



Effect of the morphology of thermally reduced graphite oxide on the mechanical and electrical properties of natural rubber nanocomposites



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ABSTRACT

Graphene materials often are obtained through thermal reduction of graphite oxide. This is due to the fact that other synthesis methods are more difficult and generally render lower yield. The structure and morphology of these graphene materials could affect their performance in different applications. Herein, thermally reduced graphite oxide (TRGO) was obtained from thermal reduction of graphite oxide prepared by using the methods reported by Brodie and Hummers. The oxidation method greatly affects the structure and morphology of the resulting TRGO. TRGO obtained by the Brodie's method generates a morphology comprised of rather exfoliated galleries while that obtained by the Hummers method presents randomly distributed sheets. The influence of structural differences on the dispersion of TRGOs in natural rubber latex (NR) and on the resulting mechanical and electrical properties of the TRGO/NR nanocomposites is studied. The TRGO prepared by the Brodie's method (TRGO-B) showed a more homogeneous dispersion in the polymer–matrix, rendering enhanced mechanical and electrical properties of their nanocomposites. TRGO-B/NR nanocomposites showed higher electrical conductivity, which is attributed to the formation of an electrically conducting filler network through the polymer–matrix. This is consequence of the morphology presented by TRGO produced by the Brodie's method.

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1. Introduction

Graphite is a carbon allotrope with planar layered structure widely available in nature [1]. An isolated layer of graphite is known as graphene. In graphene the carbon atoms are bonded by sp^2 hybridization and the single atomic layer character renders its outstanding physical properties [2]. Although an isolated layer of graphene is normally not found in nature, the group of Novoselov and Geim [3] are well known for isolating stable graphene. The micromechanical exfoliation used by Novoselov et al. is not feasible for large scale preparation of graphene. Therefore, other methods to produce graphene or a few layers of exfoliated graphene materials have been proposed [3,4]. The method known as “top-down” comprises in the production of graphene materials from graphite.

Examples of “top-down” methods are ultrasound treatment of graphite in suspension [4] and the exfoliation of graphite oxide by thermal or chemical reduction [5]. The exfoliation process of graphite oxide through a quick thermal expansion is probably the most used method owing to facility, viability and high yield [6]. The graphite oxide frequently used for obtaining graphene materials are those obtained by oxidation of graphite by methods reported by Brodie [7], Staudenmaier [8] or Hummers and Offerman [9].

Brodie [7] proposes the use of potassium chlorate ($KClO_3$) and fuming nitric acid (HNO_3), without formation of perchlorates, where the chloric acid ($HClO_3$) is probably the main oxidizing species [10]. The Hummers' method [9] consists in the use of potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$) and concentrated sulfuric acid (H_2SO_4). The oxidizing species in the Hummers' method could correspond to manganese heptoxide (Mn_2O_7) [11]. Botas et al. [12] studied the thermal reduction of graphite oxide prepared by the Brodie's (GO-B) and Hummers' (GO-H) methods, demonstrating that GO-H presents higher oxygen

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content than GO-B. However, thermal reduction of GO-H and GO-B upon 1000 °C produced TRGO-H with lower oxygen content than TRGO-B.

The excellent intrinsic properties of graphene [13] are probably the main reason for the huge interest of using graphene materials as mechanical reinforcement and/or electro-conducting filler for polymer matrices [14]. However, the difficulty to produce graphene monolayer and to prevent such an individual layers from recombining within the polymer–matrix has induced researchers to employ graphene materials obtained either by chemical (CRGO) or thermal (TRGO) reduction of graphite oxides as fillers for polymer matrices [15–23]. Different authors have reported the use of natural rubber (NR) as matrix for the preparation of electrically conducting elastomeric nanocomposites by using TRGOs or CRGOs as fillers [24–31]. Some of these reports have employed natural rubber latex at some stage of the nanocomposite preparation [26–33]. Zhan et al. [26] reported the homogeneous dispersion of CRGO in NR obtaining nanocomposites with excellent mechanical properties. These nanocomposites were prepared by coagulation of NR latex in presence of CRGO, mixed in a two roll mill and then vulcanized. Similar works were developed by Potts et al. [28,29], where they observed that processing of coagulated NR containing TRGO in a two roll mill yields better mechanical and electrical properties compared with the properties of those prepared by the direct addition of TRGO to NR during two roll milling. Aguilar-Bolados et al. [31] reported a simple and more efficient method for the preparation of TRGO/NR nanocomposites by the addition of aqueous suspension of TRGO and surfactant to prevulcanized natural rubber latex. The use of prevulcanized natural rubber latex allows the production of homogeneous films with improved mechanical and electrical properties, without the need of post-processing stages.

