



Constructing a segregated graphene network in rubber composites towards improved electrically conductive and barrier properties



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ABSTRACT

A simple and effective approach, *i.e.* pre-construction method, was developed to fabricate a three-dimensional segregated graphene network (IL-3DGE) in a styrene butadiene rubber (SBR) matrix. Such segregated 3D-GE network dramatically enhanced the electrical conductivity, mechanical properties and gas barrier property of SBR composites. With the incorporation of 1.66 vol% IL-3DGE, the electrical conductivity of the composites was significantly enhanced by 10 orders of magnitude, the tensile strength was increased by 516%, and gas permeability was effectively reduced by 75.5%, as compared with those of neat SBR. Specifically, SBR/IL-3DGE with a segregated morphology showed a much low electrical percolation threshold (0.39 vol%), which is approximately 9-fold lower than that of the non-segregated SBR/IL-GE (3.78 vol%). The excellent properties of the composites were attributed to the construction of a 3D segregated conductive structure and strong interfacial interactions. This work provides a new insight into the fabrication of high-performance rubber composites for versatile practical applications.

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1. Introduction

Polymer composites with high electrical conductivity are of considerable attention because of their versatile applications such as sensor [1,2], photovoltaic devices [3,4], conductor [5,6], actuators [7,8], and electromagnetic shielding [9,10]. Graphene (GE) has attracted a considerable amount of interest because of its two-dimensional structure, large specific surface area, and superior properties [11,12]. There have been a theoretical study reporting that GE is more effective for conductivity enhancement than other competing nanofillers such as carbon nanotubes due to its special structure characteristics [13]. Particularly, GE has been widely utilized as electrically conductive filler in polymer composites in view of its potential to dramatically confer upon host polymer the high electrical conductivity and low percolation threshold. For example, Xing et al. [14] reported that a styrene butadiene rubber-GE composite had achieved an electrical conductivity that could already satisfy the antistatic criterion (10^{-6} S/m) with a GE content of 3 phr. Das et al. [15] developed a mechanical mixing process to fabricate the conductive solution styrene butadiene rubber/GE composites

with a percolation threshold of 6.24 vol%. However, the electrical conductivity of these fabricated composites is still far below an expected level, even if homogeneous dispersion of GE has been achieved. Its obstacle lies in the fact that there still exists high junction contact resistance between GE in the composites, greatly lowering the conductivity enhancement of GE towards the host polymer.

To date, constructing a three-dimensional (3D) segregated GE network in polymer matrix provides a new strategy for fabricating highly conductive GE-based composites with low percolation threshold [16–18]. 3D segregated GE network can dramatically reduce the junction contact resistance between GE, and significantly enhance the electrical conductivity of polymer composites. For these segregated GE-based polymer composites, the GE sheets are primarily located at the interfaces between the polymer matrix particles instead of being randomly dispersed throughout the matrix. Recently, Luo et al. [19] reported that 3D segregated GE networks in natural rubber (NR) matrix were framed with self-assembly integrating latex compounding technology, efficiently endowing the nanocomposites with excellent electrical conductivity of 7.31 S/m with a GE content of 4.16 vol%, extremely low percolation threshold of 0.21 vol%. Also, Wu et al. [20] fabricated a highly conductive polymer nanocomposite with 3D compactly segregated GE networks by a self-assembly process, and a

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percolation threshold was achieved as low as 0.15 vol%. Although 3D segregated GE network have been constructed in some previous reports [20–22], the attention paid to design and construct 3D GE network in a polymer matrix is still scarce so far. Unfortunately, what is noteworthy is that these conductive composites always suffer from various drawbacks: (i) imperfect segregated GE network, and (ii) poor interfacial interaction between the matrix and fillers, and relatively inferior mechanical performance. Therefore, it remains a challenge to develop a simple method to achieve highly conductive composites with a compact segregated GE networks, as well as comparable mechanical performance.

Herein, we present a simple and effective route, *i.e.* pre-construction method, to fabricate the SBR composites with 3D segregated GE networks, synchronously having high electrical conductivity, comparable mechanical strength and gas barrier property. This approach exhibits very competitive for applying to highly conductive materials in electronic industry, and gas transport and storage devices, *etc.*

2. Experimental

2.1. Materials

SBR latex (solid content of 60 wt%), was manufactured by Lanzhou Petrochemical Co. Ltd. Graphite powder was purchased from Shanghai Colloidal Co. Ltd. Calcium chloride (CaCl₂), toluene, sodium hydroxide (NaOH) and hydrazine hydrate was provided by Guangzhou Chemical Reagent Factory. 1-vinyl-3-ethylimidazolium bromide (IL) was supplied by Shanghai Cheng Jie Chemical Co., Ltd. Rubber additives such as zinc oxide, stearic acid, accelerant CZ, accelerant DM, antioxidant MB and sulfur were obtained from Guangzhou Longsun technology Co., Ltd. All the rubber ingredients were industrial grade and were used as received.

