High performance natural rubber/thermally reduced graphite oxide nanocomposites by latex technology

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ABSTRACT

The latex technology is an innovative alternative for the preparation of composites of natural rubber (NR) and thermally reduced graphite oxide (TRGO). To achieve an improvement of material properties is indispensable to prepare stable suspensions of TRGO. In this work the influence of two surfactants, such as sodium dodecyl sulfate (SDS), as ionic, and Pluronic F 127 as non-ionic surfactant, on the dispersion of TRGO in NR latex and the mechanical and physical properties of the composites were studied. The results showed that the SDS surfactant is ideal for preparing latex NR/TRGO nanocomposite. An optimum dispersion of the nanoparticles in the polymer matrix was achieved in the presence of SDS, as reflected in a considerable improvement of the physical and mechanical properties of the material. Thus, the nanocomposites with 3 phr of TRGO exhibited an improvement of nearly 400% in the maximum strength and an electrical percolation threshold with values around 10^{-6} S/cm, above the static limit.

1. Introduction

Since its discovery [1], graphene has attracted enormous interest as reinforcement of polymeric matrices due to its excellent intrinsic properties such as high thermal and electrical conductivity, excellent mechanical properties and high surface area [2]. All this makes graphene an ideal candidate to improve the mechanical, thermal and electrical properties of polymeric composites [3–6]. Graphene is an allotropic form of carbon with planar sheet of sp2 bonded carbon atoms that are densely packed in a honeycomb crystal lattice [7]. Graphene can be obtained by different methods such as micromechanical exfoliation [1], ultrasound treatment [8], chemical or thermal exfoliation of graphite oxide [9] or chemical vapor deposition (CVD) of methane [10]. Among these methods, the process of oxidation of the graphite and its subsequent reduction by rapid thermal expansion is the most used method because of its simplicity and viability [11].

Few studies on the preparation and characterization of natural rubber nanocomposites reinforced graphene are reported in the literature [12–17]. Zhan et al. [13,14] prepared NR/graphene composites, where graphite oxide was dispersed in the natural rubber latex using ultrasound followed by *in situ* reduction of graphene oxide with hydrazine hydrate and coagulation of the

latex to obtain a masterbatch. Subsequently, the nanocomposites were prepared in an open two-roll mill at room temperature, where the vulcanizing ingredients were added. The authors observed a homogeneous dispersion of graphene in the rubber matrix which contributed to an improvement in mechanical properties over the conventional direct mixing method.

Potts et al. [16,17] compared the properties of nanocomposites prepared by two methods. They observed that the materials prepared directly in a roll-mill had almost the same properties as those of NR. However, the pre-mixing of TRGO with NR latex by a co-coagulating process of the latex assisted by sonication and followed by mixing in a roll-mill improved the dispersion of the graphene in NR matrix and thus the properties of the nanocomposite.

Due to the chemical nature of graphene, stability of its aqueous suspension is relatively low, so it tends to agglomerate. The stability of graphene suspensions has been successfully obtained by using surfactants [18]. However, the selection of the type of surfactant is critical since it can influence on the morphology and properties of the composite, and even it could affect the percolation threshold [18].

In this work, the preparation of nanocomposites of thermally reduced graphite oxide and pre-vulcanized natural rubber, by applying the latex technology, is studied. For the first time the influence of the type of surfactant on the morphology and the physical and mechanical properties of the composites was

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analyzed. Sodium dodecyl sulfate (SDS) was used as ionic surfactant and Pluronic F 127 as non-ionic surfactant.

2. Experimental

2.1. Materials

A double centrifuged pre-vulcanized natural rubber latex (NR) with high ammonia content and with total solid content of 56.87% (49.08% of natural rubber) was used. This latex was kindly supplied by TECNILATEX S.A., Spain. This type of latex was chosen because it is widely used at industrial level. Also, the use of latex avoids the chewing process which can distort the elastomeric network formed by addition of the fillers. Moreover, it allows obtaining thin films with an adequate degree of curing after a simple drying process.

The thermally reduced graphite oxide (TRGO) was produced in-house by rapid adiabatic expansion of graphite oxide at 1000 °C under inert atmosphere [19]. Graphite oxide was synthesized from natural graphite by the method of Brodie [20]. A thorough characterization of the material has been already reported [19]. SDS ($NaC_{12}H_{25}SO_4$) and Pluronic F 127 $HO(C_2H_4O)_a(C_3H_6O)_b(C_2H_4O)_a$H (where $a = 100$ polyoxyethylene portion and $b = 65$ polyoxypropylene) supplied from Sigma–Aldrich were used as received. The molecular structural formulas of the surfactants are shown in Fig. 1.

2.2. Preparation of nanocomposites of natural rubber and TRGO

First, the aqueous dispersions of TRGO containing 0.3 wt.% of TRGO were prepared by using either SDS or Pluronic F127 as surfactants, the ratio TRGO to surfactant was 1:3. The TRGO was dispersed in a 1 wt.% sodium dodecyl sulfate solution or in 1 wt.% Pluronic F 127 solution followed by sonication for 1 h. Known volumes of the TRGO suspensions were added to pre-vulcanized natural rubber latex to obtain nanocomposites containing between 1 and 4 phr of TRGO. Subsequently, the samples were dried for 24 h at 70 °C.

