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Dispersion of graphene in chlorosulfonated polyethylene by slurry compounding

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ABSTRACT

It remains a huge challenge to realize the homogeneous graphene dispersion in elastomer matrix by a simple and general compounding method. Herein, we develop a straightforward slurry compounding method for preparation of rubber/graphene composites with well-dispersed graphene. Specifically, TPG (tea polyphenol reduced graphene)/ethanol slurry was first collected by solvent exchange after the reduction of graphene oxide by tea polyphenol and then directly melt compounded with chlorosulfonated polyethylene (CSM) in a two-roll mill to produce the composites. As revealed by the XRD and morphological studies, TPG homogeneously dispersed in CSM matrix, which together with the strong interfacial interaction between TPG and CSM contribute to the remarkable improvement in mechanical properties of the resulted composites. We envision that the present work offers a straightforward yet effective methodology for preparing high-performance elastomer/graphene composites via conventional melt compounding.

1. Introduction

Rubbers are strategically important elastic materials for their indispensable applications, such as tires, transmission belts and seals. However, most neat rubbers are mechanically weak, which largely limits their practical applications. Reinforcement of rubbers by incorporation of various nanoparticles such as carbon black and silica have been widely adopted in rubber industry. Recently, graphene and its derivatives have been intensively pursued, due to their much higher efficiency in reinforcing rubber composites than the above mentioned traditional fillers [1–3]. However, graphene tends to aggregate in rubber matrix due to the high specific surface area and strong van der Waals forces, which will inevitably deteriorates the ultimate performance of the prepared rubber composites.

To date, several methods such as solution blending, latex mixing and melt compounding have been developed to address the issue of graphene dispersion in rubber matrices [4,5]. Generally, the first two approaches have been demonstrated to be effective in achieving homogeneous graphene dispersion in rubber composites, resulting in significantly improved mechanical properties [6,7]. However, these methods could have limitations. For example, the consumption of abundant solvents and the removal of solvents after compounding are not suitable for practical industrial applications. In contrast, melt compounding, which is referred to directly disperse fillers into rubber matrix by shearing force in an internal mixer or two-roll miller, has long been the most commonly used processing method for preparing rubber composites in rubber industry due to its advantages of simplicity, cost-effective and environmental friendly. However, this processing method still face considerable difficulties in achieving homogeneous graphene dispersion due to the low packing density of graphene, high viscosity of rubber matrix and strong tendency to self-aggregate of graphene sheets, which largely reduces the reinforcing efficiency of graphene and leads to inferior mechanical performances of the as-prepared rubber/graphene composites. For example, Potts et al. prepared natural rubber/thermally expanded graphite oxide (NR/TEGO) composites by a conventional two-roll mill in order to evaluate the effectiveness of melt compounding method [8]. And the results indicate that the property improvements achieved by this method were small and only comparable to those provided by carbon black. Although appropriate surface treatment of graphene can help improve graphene dispersion during melt compounding [9], the outcome is still unsatisfactory. In summary, it is critically important, but remains challenging, to realize the homogeneous graphene dispersion in elastomer matrix by a simple and general compounding method.

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Previously, a modified melt compounding method, namely, slurry compounding has been developed to prepare polymer/layered clay composites [10–13]. In this method, the layered clay is first exfoliated in water to form clay slurry and then directly added into the extruder. With the evaporation of water, the exfoliated clay layers are accordingly fixed into the polymer matrix and almost maintain their exfoliated state as in the slurry. The resulting composites exhibit improved clay dispersion as confirmed by the enhanced mechanical properties. Recently, we also reported on the scalable fabrication of rubber/boron nitride nanosheets (BNNSs) composites by slurry compounding, which resulted in a significant enhancement of mechanical properties and thermal conductivity of the composites [14]. Considering the structure similarity, we suspect that this approach may also be employed to prepare rubber/graphene composites after appropriate modification.

In the present work, a novel processing method i.e. slurry compounding was developed for preparation of CSM/TPG composites. Specifically, the graphene oxide was first reduced and modified by TP, resulting in TP-reduced graphene (TPG). Subsequently, TPG slurry was collected by solvent exchange with ethanol. TPG slurry was then directly subjected to melt compounding with CSM in a two-roll mill to produce composites. The dispersion of TPG and the interfacial interaction between TPG and CSM matrix were characterized. The greatly enhanced mechanical properties verified the effectiveness of this methodology.

2. Experimental section

2.1. Materials

Chlorosulfonated polyethylene (Grade: CSM 3304) with a Mooney viscosity (ML (1 + 4) at 100 °C) of about 40–50, a chlorine content of about 33–37%, and a sulfur content of about 0.8–1.2% was obtained from PetroChina Jilin Petrochemical Co. Ltd, China. Graphite power was purchased from Shanghai Colloidal Co. Ltd, Shanghai, China. Tea polyphenols (TPs) was supplied by Xuancheng Baicao Plant Co. Ltd, Anhui, China. The chemical reagents used in the oxidation of graphite including concentrated sulfuric acid, potassium permanganate, sodium nitrate and hydrogen peroxide, were analytical reagents and used as received. Rubber ingredients were industrial grade and used as received.

