Composites Science and Technology 73 (2012) 40–46

Contents lists available at SciVerse ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Overall performance of natural rubber/graphene nanocomposites

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ARTICLE INFO

Article history:
Received 31 May 2012
Received in revised form 1 August 2012
Accepted 22 August 2012
Available online 5 September 2012

Keywords:
A. Nanocomposites
B. Mechanical properties
B. Electrical properties
Graphene

ABSTRACT

Natural rubber (NR) and functionalized graphene sheets (FGSs) nanocomposites were prepared by conventional two-roll mill mixing. The morphology and structure of the FGS was characterized confirming the successful exfoliation of the FGS. The strong rubber-to-filler interactions accelerate the cross-linking reaction, increase the electrical conductivity and cause an important enhancement on the mechanical behavior of the NR nanocomposites. The nanofiller does not affect the molecular dynamics of NR, while the presence of vulcanizing additives slowdowns the segmental motions and decreases slightly the time scale of the global chain dynamics in NR/FGS nanocomposites. These functional properties make NR/FGS nanocomposites a promising new class of advanced materials.

1. Introduction

Elastomers are usually reinforced with mineral fillers in order to get substantial improvements in strength and stiffness. Without the filler, rubber formulations would yield resilient products having elastic properties but very little strength. The extent of property improvement depends on several parameters including the size of the particles, their aspect ratio, their degree of dispersion and orientation in the matrix and the degree of adhesion with the rubber chains [1]. At present, nanometer-scale reinforcing particles have received considerable attention from rubber scientists because of their small size and the corresponding increase in the surface area, achieving the required mechanical properties at low filler loadings [2,3].

Recently, graphene has attracted a tremendous amount of attention and has emerged to be an exciting material with potential applications as a reinforcing material for polymer nanocomposites [4,5]. Graphene is considered a two-dimensional carbon nanofiller with a one-atom thick planar sheet of sp^2 bonded carbon atoms that are densely packed in a honeycomb crystal lattice [6]. Defect-free graphene presents outstanding physical properties, such as high thermal conductivity (5000 W/m K), Young's modulus (1 TPa) and ultimate strength of 130 GPa. Furthermore, graphene possesses a large specific area (theoretical limit: 2630 m^2/g), gas permeability and high electron mobility [4,7]. Thus, it can be a good nanofiller candidate to enhance mechanical, thermal, and electrical properties of composite materials. To produce graphene, various approaches have been used including chemical vapor deposition (CVD) of methane gas [8], graphite oxide thermal reduction [9], and one-step graphite exfoliation [10]. Among these, the process of obtaining graphite oxide (GO) from natural graphite powder and its further reduction to graphene has been extensively studied due to its elaboration simplicity and to its economic feasibility. This method consists on the oxidation of graphite powder in the presence of concentrated mineral acids and oxidizing agents which yields a large variety of GO. In particular, the subsequent adiabatic thermal expansion of GO renders functionalized graphene sheets (FGSs) [11].

Few interesting studies have already been reported illustrating the potential of graphene nanocomposites based on rubber matrices [12–16]. Surprisingly, almost no studies have involved the preparation and characterization of NR/graphene nanocomposites. To the author's best knowledge, only a patent [17] and a recently published work made by Yuan et al. [18] have been reported using a NR matrix. Yuan et al. [18] have proposed a new method, i.e., ultrasonically-assisted latex mixing and *in situ* reduction (ULMR) process to prepare NR/graphene composites. GO was dispersed into NR latex using an ultrasonic field and was then reduced *in situ*, followed by latex coagulation to obtain the NR/graphene masterbatch. The results show that this method produces a better dispersion and exfoliation of graphene in the matrix and contributes to an increase in the tensile strength compared to conventional direct mixing.

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http://dx.doi.org/10.1016/j.compscitech.2012.08.012

Other aspect of paramount importance when dealing with rubber nanocomposites is the effect that can exert the vulcanization additives (accelerant, activator, vulcanizing agent) on the final properties of the material. The special character of rubber, being a multi-component system, complicates the analysis of the parameters affecting the rubber/nanoparticle composite formation.

Within this context, the present work is focused on the study of the overall performance of NR and functionalized graphene sheets (FGSs) nanocomposites. Results of this comprehensive study are provided in the following sections, mainly characterizing the structural characteristics, cure behavior and mechanical properties of the prepared nanocomposites, but also analyzing the dielectric behavior. The relationships between these properties and nanoparticle nature are presented in this work. The influence of the vulcanizing additives on the dynamics of the nanocomposites is also analyzed.

2. Experimental details

Natural rubber (NR) supplied by *Malaysian Rubber*, under the trade name SMR CV60 was the polymer matrix employed in this study. The nanocomposites and the vulcanizing additives: zinc oxide (ZnO), stearic acid (SA), mercapto benzothiazyl disulfide (MBTS) and sulfur (S) are listed in Table 1, expressed as parts per hundred parts of rubber (phr). FGS were produced in-house from the adiabatical expansion [14] of graphite oxide at 1000 °C under an inert atmosphere. Graphite oxide was synthesized from natural graphite according to the Brödie method [19].

