8 from Undesa.

2.2. Preparation and morphological characterization of SiO_2@POSS hybrid filler

SiO_2@POSS hybrid filler was prepared by the double-step functionalization procedure reported in the previous work [12]. Firstly, SiO_2 (30 phr, i.e. parts of hundreds of rubber) were functionalized with 20 wt.% of TMMS with respect to silica in a methanol/water solution (4/1 v/v); secondly SiO_2-TMMS NPs were suspended in toluene (150 mL) and then POSS nanounits (10 wt.%) were introduced into the solution in the presence of a suitable amount of DCP (2 wt.%, molar ratio POSS/DCP = 20/1). The peroxide promotes the activation of the methacrylate groups of both silane and POSS units, favoring the anchoring of the nanocages onto the silica surface and their partial condensation to form, possibly, nanometric networks [29].

Morphological characterization of SiO_2@POSS and SiO_2 TMMS powder was performed on a Jeol 3010 HRTEM operating at 300 kV with a high-resolution pole piece (0.17 nm point to point resolution) and equipped with a Gatan slow-scan 794 CCD camera.

Nitrogen physisorption measurements on SiO_2-TMMS and SiO_2@POSS hybrid filler were carried out by a Quantachrome Autosorb-1 apparatus [32,33]. The specific surface area (SSA_{BET}, BET method) was measured after evacuation at 150 °C for 16 h.

2.3. Preparation of uncured and cured nanocomposites

In order to prepare uncured rubber nanocomposites, SiO_2@POSS hybrid filler was mixed by *ex-situ blending* with SBR in a Brabender Plasti-corder lab station (mixing chamber of 50 mL, filling factor of 0.7) [12].

SBR polymer (32.0 ± 0.5phr) was first introduced into the mixer and plasticized for 30 s at 60 RPM at 145 °C, then 30phr of SiO_2-TMMS or 33phr SiO_2@POSS hybrid filler was introduced, mixed for about 4 min and then discharged.

Vulcanization chemicals were then added to the composites in two further steps. Firstly, stearic acid (2 phr), zinc oxide (3.5 phr) and 6-PPD (2 phr) were mixed with the obtained composites at 60 rpm for 5 min at 145 °C. Successively, DCP (1.5 phr) was introduced at a working temperature of 90 °C and by mixing at 60 rpm for 3 min.

Since both the filler networking and distribution are related to the DCP during the curing process, composites have been cured at different temperature. In detail, cured composites were obtained by vulcanization using a hydraulic press at 155 °C, 170 °C and 185 °C for 10 min running time under a pressure of 200 bar. Hereafter, cured nanocomposites are labelled as C-SBR/SiO_2@POSS_X where X refers to the different curing temperature.

In order to find a relation between the peculiar structure of the SiO_2@POSS hybrid filler and the features of the resulting composites, the properties of SBR/SiO_2@POSS, both uncured and cured, were compared to those of nanocomposites prepared by simply mixing SiO_2, TMMS and OctaMethacrylPOSS in the same polymer matrix, under the same experimental conditions (i.e. curing chemicals, temperature, rotor speed) described above.

Uncured and cured SBR/SiO_2 + POSS composites were prepared by blending SBR with a filler mixture composed by SiO_2 Rhodia (30 phr), a TMMS coupling agent (2 phr) and 10phr of OctaMethacrylPOSS. These composites, before and after curing, are labelled as SBR/SiO_2 + POSS and C-SBR/SiO_2 + POSS_X, respectively, where X refers to the different curing temperature. A reference material without any filler was prepared by the same experimental conditions (i.e. curing chemicals, temperature, rotor speed) described above. These composites, before or after curing, are labelled as SBR pure or C-SBR pure, respectively.

2.4. Morphological characterization of silica nanofillers and silica–SBR nanocomposites

Morphological study of both uncured and cured SBR/SiO_2@POSS and SBR/SiO_2 + POSS composites was carried out by Transmission Electron Microscopy (TEM) with a Zeiss EM 900 microscope working at an acceleration voltage of 80 kV. Ultrathin sections (about 50 nm thick) of composites were obtained with a Leica EM FCS cryo-ultramicrotome equipped with a diamond knife (samples kept at −130 °C).

Light microscopy (LM) was employed to visualize the overall morphology of the cured composites. Two LM microscopes were used: stereomicroscope SMZ-2T (Nikon) for the lowest magnifications and the highest depth-of-focus, and wide-field light microscope Nikon Eclipse 80i (Nikon) for higher magnifications up to 40 ×. The surface of the samples was observed directly in reflected light. Under these conditions, the micrographs showed brighter agglomerates of the fillers on darker background.

The investigation of the interfacial adhesion between hybrid nanofiller and rubber of the nanocomposites cured at different temperature was carried out by SEM using Microscope Quanta 200 FEG (FEI). The samples were fractured in liquid nitrogen, sputtered with a thin platinum layer (4 nm of Pt, deposited using vacuum sputter coater SCD 050 (Leica)) and observed at an accelerating voltage 30 kV using both secondary electrons detector (SE) and backscattered electrons detector (BSE). SE and BSE micrographs showed mostly topographic and material contrast, respectively.

The investigation of the topography and the heterogeneity relief was