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Fabrication of conductive elastic nanocomposites via framing intact interconnected graphene networks

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ABSTRACT

Electrically conductive elastic nanocomposites with well-organized graphene architectures offer significant improvement in various properties. However, achieving desirable graphene architectures in cross-linked rubber is challenging due to high viscosity and cross-linked nature of rubber matrices. Here, three dimensional (3D) interconnected graphene networks in natural rubber (NR) matrix are framed with self-assembly integrating latex compounding technology by employing electrostatic adsorption between poly(diallyldimethylammonium chloride) modified graphene (positively charged) and NR latex particles (negatively charged) as the driving force. The 3D graphene structure endows the resulted nanocomposites with excellent electrical conductivity of 7.31 S/m with a graphene content of 4.16 vol.%, extremely low percolation threshold of 0.21 vol.% and also analogous reinforcement in mechanical properties. The developed strategy will provide a practical approach for developing elastic nanocomposites with multi-functional properties.

1. Introduction

Electrically conductive elastic nanocomposites with excellent abrasive resistance, high elasticity and good tightness have been widely used in various fields including sealing [1], electrostatic paints [2], electromagnetic shielding [3], stretchable electronics [4], flexible displays [5], smart skin [6], and implantable devices [7]. With low density, good chemical resistance, excellent electrical property, carbon-based fillers, such as carbon blacks [8], carbon fibers [9], carbon nanotubes (CNTs) [10] and graphene [11], have been introduced into elastomers (or rubbers) to take the advantages of the synergetic effect from the conductive carbon fillers and elastomers. Graphene, a quasi-two dimensional sp^2-hybridized carbon based nanoscale building blocks, has particularly been a good candidature for this purpose due to its large specific surface area, excellent mechanical flexibility, extremely high electron mobility and fascinating transport phenomena [12]. It has been found that graphene, compared with other nanofillers, could endow polymer nanocomposites with lower percolation threshold, higher electrical conductivity, greater critical exponent, and maintain the excellent flexibility of elastic matrices [13]. Although graphene-based elastic nano-composites have been fabricated with various methods [14,15], fabrication of continuous graphene conductive network in the cross-linked rubber matrices with high viscosity remains to be a major challenge in the development of highly conductive composites with desirable electrical percolation behavior.

Theoretically, an inspiring electrical percolation behavior, i.e. high conductivity combined with low percolation threshold, mainly depends on the geometrical conduction pathway stemmed from an intact infinite network of conductive fillers that are connected in some senses [16,17]. Dispersion of the fillers and interfacial interaction between fillers and polymer molecules are the two key factors that may affect the conductivity of the composites. To achieve a good dispersion of graphene, a great number of efforts have been made by surface modification with dispersants or polymers [18,19]. For example, surfactant stabilized graphene is individually incorporated in styrene butadiene rubber, which improves its conductivity even with a low percolation threshold [20]. However, the composites still show unfulfilling electrical conductivity and have high inter-sheet junction contact resistance

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between graphene sheets. Furthermore, it is found that highly dispersed graphene in matrix does not always guarantee a significant improvement in electrical property when graphene is dispersed within matrix in an inconsecutive manner [21]. Recently, assembling individual graphene nanosheet into layered or porous 3D microstructures and ultimately embedding them in polymer matrices provide graphene-based materials with large accessible specific surface areas, interconnected conductive network and excellent electrical properties [22]. Several strategies including porosity engineering [23], chemical vapor deposition [24], and in situ gelation [25] have been used to construct 3D graphene networks in synthetic polymer, however, few efforts have contributed to construct such networks in cross-linked natural rubber (NR).

Table 1
The experimental formula of graphene/NR composites.

Compounds	Content/phr[a]
NR	100
PDDA-graphene	0, 0.5, 1, 2, 3, 5
Sulfur	2.3
Zinc oxide	5
Stearic acid	3
Accelerator NS[b]	0.7
Antioxidant MB[c]	2
Diffusant NNO[d]	0.27
Triton-100[e]	3
Casein	0.43

[a] Parts per hundred parts of rubber.
[b] 2-Mercaptobenzothiazole.
[c] 2-Mercaptobenzimidazole.
[d] Sodium salt of polynaphthalene sulfonic acid.
[e] t-Octylphenoxypolyethoxyethanol.

