



New evidence disclosed for the engineered strong interfacial interaction of graphene/rubber nanocomposites



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ABSTRACT

Interfacial interaction is of crucial importance for polymer nanocomposites. To improve interfacial interaction between graphene (GE) and isoprene rubber (IR), we grafted a silane coupling reagent, (bis- $[\gamma$ -(triethoxysilyl) propyl]-etrasulfide), onto graphene oxide (GO). The modified GO was mixed with IR by solution blending and then reduced *in situ* to prepare IR/surface modified GE nanocomposites (IR/SGE). Raman mapping illustrates that the bound rubber on SGE is much thicker than that on unmodified GE, suggesting a strong interfacial interaction between SGE and IR. As a result, IR/SGE shows slower chain dynamics and lower strain-induced crystallinity than IR/GE. However, on-line Raman measurements show that the G band of IR/SGE shifts more noticeably during uniaxial tensile deformation than that of IR/GE; this suggests more efficient load transfer between SGE and IR. Consequently IR/SGE has better mechanical properties than IR/GE.

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1. Introduction

For practical applications, elastomers are usually reinforced with certain particles such as carbon black, silica, montmorillonite, carbon nanotubes and graphene (GE) to get substantial improvements in strength and stiffness. Without the filler, rubber formulations would yield resilient products having elastic properties but very low strength [1,2]. Among various fillers, GE is particularly interesting and considered as an ideal filler for elastomers, due to its high specific surface area (2600 m²/g), and extraordinary mechanical, electrical, thermal and gas barrier properties [3–8]. Increasing number of works have attempted to incorporate GE (or its derivatives) into elastomers and confirmed the excellent potential of using GE as a multifunctional nanofiller for rubber materials [9–15]. However, maximizing the reinforcing efficiency of GE in elastomers is still confronted with two challenges, i.e., poor dispersion of GE in the matrix and weak interfacial interaction between GE and elastomers [3]. Actually, the dispersion state of fillers also strongly depends on the interfacial interaction, in

addition to the mixing methods [12–14,16,17]. Therefore, it is crucial to engineer the interfacial interaction and investigate the effect of interfacial interaction on physical and mechanical properties of GE-filled elastomer materials.

To improve the interfacial interaction of GE with rubber matrix, one of the most versatile and easily scalable strategies is surface modification of GE. But direct chemical modification of defect-free GE to obtain a large amount of functionalized GE is not practical. The current state of the art is still based on the modification and reduction of graphene oxide (GO). Various functional reagents (such as organic isocyanates [18], perylene [19], amino acids [20] and alkyl-chlorosilanes [21]) and some macromolecules (like conjugated-polyelectrolyte [22] and poly(vinyl alcohol)) [23] have been used to modify GO. These modifications allow tailoring the interfacial interaction of the filler with host matrices. For example, Kim et al. [17] utilized isocyanate to covalently modify GO and then employed the functionalized GO to prepare polyurethane/GE composites by solution blending. 10-fold increase in tensile strength and 90% decrease in nitrogen permeation were achieved by adding 3 wt % modified GE. Qiu et al. [24] modified the GE with methylene diphenyl diisocyanate and they found the modified GE could enhance not only the tensile strength but also elongation levels of the thermoplastic polyester elastomer nanocomposites. Guo et al. [25] reported modifying GO with alkylamines, which significantly improved its interfacial interaction with styrene-

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butadiene rubber by the crosslinking reaction between sulfur and the double bonds of alkylamines. In their another work [26], a novel covalent interface in SBR/GE nanocomposites based on ortho-quinone-thiol chemistry was developed. The developed rubber/GE nanocomposites were applied to the typical dynamic elastomeric product, auto tires, which exhibited an extremely low rolling resistance coefficient. Considering the practical applications, an ideal surface modifier is required to be cost-effective as well as easy to operate. Bis(triethoxysilylpropyl)tetrasulfide (BTESPT), as an industrial accessible silane coupling agent, is just such a cheap yet versatile surface modifier. The ethoxysilylpropyl groups and polysulfide group on BTESPT could react with the functional groups on filler particles and the double bonds of rubber molecules, respectively. These reactions could result in the formation of additional chemical bonds between GE plates and rubber matrix, which will eventually lead to enhanced interfacial interaction of the resulting composites. In fact, Wu et al. [12] have already grafted BTESPT onto the surface of GO and studied its effect on the mechanical and gas barrier properties of NR/GO nanocomposites. However, their research just involved the test of the bulk mechanical properties like tensile strength, Young's modulus and gas permeability. From such macroscale characterization it is difficult to infer the local structure information at the rubber/GO interface. Actually, it is still a challenge to acquire a conclusive relationship between the enhanced microscopic interfacial interaction and the superior macroscopic performance, which is of primary importance to understand the reinforcing mechanism of functionalized nanoparticle.

