



A slurry compounding route to disperse graphene oxide in rubber



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ABSTRACT

In polymer composites, filler dispersion and interfacial adhesion are two critical factors in determining their properties. To date, it still remains a challenge to achieve uniform filler dispersion and implement interfacial tailoring in rubber composites by direct melt mixing. In this study, we prepared graphene oxide (GO) slurry in acetone via a simple solvent exchange method and modified GO in the slurry. Then the slurry was compounded with nitrile rubber on two-roll mill to produce composites. Morphological and interfacial structural studies revealed that GO was dispersed at nano-scale in the composites, and the dispersion of GO and interfacial adhesion were further improved upon the modification of GO with silane. Consequently, the mechanical properties of the composites were remarkably enhanced by adding GO.

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1. Introduction

Rubbers are strategically important materials due to their indispensable applications in tires and seals. To fulfill their practical applications, compounding rubbers with diverse fillers is necessary because almost all neat rubbers suffer from poor mechanical properties and low transport behaviors. In recent years, graphene and its derivatives have been widely incorporated into rubbers, from the viewpoints of the spectacular improvements in mechanical and functional properties at low filler loading [1,2]. However, due to large surface area and strong van der Waals force among the sheets, graphene and its derivatives tend to severely aggregate in rubber matrices, which inevitably deteriorates the properties of the composites.

To date, various processing methods have been explored to address the issue of graphene dispersion in rubber composites. Generally, solution mixing and latex compounding can achieve uniform dispersion [3,4]. However, the use of large amounts of organic solvents causes additional costs and environmental pollution, and there are no latex forms for many rubbers. These disadvantages pose persistent obstacles for their practical implementation. Alternatively, melt mixing is highly pursued because it is cost-effective and compatible with current industrial practices. Unfortunately, direct melt mixing yields a rather poor filler dispersion [5]. In summary, it is critically important, but still

challenging, to achieve a homogeneous filler dispersion through a simple and universal processing method.

In this work, we prepared graphene oxide (GO, a precursor of graphene) slurry in acetone through a simple solvent exchange method and modified the GO slurry with silane. The slurry was then compounded with nitrile rubber (NBR) on a two-roll mill to produce composites. The highlights of this novel methodology in dispersing GO and facilitating interfacial modification are demonstrated by investigating the morphologies, interfacial adhesion and mechanical properties of the resulting composites.

2. Experimental section

2.1. Materials

Graphite powder was purchased from Shanghai Colloidal Co., Ltd. NBR with acrylonitrile content of 33% was provided by Jiangsu Nandi Chemical Co., Ltd. Bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT) was purchased from Alfa Aesar. Other chemical reagents were obtained from Tianjin Fuyu Fine Chemical Co. Ltd. Rubber ingredients were industrial grade.

2.2. Preparation of GO slurry and TESPT-modified GO (TGO) slurry

GO was synthesized by oxidizing graphite according to a modified Hummers method [6]. GO slurry was prepared by a solvent exchange method [7]. Typically, GO aqueous dispersion (2 mg/mL) was first subjected to centrifugation to yield wet GO sediment

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(50 mg/mL). The wet sediment was then diluted with acetone to obtain GO dispersion (1 mg/mL) in a mixture solvent of water and acetone, in which the concentration of water is 2 vol%. Subsequently, the GO dispersion was subjected to two cycles of centrifugation and dilution with acetone, and a homogeneous GO slurry in acetone (50 mg/mL) was obtained. After each cycle, the concentration of water was diluted by a factor of 50, and thus the water content in the final GO slurry was a trace concentration of approximately 0.008 vol%. It should be noted that GO cannot be directly exfoliated in acetone because the hydrogen bonds of GO layers prevents the entrance of acetone molecules.

TGO slurry was prepared by adding 2 wt% (relative to rubber) TESPT into GO slurry, followed by stirring for 3 h at room temperature. To envisage the modification of GO with TESPT, TGO slurry model compound (weight ratio of TESPT/GO is 10) was repeatedly washed with ethanol and acetone, followed by drying at 50 °C for 12 h. The obtained TGO powder was used for XRD and FTIR measurements.

2.3. Preparation of NBR/GO and NBR/TGO composites

To prepare NBR/GO composites, a desired amount of GO slurry was compounded with NBR on a two-roll mill, and then rubber ingredients were added. During mixing, rubber chains were intercalated into the GO layers, accompanied by the evaporation of acetone. *Caution: Acetone is irritating and has acute and chronic toxicity. Therefore, the two-roll mill should be equipped with a vent system to prevent inhalation of acetone!* After compounding, the resulting compounds were subjected to compression at 160 °C for the optimum curing time determined by a vulcameter. Following similar protocols, NBR/TGO composites were prepared by adding TGO slurry to NBR. The formulation for the composites was as follows: NBR 100 g; GO was variable (1, 3, 5, or 7 g); zinc oxide 5 g; stearic acid 1.5 g; dibenzothiazole disulfide 1 g; N-cyclohexyl-2-benzothiazole 1.5 g; sulfur 1.5 g. In this context, the term “x” in NBR/GO-x and NBR/TGO-x represents the composites with x phr (per hundred parts of rubber) GO.