In spite of these research progresses, there is no clear understanding of how the method of synthesis of TRGO affects the electrical and mechanical properties of nanocomposites. Therefore, this work reports on the synthesis of graphite oxides produced by using the methods reported by Brodie [7] and Hummers [9]. The graphite oxides are subsequently thermally reduced to obtain TRGO for investigating their effect on the mechanical and electrical properties of NR composites. The aim of this work is to study the effect of the morphology of both TRGO on the mechanical and electrical properties of TRGO/NR nanocomposites prepared by latex technology.

2. Materials and methods

2.1. Materials

Commercial natural graphite powder supplied by Sigma–Aldrich was used for the preparation of graphite oxides. The carbon content was 99.9 wt.%. Fuming nitric acid ($\geq 99.5\%$), potassium chlorate ($\geq 99\%$), sulfuric acid (98%), sodium nitrate ($\geq 99.5\%$) and potassium permanganate ($\geq 99\%$) were from Sigma–Aldrich and were used as received.

2.2. Synthesis of graphite oxide

2.2.1. Brodie's method

5 g of graphite were added to 100 ml of fuming nitric acid into a flask with a cooling jacket and cooled to 0 °C in a cryostat bath. Next, 40 g of potassium chlorate was slowly added for 1 h and the reaction mixture was stirred for 21 h at 0 °C. Once the reaction finished, the suspension was centrifuged (3700 rpm for 30 min), washed with distilled water and vacuum filtered until the pH of the filtrate was neutral.

2.2.2. Hummers' method

44 ml of sulfuric acid, 1 g of sodium nitrate and 2 g of graphite were added to a refrigerated reactor and cooled down to 0 °C. Next, 6 g of potassium permanganate was slowly added to keep the reaction temperature below 20 °C. This mixture was then heated to 37 °C under stirring for 3 h, followed by the addition of 88 ml of distilled water. Then, 3% H₂O₂ was slowly added until a color change was observed. The mixture was then washed with distilled water and vacuum filtered until the pH was neutral. Finally, the suspension was dried at 70 °C.

2.3. Synthesis of thermally reduced graphite oxide

The thermal exfoliation and reduction of GO-B and GO-H for the preparation of thermally reduced graphite oxide (TRGO) was performed in a Carbolite® TZF 12/65/550 horizontal furnace tube at 1000 °C under an argon atmosphere (500 ml/min). 0.3 g of GO was introduced into the furnace and heated first to 200 °C at a rate of 20 °C/min and then at 10 °C/min up to 1000 °C, maintaining this temperature for 1 h. The corresponding samples obtained were labeled as TRGO-B and TRGO-H, where the last letter indicates the oxidation method used.

2.4. Preparation of TRGO/NR nanocomposites

For the preparation of TRGO/NR nanocomposites, a colloidal suspension of TRGO in an aqueous solution of 22.5 mM of dodecyltrimethylammonium bromide (DTAB) from Merck was prepared and subjected to ultrasound for 30 min at room temperature. This suspension was added to prevulcanized natural rubber latex from Química Miralles S.A. with 49.62 wt.% rubber content. This suspension was immediately poured to a Petri dish and then dried at 70 °C to form a film. The diameter and thickness of the films were around 15 cm and 200 μm , respectively. Specimens for mechanical and electrical testing were obtained from these films. The content of TRGO in the nanocomposites was 2, 3 and 4 wt.% with respect to the NR. Each of these nanocomposites contained 4.6, 6.9 and 9.3 wt.% of DTAB as surfactant with respect to the NR.

2.5. Characterization of TRGOs and TRGO/NR nanocomposites

TRGOs were characterized by Raman spectroscopy using a Renishaw Invia Confocal Raman Microscope equipped with an argon laser of 514.5 nm excitation wavelength and 0.02 cm^{-1} resolution. The spectra were recorded from 750 to 3500 cm^{-1} . To determine the interlayer distance of TRGO, X-ray diffraction (XRD) analysis of the powdered samples was performed using a Bruker D8 Advance diffractometer with a CuK α radiation source, wavelength $\lambda = 0.154 \text{ nm}$ and a power supply of 40 kV and 40 mA. The incidence angle (2θ) was varied between 1° and 60° and the scan rate was 0.02°/s. The interlaminar sheet distance was obtained from the (002) reflection of the XRD patterns of the TRGOs. The morphology of the TRGOs was studied using a scanning electron microscope (SEM) Vega 3 Tescan.

Tensile stress–strain properties of vulcanized NR latex and its nanocomposites were measured in an Instron dynamometer model 3366 at 25 °C using a cross-head speed of 500 mm/min and following the ASTM D412 specification [34]. Rectangular-shaped specimens were cut from the vulcanized films. Five specimens of each material were tested.

Broadband dielectric spectroscopy (BDS) measurements were performed in a Novocontrol ALPHA high resolution dielectric analyzer. Vulcanized film disc-shaped samples were mounted in the dielectric cell between two parallel gold-plated electrodes. The film thickness (nominally 100 μm) was considered as the distance

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