2.2. Preparation of TP-reduced graphene (TPG) slurry

Graphene oxide (GO) was firstly synthesized through oxidation of graphite according to a modified Hummers method [15]. TPG aqueous suspension was prepared according to our previously published method [16]. Typically, a certain amount of GO was dispersed in water under sonication to obtain a stable GO dispersion (2 mg/mL), and then TPs (300 wt % relative to GO) were added. The mixture was vigorously stirred at 80 °C for 8 h to realize the reduction and modification of GO. The resulted suspension was washed and centrifuged twice with abundant deionized water to remove residual TPs. Following the above-mentioned procedure, we noted that about 0.95 g of GO and 2.85 g of TPs were required for the production of 1 g of TPG. The TPG sediment was collected to prepared TPG slurry by our previously reported solvent exchange method. Typically, desired amount of wet TPG was diluted with ethanol to obtain TPG dispersion (1 mg/mL) in a mixture solvent of ethanol and water, in which the concentration of water is 2 vol%. Subsequently, the TPG dispersion was further subjected to centrifugation and dilution with ethanol twice to exchange and remove the residual water, and a uniform TPG slurry in ethanol (solid content: 50 mg/mL) was obtained.

2.3. Preparation of CSM/TPG composites

CSM/TPG composites were prepared by conventional melt mixing. Typically, a desired amount of TPG slurry was directly compounded with CSM using a two-roll mill at room temperature, followed by addition of other rubber ingredients. Note that the cooling water for the mill was turned off during the compounding of TPG slurry with CSM and thus the heat generated during melt mixing can help to evaporate the ethanol. The as-prepared compounds were subjected to compression at 150 °C for the optimum curing time, which was determined by a vulcameter. The basic recipe for the composites was listed as follows: CSM 100 phr (per hundred parts of rubber); PbO-80 (containing 80% of lead oxide), 25 phr; Dipentamethylene thiuram hexasulfide, 2 phr; Dibenzothiazyl disulfide, 0.5 phr. The samples are referred to as CSM/TPG-*x*, where *x* represents the TPG content (phr) in the composites.

2.4. Characterizations

The cryogenically fractured surfaces of CSM composites were performed on a field emission scanning electron microscope (FESEM, Hitachi SU-70, Japan). Transmission electron microscope (TEM) images were carried out with a Tecnai G2 F30 S-Twin electron microscope at an accelerating voltage of 200 kV. X-ray diffraction (XRD) analysis was performed on X'pret Pro diffractometer with Cu-Kα radiation (λ = 0.1542 nm). Fourier transform infrared spectra (FTIR) spectra were investigated by a Bruker Vertex 70 FTIR spectrometer. Dynamic mechanical analysis (DMA) measurements were conducted on a TA DMA Q800 instrument. The curing characteristics of CSM and CSM/TPG compounds were obtained from a U-CAN UR-2030 vulcameter (Taiwan) at 150 °C. The volume fraction of the rubber in the swollen rubber (V_r) and crosslinking density were determined by equilibrium swelling measurements according to previous reports [2,17]. Tensile tests for all the samples were performed on U-CAN UT-2060 instrument (Taiwan) according to ISO standard 37–2005. Shore A hardness was tested using an XY-1 sclerometer following ISO standard 7619-1997 (Shanghai). The abrasion tests were carried out with an Akron abrader according to GB/1689-1998.

3. Results and discussion

3.1. Dispersion of graphene and interface in CSM/TPG composites

The structures of GO, TPG and TPG slurry are investigated by XRD analysis. As presented in Fig. 1, XRD pattern of GO exhibits a typical diffraction peak at about 10.3°, corresponding to an interlayer spacing of ~0.86 nm, which is considerably larger than that of graphite and this increased interlayer spacing should be ascribed to the presence of

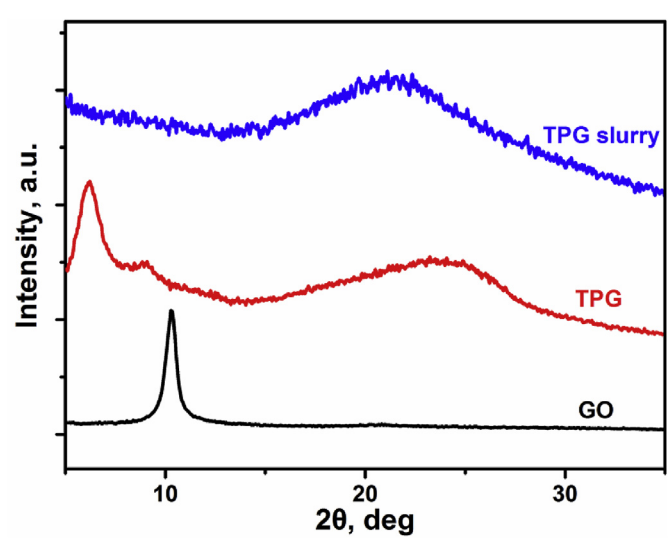

Fig. 1. XRD patterns of TPG slurry, dried GO and TPG.