Various methods such as dielectric relaxation spectroscopy (DRS) [27], rheometry and thermal measurements have been carried out to detect the interfacial information of polymer composites in the last decades, but the majority of them are indirect. For directly measuring the strength of interfacial adhesion between polymer and nanofiller, the most popular method is fiber pull-out test [28–30], which uses a single fiber in the matrix and records the load during pull-out. However, this method is only applicable to fiber-shaped fillers. Atomic force microscopy (AFM) is another powerful technique widely used to probe the interfacial information between fillers (especially 2-dimensional nanofiller, like GE) and polymers [31–34]. For example, Cai et al. [31] laminated sheets of two different polymers with GE, and then peeled the sheets apart. Since the GE sheets will adhere on the surface upon strong interfacial interaction, AFM topographic images of both failure interfaces were used to qualitatively compare the strength of interfacial adhesion of GE on different polymer surfaces in their work. However, these measurements require samples with relatively flat surface and thus are not suitable to investigate the GE sheets that absorb thick and rough bound rubbers. Different from the methods mentioned above, Raman spectroscopy is known as a nondestructive and sensitive tool for investigating the interfacial load transfer between polymer matrix and GE nanosheets [35–38]. Since the load transfer depends on the interfacial shear stress between the filler and the matrix, studying the load transfer efficiency of modified and unmodified GE filled composites could enable us to reveal the enhanced interfacial interaction. Moreover, Raman mapping mode allows us to portray the surface chemical composition distribution, which furthermore enables us to visually observe the surface of GE with absorption of rubber molecules.

In the present work, GO was successfully modified by the silane coupling reagent, BTESPT. We used the modified GO to prepare IR/SGE by solution blending and in-situ reduction. On-line Raman spectra during tensile tests and Raman mapping measurements were performed to reveal the reinforcement mechanism of surface-functionalized GE in IR. Results demonstrate that the modification of GE significantly improves the interfacial interaction of IR/SGE

nanocomposites. This strong interfacial interaction results in efficient load transfer and thus endows IR/SGE with superior mechanical properties.

2. Experiment

2.1. Materials

Highly purified graphite flakes (99.99%) with an average diameter of 40 μm were purchased from Qingdao Ruisheng graphite company, Qingdao, China. Isoprene rubber (IR) was purchased from Shanghai Sanlian Co., Ltd. Bis(triethoxysilylpropyl)tetrasulfide (BTESPT) with a purity of 95% was obtained from Chengdu Best Chemical Reagent Co., Ltd. Curing reagents including sulfur, zinc oxide (ZnO), *N*-cyclohexyl-2-benzothiazolesulfenamide (CZ), stearic acid (SA), and antioxidant *N*-isopropyl-*N'*-phenyl-*p*-phenylene diamine (4010 NA) were all kindly provided by Sichuan Haida Rubber Group Co., Ltd. *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were supplied by Tianjin Bodi Chemical Holding Co., Ltd., China. Other reagents were all of analytical-grade and commercially available.

2.2. Preparation of BTESPT-modified graphene oxide (SGO)

In this experiment, graphite oxide was synthesized from graphite flakes by using the Hummers method [39], then dispersed in deionized water by ultrasonic-treatment. The suspension was centrifuged at 10,000 r.p.m for 10 min to remove any unexfoliated graphite, thus a suspension of fully exfoliated graphene oxide (GO) was obtained and subsequently placed in a vacuum oven at 70 °C for several days to remove water. Dried GO was then modified by silane coupling agent BTESPT: GO (1.5 g) was dispersed in 300 mL DMF through ultrasonication and 0.15 g BTESPT was added to the suspension. The suspension was further sonicated for half an hour and then maintained at 70 °C for 24 h under agitation. The resulting modified GO was collected by filtration and washed with pure DMF, and then re-dispersed in DMF by ultrasonic exfoliation at a concentration of 5 mg/mL. As is determined by weighing the weight of GO, BTESPT and SGO, the grafting efficiency is about 91%.

2.3. Preparation of IR/SGE nanocomposites

12 g of IR was completely dissolved in 700 mL of THF under agitation for 24 h. Different amounts of SGO in DMF were added into the IR solution under vigorous agitation to produce homogeneous mixtures with different SGO loading. Then, hydrazine hydrate with a ratio of 30 μL per 1 mg SGO was added into the solution, which was stirred for 24 h at 70 °C to reduce SGO *in situ*. Subsequently, most of the solvents in resulting mixture were evaporated at 60 °C while keeping stirring. The mixture was then placed in a vacuum oven at 60 °C for 48 h to remove the residual solvent. The loadings of SGE in the rubber matrix, including 0.1, 0.2, 0.5, 1 and 2 parts per hundred rubber (phr), were calculated according to initial SGO weight fractions.

To cure the mixture, curing agents were added in an open twin-roll mill (SK-160B, Shanghai Huaxing Machinery Co. Ltd, China) at room temperature with a friction ratio of 1:1.2 and a nip gap of ca 1 mm. Then the mixed pastes were compression molded at a temperature of 143 °C and a pressure of 15 MPa for their optimum cure time (t_{90}) determined by the curing curve. The formula of the curing agents is shown in Table 1. For comparison, samples of IR filled with GE reduced from GO but without modification were also prepared in the same way.

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