2.3. Nanocomposite characterization

The nanocomposites were characterized by Raman spectroscopy, which was performed on a Renishaw Invia Raman microscope with a laser wavelength of 514.5 nm and a spectral resolution of 0.02 cm^{-1}. The degree of dispersion of the nanoparticles and nanocomposite morphology was analyzed by transmission electron microscopy by using a Philips Tecnai 20 microscope at an accelerating voltage of 200 kV. Ultrathin sections of the samples were prepared by crioultramicrotomy at −140 °C using Leica EM UC6 crioultramicrotome equipment.

Thermogravimetric analysis was performed on a Mettler Toledo SDTA model 851. A sample of about 8 mg was heated at

20 °C min^{-1} under nitrogen atmosphere. TGA curves were recorded from 30 °C to 700 °C.

Mechanical tests were performed on an Instron model 3366 dynamometer according to ASTM D 412 specifications. The tests were conducted at room temperature and a pulling speed of 500 mm min^{-1}. The elongation of the material, corresponding to the displacement of two marks 2 cm apart on the samples, was determined by optical measurements using a video extensometer. The results are the average of at least five measurements for each sample.

Dynamic mechanical analysis was performed on a Mettler Toledo 861e DMA in tension mode at 1 Hz in a temperature range between −100 and 0 °C at a heating rate of 2 °C min^{-1}. The experimental error is less than 5%.

The electrical conductivity of the nanocomposites was measured on a high resolution Alpha-Novocontrol dielectric spectrometer. The films were placed in the dielectric cell between two parallel gold electrodes. The conductivity measurement is given directly by the analyzer. In a composite material, the conductivity is given by two terms:

$$\sigma(F) = \sigma_{dc} + AF^x$$

where σ_{dc} is the direct measurement of the conductivity, A is a constant and x is an exponent which describes the dependence of $\sigma(F)$ with the frequency.

3. Results and discussion

Fig. 2 shows the Raman spectrum of TRGO and natural rubber nanocomposites (NRL) and TRGO. The TRGO shows the two distinctive bands of carbonaceous materials, the G band (in-plane tangential stretching of the carbon–carbon bonds in graphene sheets) at around 1592 cm^{-1} and the D band associated to the presence of disorder or amorphous carbon in graphite materials at 1347 cm^{-1} [21] (Fig. 2(a)). It can be seen that both bands remain in the nanocomposite indicating the presence of TRGO. The D and G bands are slightly shifted to higher frequencies in the nanocomposites and this can be associated to the presence of possible polymer–filler interactions.

TEM images (Fig. 3) show that TRGO nanoparticles are homogeneously dispersed and completely embedded in the matrix of natural rubber, being this effect more evident when SDS is used as surfactant. This indicates that the nature of the dispersion of TRGO
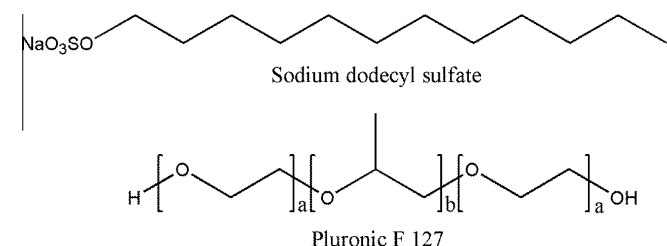

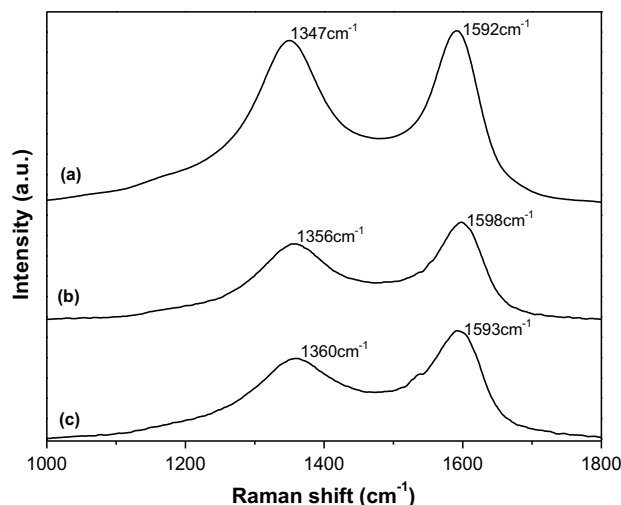Fig. 1. Sodium dodecyl sulfate a ionic surfactant and Pluronic F 127 a non ionic surfactant.

Fig. 2. Raman spectra of TRGO (a) and NR/(3 phr) TRGO nanocomposites dispersed in SDS (b) and Pluronic F127 (c).