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Research paper

Size-controlled self-assembly of anisotropic sepiolite fibers in rubber nanocomposites

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ABSTRACT

The development of advanced polymer nanocomposites requires a strong filler-polymer interfacial interaction and an optimal filler nanodispersion. The incorporation of the clays into a polymer matrix frequently does not improve the composite mechanical properties, owing to both poor dispersion and macroscopic particle dimensions. In this work, pristine and organically-modified sepiolites (Sep) were structurally modified by an acid treatment, which provides nano-sized sepiolite (NS-Sep) fibers with reduced particle size and increased silanol groups on the surface layer. NS-Sep fibers were used to prepare styrene-butadiene rubber nanocomposites with enhanced mechanical properties.

Dynamic-mechanical analysis of clay polymer nanocomposites demonstrated that the NS-Sep fibers provided an excellent balance between reinforcing and hysteretic behavior, compared to the large-sized pristine Sep and isotropic silica. This was related to the enhanced interfacial chemical interaction between NS-Sep and rubber, as well as to the size and self-assembly of anisotropic nanofibers to form filler network structures, as supported by transmission electron microscopy analysis.

The preparation of nanocomposites, based on Sep nanofibers obtained by a simple and versatile acid treatment, can thus be considered an alternative approach for the designing of advanced clay polymer nanocomposites.

1. Introduction

Mechanical properties of rubber based materials critically depend on vulcanization (Scotti et al., 2014; Susanna et al., 2015) and addition of reinforcing fillers (Heinrich et al., 2002; Sabu and Ranimol, 2010). The most widely used fillers are carbon black and silica, though in the last decades clay fillers consisting of two-dimensional layers with plate-like geometry, *e.g.* talc, mica, or layered silicates, have been frequently considered as promising candidates for the strengthening of various types of polymer matrices (Krishnamoorti et al., 1996; Alexandre and Dubois, 2000).

It is commonly accepted that, beside the hydrodynamic effect due to filler volume fraction, the reinforcement mechanism consists of two main contributions (Kraus, 1965; Frolich et al., 2005). The first one is related to the *filler network structure*, and contributes to the total modulus together with the polymer network (Vilgis et al., 2009). The rationale of this is that, in a given range of particle loading, the filler gives rise to interconnected structures, through both direct particles interactions, and their bridging by polymer chains (Kluppel et al., 1997). In this respect, the size and shape of the filler have a pronounced significance. In fact, it is clearly demonstrated that the reinforcing effect varies with the particle shape (Donnet and Custodero, 2005). Specifically, clay fillers impart larger reinforcing effect than spherical particles, due to the high aspect ratio (AR) of the lamellar particles having layers approximately of 1 nm thickness and 1000 nm length (Galimberti, 2011). The second contribution is associated to the *interfacial interaction* between filler and polymer, which induces the slowing down of the chain mobility, increasing the fraction of the polymer rigid

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phase (Dutta et al., 1994). Recently, our group reported that rod-like silica particles with high AR (i.e. 2–7) provide significant rubber reinforcement (Scotti et al., 2014; Tadiello et al., 2015) thanks to the self-alignment of the anisotropic particles and to the consequent increased filler/polymer interface. These results suggest the possibility of tuning the formation of the filler network improving the filler-rubber interaction by using high AR fillers, like clays. These latter are of high applicative interest because they are environmental friendly, naturally occurring and readily available in large quantities at lower cost compared to other fillers.

Unfortunately, the incorporation of clays into a polymer matrix frequently does not improve the composite mechanical properties as sought after (Bandyopadhyay et al., 2006). This is basically due to the poor dispersion aptitude of the clay minerals because of the low affinity between the *inorganic* layers and the *organic* polymer. Thus, a modification of the filler surface is required to favor the *interfacial interactions*. To this aim, the hydrophilic pristine clays are generally modified by organic molecules (typically cationic surfactants), *via* ion exchange reaction (Kojima et al., 1993; Li et al., 2008) or by grafting reaction with silane-based coupling agents (Herrera et al., 2005; Yang et al., 2012).

It might also be noted that up to now clay fillers employed in the preparation of clay-based rubber composites have dimensions in micrometric scale, which might not be fully exfoliated during mixing. This may be a drawback, since nano-sized particles with high surface area lead instead to wider filler-matrix interfaces, modifying the molecular mobility of polymer chains and thus inducing a stronger reinforcing effect. To face with this issue, several research groups have performed chemical modifications of specific clays (Ruiz-Hitzky and Van Meerbeek, 2006), but only few ones managed to decrease their average size toward the nanometric scale (Zha et al., 2014).

