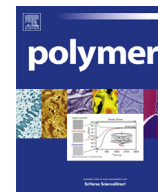




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# Molecular-level dispersion of graphene into epoxidized natural rubber: Morphology, interfacial interaction and mechanical reinforcement

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## ABSTRACT

The interfacial interaction of composites dominates the properties of polymeric/inorganic nanocomposites. Herein, epoxy and hydroxyl groups are introduced into the natural rubber (NR) molecular chains to anchor oxygenous functional groups on the surface of graphene oxide (GO) sheets and therefore enhance the interfacial interaction between GO and rubber. From the morphological observation and interaction analysis, it is found that epoxidized natural rubber (ENR) latex particles are assembled onto the surfaces of GO sheets by employing hydrogen bonding interaction as driving force. This self-assembly depresses restacking and agglomeration of GO sheets and leads to homogenous dispersion of GO within ENR matrix. The formation of hydrogen bonding interface between ENR and GO demonstrates a significant reinforcement for the ENR host. Compared with those of pure ENR, the composite with 0.7 wt% GO loading receives 87% increase in tensile strength and 8.7 fold increase in modulus at 200% elongation after static in-situ vulcanization.

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## 1. Introduction

Due to its significant nature of carbonic monolayer in atomic level, graphene with outstanding mechanical, chemical, and electronic properties finds great potential in many applications, such as electrodes [1], photovoltaic devices [2], energy storages [3], flexible electronics [4] and nanocomposites.

Perfect graphene is not naturally available and usually developed from a precursor, graphene oxide (GO), by treating graphite flakes with oxidizing agents. After oxidation process, oxygenous functional groups including hydroxyls, epoxides, diols, ketones, and carboxyls are introduced onto the graphite surface [5–7]. These polar groups significantly alter the van der Waals interactions between GO sheets which can therefore be easily exfoliated to

monolayer, and then further reduced to graphene with reducing agents [8].

The unique monolayer structure of graphene has been attracting tremendous attention on developing graphene-filled polymer nanocomposites (PGNs) with solution mixing, melt blending and in situ polymerization method [9]. Nevertheless, the manufacturing of PGNs faces a number of challenges in terms of dispersion and interfacial interaction. Solution mixing has been demonstrated to be an effective way to obtain desired dispersion [10–12]. For example, Ozbas et al. [10] prepared natural rubber (NR)/GO nanocomposites using solution mixing technique, where both functionalized graphene sheet and NR were well dispersed in tetrahydrofuran (THF) solution. After completely mixed, THF was removed to obtain the composite. Similarly, Huang and co-worker [11,12] successfully prepared few-layer graphene (FG)/thermoplastic polyurethane (TPU) composites with improved mechanical and self-healing properties by solution mixing method. However, the use of large amounts of solvent and the associated environmental pollution poses a persistent problem for the fabrication of composites. In situ polymerization is an efficient method to prepare GNPs, where the monomer is polymerized in the presence of the filler [13–18]. However, a lot of electrical energy is needed to disperse the filler in

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the polymer matrix during processing and difficult to be used for the mass production of polymer nanocomposites. Melt blending is a direct and cost-effective process technique, since no solvents are involved during the preparation of the composite [19–21], but the structure of GO sheets will be destroyed by the high shearing forces employed during melt compounding.

As GO sheets can be completely exfoliated to individual sheets in water to form a stable GO solution [5,6,22–24], it is realizable to achieve fine dispersion of GO in a water-soluble polymer matrix. Accordingly, Tang et al. [25] and Zhan et al. [26] proposed that aqueous polymer latex can be used to synthesize PGNs using a latex mixing and co-coagulation process. Among the candidates of aqueous polymers, natural rubber (NR) is a promising one as NR latex is a colloidal dispersion of polyisoprene latex particles and non-rubber components in an aqueous serum phase [27]. Zhan [28] and his co-workers successfully prepared NR/GO nanocomposites by ultrasonically assisted latex mixing method. It was found that the crosslink density, elastic modulus, and thermal conductivity of NR/GO composites increased compared to those of pure NR. However, due to the non-polar character of NR molecules, NR could not efficiently react with the polar oxygenous groups of GO. These mixtures of NR and GO were only physically blended with poor interfacial interaction and therefore achieved limited improvement in the properties.

Therefore, interfacial interaction between GO and polymer plays a vital role in the development of high performance PGNs [29]. This interaction not only weakens the intrinsic van der Waals between GO sheets to depress their self-agglomeration, but also more importantly enhances the reinforcing efficiency of GO as the strong interfacial interaction may block the movement of polymer chains when external force is applied. In addition to the chemical bonds, the hydrogen bonding is an ideal candidate to enhance the interfacial interaction between GO and polymers as the abundant oxygenous groups on the surface of GO sheets can interact with polar polymer molecules [30,31].