2.4. Characterizations

XRD pattern was collected using a Rigaku D/max IIIA X-ray diffractometer with Cu K α radiation. FTIR measurement was carried out on a Bruker Vector 33 spectrometer. SEM and TEM measurements were performed on Hitachi S-4800 and Tecnai G2 F30

S-Twin electron microscope, respectively. Swelling experiment was conducted by immersing vulcanizations in toluene, as described elsewhere [8]. Mechanical properties were determined with a Gotech testing machine.

3. Results and discussion

In Fig. 1(a), the XRD pattern of GO exhibits a sharp diffraction peak at $2\theta = 10.6^\circ$, corresponding to an interlayer spacing of 0.83 nm. The interlayer spacing in the GO slurry is increased to 1.41 nm ($2\theta = 6.3^\circ$) due to the intercalation of acetone molecules into the GO interlayer. This diffraction peak disappears in TGO slurry, suggesting that GO sheets are exfoliated due to the further intercalation of TESPT into the GO interlayer. In addition, the dried TGO powder exhibits an interlayer spacing of 1.01 nm ($2\theta = 8.8^\circ$), which is larger than that in GO. Considering that TGO is repeatedly washed with solvents to remove un-grafted TESPT, the increased interlayer spacing in TGO powder indicates the intercalation and covalent grafting of TESPT onto GO sheets.

The modification of GO with TESPT is explicitly confirmed by FTIR spectra. In Fig. 1(b), GO shows absorption peaks at approximately 3400, 1730 and 1235 cm^{-1} characteristic of the stretching vibrations of -OH and C=O in carboxyl moieties and to C-OH, respectively [6]. In the FTIR spectrum of TGO powder, the newly emerging absorptions at 2926, 1064, 790 and 690 cm^{-1} originate from the stretching vibrations of -CH₂-, Si-O, Si-C and Si-O-C, respectively [4]. Furthermore, the absorptions associated with the hydroxyl and carboxyl groups of GO are absent or suppressed in TGO. These results demonstrate the chemical reaction of TESPT with GO through condensation between the hydroxyl and carboxyl groups of GO and silanol groups of TESPT.

Due to the enhanced interlayer spacing and facile implementation of modification in GO slurry, we envision that GO can be finely dispersed and interfacial adhesion is readily strengthened by directly compounding GO slurry with rubber on a two-roll mill. As a proof of concept, we prepared NBR/GO composites by adding GO or TGO slurry via twin-roll mixing.

Dispersion status of GO in the composites is evaluated by TEM measurement. As shown in Fig. 2(a), GO tends to stack and exists as multilayer in NBR/GO7. However, the thickness of the stacking is less than 10 nm, indicating that GO is dispersed at nanoscale in the composites. Previous studies reported that only a microsized dispersion of GO in rubber was obtained by direct melt mixing [9,10]. In NBR/TGO7 (Fig. 2(b)), GO is uniformly dispersed and

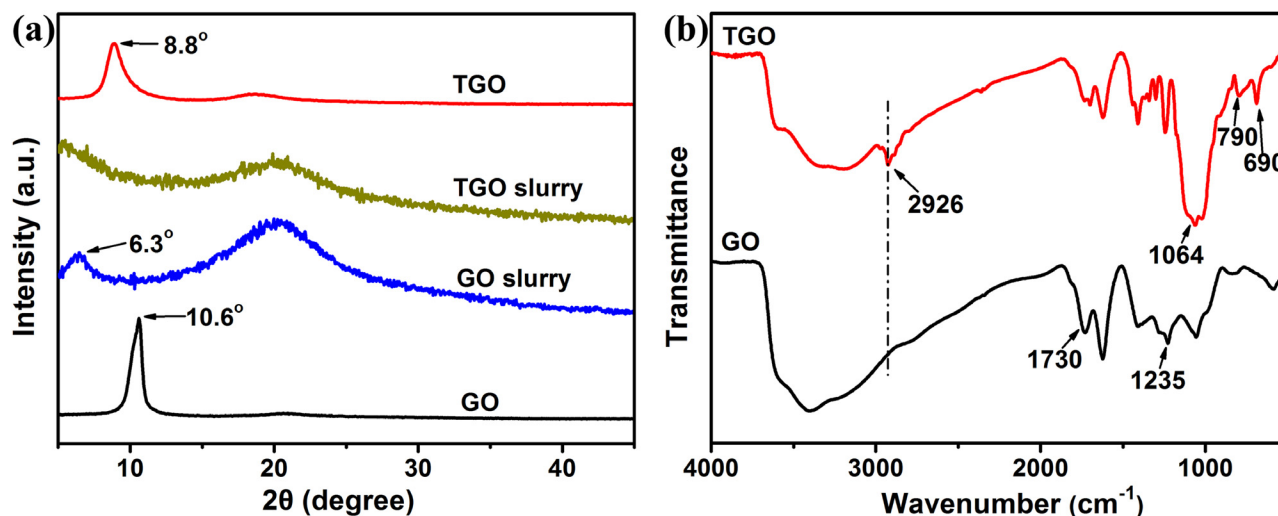


Fig. 1. (a) XRD patterns of dried GO and TGO powder, GO and TGO slurry, (b) FTIR spectra of dried GO and TGO powder.

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