2.2. Preparation of 3D graphene oxide (3D-GO)

Firstly, graphite oxides were prepared according to our previous work and the yield of GE is about 45% from GO [23]. And polystyrene (PS) microspheres were synthesized by dispersion polymerization, details of which were consulted from our previous work [24]. Then, 3D-GO was synthesized by a self-assembly process. Specifically, 200 g GO suspensions (0.25 wt%) and 500 g PS microspheres suspensions (0.2 wt%) were obtained by a sonication process, respectively. Afterwards, PS@GO hybrids were fabricated by mixing GO and PS solution at PH = 6 accompanied with vigorous stirring. The obtained hybrids were purified by repeated washing, and then freeze-dried under vacuum for 12 h. Finally, the 3D-GO was achieved by removing the PS microspheres with toluene exposure.

2.3. Preparation of IL modified 3D graphene (IL-3DGE)

IL-3DGE was prepared by reducing 3D-GO with hydrazine hydrate in the presence of IL, thereinto, the mass ratio of IL and 3D-GO was set at 8/1. The reducing temperature and time were set as 95 °C and 2.5 h, respectively. As a comparison, 3D-GE was synthesized by direct chemical reduction of 3D-GO with hydrazine hydrate in aqueous solution. The IL-3DGE suspensions were firstly obtained by sonication, and then evenly dispersed in SBR latex. Subsequently, the rubber additives (sulfur, accelerator, *etc.*) and OP emulsifier were well-dispersed into the latex and then the mixed latex was coagulated. After filtering, the solid mixture was vacuum dried at 50 °C for 24 h. The obtained compounds were directly hot pressed and vulcanized at 160 °C to obtain the SBR/IL-3DGE-x. For comparison, SBR/IL-GE-x without segregated network was prepared

following the same procedures of the SBR/IL-3DGE-x. Herein, x represents the IL-3DGE or IL-GE content as parts per hundred parts of rubber, set to be 0.5, 1.0, 2.0, 4.0, 6.0, 8.0 and 10 phr in the composites. The formulation of the SBR composites is shown in the Table 1. Note that the pre-construction method for fabricating SBR composites with a segregated 3D-GE network is schematically illustrated in Scheme 1.

2.4. Characterization

Transmission electron microscopy (TEM) was performed on a JEOL2100 microscope. Scanning electron microscopy (FESEM) was analyzed by a Nova NANOSEM 430. Zeta potential measurements were performed using a Zetasizer Nano-ZS. Fourier transform infrared spectroscopy (FT-IR) was recorded on a Bruker Vertex Fourier Transform Infrared Spectrometer. Thermogravimetric analysis (TGA) was collected on a Netzsch TG209F1 apparatus with a heating rate of 20 °C/min under nitrogen atmosphere. The mechanical performances for all the samples were tested on a U-CAN UT-2060 Testing Machine (Taiwan) at room temperature with relative humidity about 65%, and all the specimens were stretched at a crosshead rate of 500 mm/min according to a China Standard GB/T 528–1998. Also, five specimens from each sample were taken for mechanical testing, and then the mechanical performances were obtained by taking an average for these five specimens. The nitrogen permeability of samples was measured with a gas permeability tester (VAC-V2, Labthink Instruments). All the samples were circular-shaped specimens with 50 mm diameter and 0.5 mm thickness. The electrical conductivity of samples was measured by a two-point measurement using a digital source-meter [21].

3. Results and discussion

To fabricate the PS@GO hybrids, the surface charges of GO and PS microspheres were examined by the zeta potential measurements. As shown in Fig. 1, PS microspheres and GO are positively and negatively charged at pH = 6, respectively. This provides a feasible opportunity for the assembly of GO sheets onto the surface of PS microspheres through the electrostatic interaction, which is evidenced by the TEM observation (Fig. 4a). For further observing the assembly behavior between the GO and PS microspheres, SEM was performed to investigate the morphology of the samples. As illustrated in Fig. 2, the synthesized PS particles are ideally spherical with particle size ~2 μm. And notice that GE sheets accomplished by the chemical reduction are inclined to agglomerate due to the high specific surface area and van der Waals interactions [25,26]. After the assembly process, the crumpled and ultrathin GE

Table 1
The experimental formula of SBR composites.

Compounds	Content/phr ^a
SBR	100
IL-3DGE/IL-GE	0, 0.5, 1, 2, 4, 6, 8, 10
Zinc oxide	5
Stearic acid	2
Accelerator CZ ^b	1.5
Accelerator DM ^c	0.5
Antioxidant MB ^d	1
Sulfur	1.5
OP-10	2

^a Parts per hundred parts of rubber.

^b N-cyclo-hexylbenzothiazole-2-sulphenamide.

^c 2,2'-dibenzothiazole disulfide.

^d 2-mercaptobenzimidazole.

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