Herein, we frame interconnected graphene 3D networks into cross-linked NR matrices by employing electrostatic adsorption as the driving force as used in our previous work on self-assembled NR/CNTs [26] and NR/silica [27] systems. This approach offers not only a uniform dispersion of graphene, but also an intact continuous 3D graphene network in cross-linked NR. Owing to the well-organized graphene microstructures, the graphene /NR composites exhibit high electrical conductivity, very low percolation threshold and comparable mechanical properties.

2. Experimental

2.1. Materials

Natural rubber latex (NRL) with a total solid content of 60 wt.% was sourced from Shuguang Rubber Farm (Maoming, PR China). Natural graphite powder (density $\rho = 2.26\ g/cm^3$, CP) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, PR China). Poly(diallyldimethylammonium chloride) (PDDA), in the form of an 20 wt.% aqueous solution, was purchased from Sigma–Aldrich (Sigma–Aldrich, Louis, MO). Other chemical reagents including sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrochloric acid (HCl), hydrazine hydrate ($N_2H_4{\cdot}H_2O$) and hydrogen peroxide (H_2O_2) were all analytical grade and obtained from Guanghua Sci-Tech. Co., Ltd. (Guangzhou, PR China). Vulcanizing agents such as sulfur, zinc oxide, stearic acid, accelerant NS, antioxidant MB, diffusant NNO, casein and Triton-X100 were CP grade.

2.2. Preparation of PDDA modified graphene

Graphene oxide (GO) was prepared according to a modified Hummers' method [28,29]. PDDA modified graphene (PDDA-graphene) was prepared by reducing GO with $N_2H_4{\cdot}H_2O$ in the

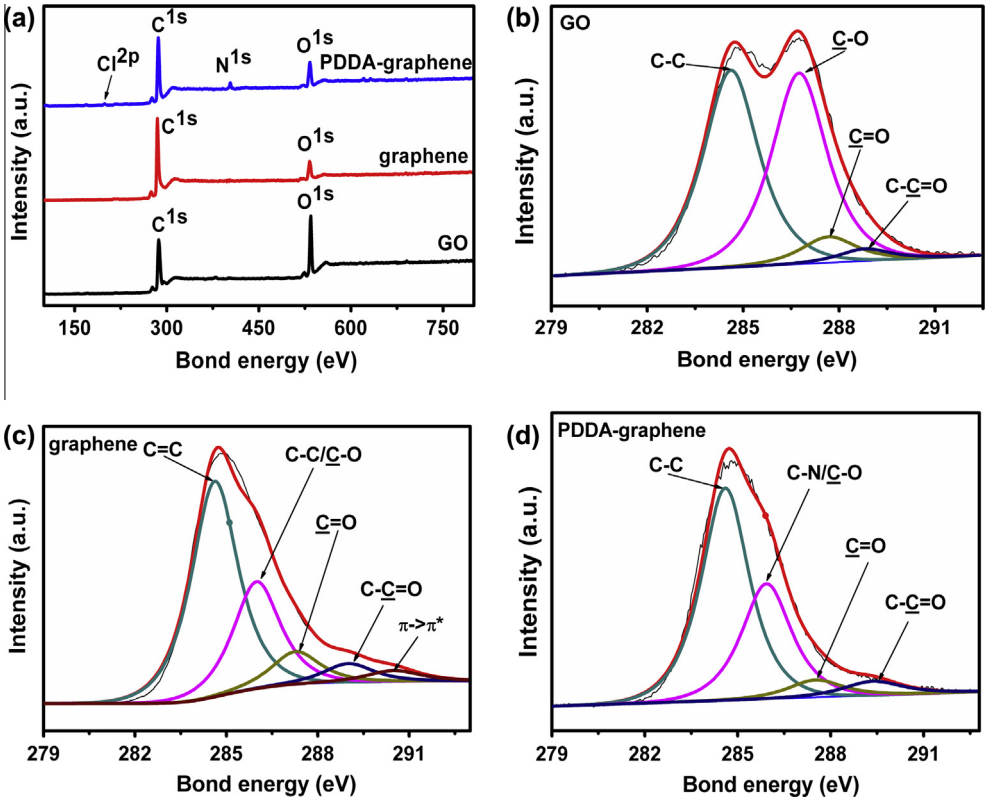

Fig. 1. (a) XPS spectra for GO, graphene and PDDA-graphene and (b–d) their corresponding high-resolution C^{1s} spectra.