Among clays, sepiolite (Sep) has attracted researcher attention because of its easy availability, low cost, high specific surface area, strong mechanical and chemical stability, and anisotropic particle shape (Miles, 2011). Sep is a 2:1 phyllosilicate with formula $[Si_{12}O_{30}\ Mg_8(OH)_4(OH_2)_4{\cdot}nH_2O]$ (Murray, 2007). It has a rather unusual structure, organized in two-dimensional silica tetrahedral sheets including one central magnesium octahedral sheet, continuous in one direction. In the third direction, sheets have a thickness of about 1.34 nm and share each edge with the neighboring one, producing a “checkerboard” type pattern. As the sheets are covalently bonded they cannot be exfoliated. The Sep elemental particle appears as tiny fibers 40–150 nm width and 1–10 μm length. Fibers usually stick together in bundles having 0.1 to 1 μm diameter. The bundles form randomly-oriented aggregates having size ranging 10–100 μm. The breaking down of these almost tightly packed aggregates is still a challenge for scientists, if they want to take advantage of the peculiar Sep shape for designing nanostructured materials. Up to now some fundamental studies have been performed in Sep/nanocomposites in order to better control the Sep dispersion (Fernandez-Barranco et al., 2016) and different functionalization treatments of Sep have been reported to prepare clay nanocomposites (Ruiz-Hitzky et al., 2010; Galán, 2011). Recently, De Lima et al. (2017) proposed the Sep modification by ionic liquids, García et al. (2011) by methoxysilanes in aqueous gels and Mejía et al. (2014) by poly(ethylene glycol). These treatments demonstrate the positive effect of Sep functionalization on improving the nanofiber dispersion in polymer matrix and the functional properties of the nanocomposites. Besides these the results are related to specific materials, very different from rubber.

In elastomer formulation instead, the use of pristine Sep is very limited due to its hydrophilic surface and to the consequent low affinity toward organic polymers. On the other hand, even if the Sep clays, organically-modified with alkyl ammonium groups, result more easily dispersible in a polymer matrix, the polymer-filler interaction is generally not improved because of hydrophilic silanol groups on the Sep surface (Gonzalez Hernandez et al., 1987). Meanwhile, surface treatment *via* silane coupling agent is poorly effective, consisting only in 10% of functionalized Sep (Nahmias Nanni et al., 2012), due to the low bonding sites number.

In this framework, we report an alternative approach to prepare Sep rubber nanocomposites based on *size-controlled Sep nanofibers*, obtained by applying a controlled surface treatment on bare Sep. In detail, moving from the literature methods (Aznar et al., 1992; Valentín et al., 2006 and Valentín et al., 2007; Esteban-Cubillo et al., 2008), a simple acid treatment was employed. This provides needle-shaped Sep fibers with nanometric size (namely nano-sized Sep, NS-Sep), preserving the filler anisotropic features and increasing the amount of bonding sites at the Sep edge surfaces. The simultaneous silanization of Sep surface, during acid treatment, was also investigated by using tri-functional silane coupling agent. Morphological, spectroscopic and thermal analyses were performed for a complete characterization of the modified Sep clays. NS-Sep fibers were used to prepare styrene-butadiene rubber (SBR) nanocomposites by *ex-situ* blending. The filler-filler and filler-rubber interactions were investigated through dynamic-mechanical tests and by assessing the NS-Sep nanocomposite structure by transmission electron microscopy (TEM) analysis. The size and the self-assembly ability of the anisotropic NS-Sep nanofibers seem to be critical to form filler network structures, which are able to attain a better balance of the reinforcing and hysteretic properties, in comparison to those obtained by using pristine Sep and conventional nanosilica. On the basis of the reported results, this approach can be considered a good alternative for an advantageous use of Sep nanofibers, as low hysteresis reinforcing filler in elastomers, making them promising material for application in rubber industry.

2. Experimental section

2.1. Materials

Sep Pangel S9 (SepS9) and the organically modified Sep Pangel B5 (SepB5, organically-modified with *N,N*-didodecyl-*N*-methyl-ammonium, DDMA) were supplied by Tolsa and extracted from the landfill of Vallecas (Spain). Silica Zeosil MP1165 (BET specific surface area 160 $m^2\ g^{-1}$) was from Solvay. Bis(3-triethoxysilylpropyl) tetrasulfide (TESPT), ammonium hydroxide, isopropanol (iPr-OH) and 37% aqueous hydrochloric acid were purchased from Sigma-Aldrich. Deionized water and aqueous ammonium hydroxide (60%) were used during washing procedures. Milli-Q water was used with a resistivity 18.2 MΩ cm.

Compounding: SBR was SLR 4630 from Styron Europe GmbH (25% styrene; 63% vinyl; 12% butadiene); Treated Distillate Aromatic Extract (TDAE) extender oil (37.5 parts per hundred rubber (phr)); *N*-(1,3-dimethylbutyl)-*N′*-phenyl-*p*-phenylendiamine (6PPD) used as antidegradant was Santoflex-6PPD from Flexsys; stearic acid was Stearina TP8 from Undesa; sulfur was from Zolfoindustria; zinc oxide was from Zincol Ossidi; *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS) was Vulkacit CZ/C from Lanxess: N-tert-butyl-2-benzothiazyl sulfenamide. Technical Compounding: (high-cis neodymium polybutadiene rubber (BR) was Europrene 40 from Versalis; synthetic polyisoprene (IR) was SKI3 from produced by Nitzhnekamsk); Carbon Black N550 was from Cabot; *N-tert*-butyl-2-benzothiazyl sulfenamide (TBBS) from Lanxess; polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) was from General Quimica S.A.

2.2. Acid treatment of SepS9 and SepB5

SepX (with X = S9 or B5, 120.0 g) was suspended in iPr-OH (1.2 L) at 65 °C and vigorously stirred (800 rpm) for 30 min. Then 37% aqueous HCl solution (480 mL) was added to the reaction mixture. The reaction mixture was stirred at 65 °C (600 rpm) for 2 h, and then filtered. The resulting solid was washed repeatedly with distilled deionized water and with aqueous ammonium hydroxide (60%) until