All the compounds were prepared in an open two-roll laboratory mill (*Comerio Ercole*) at room temperature. First, the mastication of the rubber took place. Afterwards, all the vulcanizing additives except sulfur were added to the rubber prior to the incorporation of the filler and, finally, sulfur was added. NR compounds were vulcanized in an electrically heated hydraulic press (*Gumix*) at 150 °C and 200 MPa. The optimum cure time, t_{90} was derived from the curing curves previously determined by means of a Rubber Process Analyzer (*Alpha Technologies*). The cross-linking density was determined on the basis of solvent-swelling measurements by application of the Flory–Rehner equation [20].

An XRD diffractometer (*Bruker*) was employed with a radiation source of Cu Kα and wave length $\lambda = 0.154$ nm operated at 40 kV and 40 mA. The incidence angle (2θ) was fixed between 1° and 60° and the scan rate was 0.02°/s. Raman spectroscopy was performed on a *Renishaw Invia* Raman microscope. The analyses were done using an argon laser at 514.5 nm excitation wavelength. XPS studies were performed on a *VG Escalab 200R* spectrometer equipped with a hemispherical electron analyzer operated on a constant pass energy mode and non-monochromatized Mg X-ray radiation ($h\upsilon = 1253.36$ eV) at 10 mA and 12 kV. Data analysis was performed with the XPS peak program. The spectra were decomposed by the least-squares fitting routine using a Gauss Lorentz product information after subtracting a Shirley background. The binding energies (BEs) were normalized by using the C_{1s} peak (284.8 eV) of carbon as an internal standard. Tensile stress–strain properties of vulcanized NR and its nanocomposites were measured in a dynamometer (*Instron*) at 25 °C and at a cross-head speed of 500 mm/min. Rectangular-shaped specimens were mechanically cut out from the vulcanized film samples. At least five specimens of each sample were tested. Broadband dielectric spectroscopy (BDS) measurements were performed on an ALPHA high resolution dielectric analyzer (*Novocontrol*). Films were mounted in the dielectric cell between two parallel gold-plated electrodes. The complex permittivity ε^* of the samples was measured over a frequency window of $10^{-1} < F/Hz < 10^7$ ($F = \omega/2\pi$ is the frequency of the applied electric field, being ω the angular frequency) in the temperature range from −100 °C to 100 °C in 5 °C steps. The imaginary part ε'' of the obtained dielectric permittivity, referred to as dielectric loss, was analyzed by the phenomenological Havriliak–Negami (HN) function [21]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)/[1 + (i\omega\tau_{HN})^b]^c \quad (1)$$

where $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$, ε_∞ and ε_s are the unrelaxed and relaxed values of the dielectric constant, τ_{HN} is a characteristic relaxation time, and b and c are shape parameters ($0 < b$, $c \leqslant 1$) which describe the symmetric and the asymmetric broadening of the equivalent relaxation time distribution function, respectively. The AC conductivity was measured in the same conditions as ε^* and the results were given directly by the dielectric analyzer. In a conducting composite, the conductivity is composed of two terms:

$$\sigma(F) = \sigma_{dc} + AF^x \quad (2)$$

where σ_{dc} is the direct current conductivity, A is a constant and x is an exponent which describes the frequency (F) dependence of $\sigma(F)$. The term σ_{dc} appears as a plateau at low frequencies in the experiments and it is obtained by extrapolating the broadband AC conductivity to 10^{-1} Hz when a plateau is reached.

Table 1
Formulation and additives used in the preparation of NR nanocomposites.

COMPOUND	NR	ZnO	SA	MBTS	S	FGS
Neat NR	100					
NR/0.1FGS	100					0.1
NR/additives	100	5.0	1.0	1.0	2.5	
NR/additives/0.1FGS	100	5.0	1.0	1.0	2.5	0.1
NR/additives/0.5FGS	100	5.0	1.0	1.0	2.5	0.5
NR/additives/1.0FGS	100	5.0	1.0	1.0	2.5	1.0

3. Results and discussion

3.1. Structural characterization of FGS

XRD data were obtained for natural graphite (NG), graphite oxide (GO) and functionalized graphene sheets (FGSs) (see Fig. 1a). The interlayer distance was calculated from the XRD data and hence the exfoliation of the FGS was assessed. XRD data of the FGS shown did not present any diffraction peak indicating an amorphous structure. TEM images of FGS (Fig. 1b) show the characteristic wrinkled structure of the particle due to the thermal shock to which it has been subjected. Raman measurements of NG and FGS were performed in order to confirm the changes on the graphite structure of the FGS due to the exfoliation [22] (see Fig. 1c). Both Raman spectra present the two well-known relative intensity bands, the *D* band (attributed to the presence of disorder or amorphous carbon in graphitic materials) and the *G* band (in-plane tangential stretching of the carbon–carbon bonds in graphene sheets). The Raman spectrum of NG displays the intensity of the *G* band at 1568 cm^{-1}, while it up-shifts towards 1582 cm^{-1} for FGS, fact that has been attributed to the single-layer graphene sheets [23]. Furthermore, it is worth noticing that both bands broaden for FGS compared to NG thereby increasing the I_D/I_G ratio (Fig. 1c). The broadening of the *G* band results from the formation of epoxy, hydroxyl and carbonyl groups during the preparation of the FGS [24]. The thermal expansion of the GO to obtain FGS leaves topological defects on graphene with the subsequent broadening of the *D* band.

XPS was employed to analyze the nature and the relative amount of oxygen-containing functional groups present on the graphene surface. The C_{1s} and O_{1s} XPS spectra are shown in Fig. 2. All peaks are decomposed into several symmetrical components (four for C_{1s}, two for O_{1s}). The most intense peak between