In the present work, we significantly enhanced the interfacial interaction between GO and NR matrix by introducing epoxy and hydroxyl groups into the NR molecular chains which acts as bridges to connect oxygenous groups of GO via hydrogen bonding interaction. The hydrogen bonding interaction enables the self-assembly between GO sheets and rubber particles and depresses restacking and agglomeration of GO sheets, resulting in a molecular-level dispersion of GO into rubber matrix and remarkable reinforcement in mechanical properties. Transmission electron microscopy (TEM), X-Ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Fourier transform infrared spectrum (FTIR), Raman spectrum, Differential Scanning Calorimetry (DSC) and Halpin–Tsai model fitting [32–34] were conducted to investigate the microstructure, interfacial interaction and reinforcement of ENR/GO nanocomposites.

## 2. Experimental

### 2.1. Materials

Natural rubber (NR) latex with a total solid content of 60 wt% was supplied by Qianjin State Rubber Farm (Zhanjiang, China). Flake graphite (average particle size <20  $\mu\text{m}$ , purity >99.8%) was purchased from Qingdao Graphite Co. Ltd (Qingdao, China). The reagents including concentrated sulfuric acid, potassium permanganate, formic acid, hydrogen peroxide and sodium nitrate were analytically pure and used as received. All the rubber ingredients including sulfur (S), zinc oxide (ZnO), steric acid (SA), *N*-tert-butylbenzothiazole-2-sulphenamide (NS), and *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (4020) were supplied by Shanghai Chemical Co., Ltd.

### 2.2. Preparation of ENR/GO composites

GO and ENR were prepared according to the previous published works [35–38], and the experimental details are fully illustrated in the Supporting information (SI). ENR/GO nanocomposites were prepared by latex compounding combining self-assembly process. A certain amount (0.3 wt%, 0.5 wt% and 0.7 wt%) of GO dispersion was added into the ENR latex under mechanical stirring for 1 h followed by 30 min ultrasonic irradiation to obtain ENR/GO latex. The ENR/GO latex was vulcanized with static in-situ vulcanization and two-roll mixing vulcanization respectively with the following formula: rubber, 100 per hundred rubber (phr); S, 1.5 phr; ZnO, 5 phr; NS, 1.5 phr; SA, 2 phr; antioxidant 4020, 2 phr.

### 2.3. Static in-situ vulcanization

The aqueous dispersion of cure agents were added into the ENR/GO latex at 60 °C under mechanical stirring for 1 h. To allow for the film formation, the mixture was then poured into a horizontal glass plates and dried at room temperature until a equilibrated weight was obtained. Finally, the film was further vulcanized for 2 h at 100 °C to obtain cross-linked ENR/GO nanocomposites, which were abbreviated as SENR, SENR/GO-0.3, SENR/GO-0.5, and SENR/GO-0.7 corresponding to a GO content of 0 wt%, 0.3 wt%, 0.5 wt% and 0.7 wt%, respectively.

### 2.4. Two-roll mixing vulcanization process

The ENR/GO latex was co-coagulated with alcohol and dried at 70 °C. The masterbatch was then mixed with cure agents at 50 °C in a two-roll miller. The vulcanizates were prepared by curing the rubber sheets under a pressure of 15 MPa at 145 °C. The prepared ENR/GO composites were abbreviated as MENR, MENR/GO-0.3,

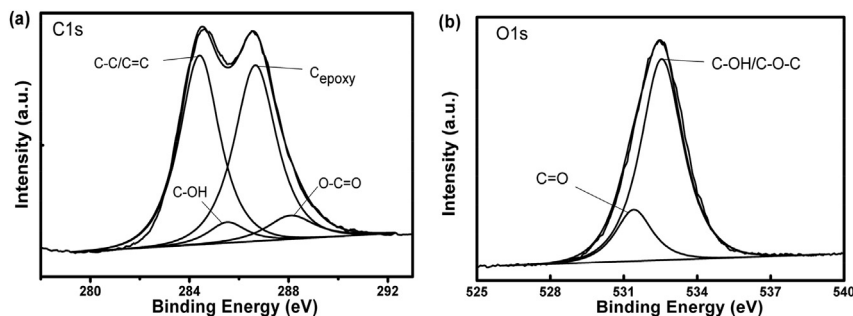


Fig. 1. (a)  $\text{C}^{1\text{s}}$  and (b)  $\text{O}^{1\text{s}}$  spectra of GO sheets.

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