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Enhanced electrical and mechanical properties of rubber/graphene film through layer-by-layer electrostatic assembly

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ABSTRACT

Despite a large amount of work have been carried out to prepare polymer/graphene hybrid nanocomposites, preparing rubber composites filled with graphene oxide via layer-by-layer (LBL) electrostatic self-assembly has not yet been reported. In this work, free-standing conductive multilayer film of $(\mathrm{PEI/XNBR/PEI/GO})_{30}$ (30 is referred to the number of deposition cycles) was fabricated on glass substrate through alternative LBL self-assembly with graphene oxide (GO), carboxylic acrylonitrile butadiene rubber (XNBR) latex, and polyethyleneimine (PEI). During the self-assembly process, negatively charged carboxyl groups on XNBR latex and GO sheets can be electrostatically bound by positively charged amino groups from PEI molecules. After thermal treatment, XNBR latex particles in each layer are gradually mixed together and became a continuous rubber film layer, and partial ionic bonds among XNBR latex, PEI and GO sheets are changed into covalent amide bonds. The formation of the multilayer XNBR/graphene film with ordered arrangement of GO sheets and XNBR latex layers was demonstrated by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The obtained XNBR/graphene film exhibited a significant improvement in mechanical properties, namely, 192% increase of the tensile strength and 215% increase of the elastic modulus. Besides, electrical conductivity of the prepared multilayer film reached 8.2E-03 S cm^{-1} after thermal reduced reaction. Hopefully, this prepared multilayer film may be potentially used as an elastomeric conductive material.

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1. Introduction

Graphene, first discovered in 2004 [1], has attracted voluminous attention in the past decade. As many theoretical and experimental researches reported before, graphene possesses many excellent properties such as excellent mechanical properties [2,3], outstanding thermal conductivity [4], large specific surface area [5] and extraordinary electronic transport performance [6]. However, the poor solubility of graphene in both polar and non-polar solvents has great limitations in the preparation and application of graphene-based nanocomposites [7,8]. Compared with graphene, graphene oxide (GO) sheets have more potential applications owing to their oxygen containing groups such as carboxylic, hydroxyl, and epoxy [9–12]. These oxygen containing groups make GO form a stable aqueous colloid through electrostatic stabilization [13]. Therefore, GO can be applied in the fabrication of the highly dispersed graphene-based polymer nanocomposites [14]. Inspired by its large specific surface area and lamellar structure, GO sheets may serve as the building blocks to enhance the mechanical and electrical properties of the nanocomposites.

A layer-by-layer (LBL) self-assembly technique [15] has been exploited to fabricate novel, multifunctional hybrid films with predetermined organization of different components with nanometer precision [16]. GO sheets are negatively charged in aqueous

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solution at pH 6.5, thus they can be employed to prepare desired multifunctional films via LBL electrostatic self-assembly by alternation with cationic polyelectrolytes [17–20]. Through this strategy, precise control over the structures of composites could be realized in nanometer scale. Recently, researches on GO sheets have progressed remarkably in a wide variety of applications by LBL self-assembly technique, such as enhancement in mechanical property [21–25], super electrical devices like battery and super capacitors [26–28], and gas barrier application [29]. It can be seen that graphene-based nanocomposites via LBL self-assembly possess great potential applications in the area of functional materials.

It is noteworthy that high-structural integrity yet solution-processable graphene sheets have been developed for polymer composites [30–32], and once compounded with elastomers, these sheets can improve both mechanical properties and electrical conductivity [33,34]. There are mainly three methods which have been used for the fabrication of graphene/rubber nanocomposites: including mechanical blending [35–37], solution mixing [38,39], and latex co-coagulation [40,41]. Mechanical blending is widely used in mass production of both laboratory and factory, but it may lead to the aggregation of GO sheets under large filling amount of GO. Although solution mixing produces good dispersion and exfoliation of GO, the process of solvent evaporation will destroy the environment. Latex co-coagulation method involves mixing of latex and other fillers, and then the polymer blends can be co-precipitated by adding flocculants. In this way, GO can be well dispersed in the rubber latex, but the random orientation of GO limits the rubber/graphene compound's application. Currently, few studies are focused on using layer-by-layer self-assembly technology to develop elastomer nanocomposites [42–46]. Generally, researches were mainly focused on the following three aspects: the modification the rubber surface to optimize its resistance to wear [42], biocompatibility with living organism [43–45] and tissue engineering and biomedicine [46]. For instance, Sruanganurak et al. [42] deposited PMMA particles onto the natural rubber (NR) latex film by LBL technique to increase the glove's roughness and hardness. Besides, the method of LBL on rubber composites can be applied in biological research area. Davi et al. [45] found that the LBL film fabricated by poly(allylamine hydrochloride) (PAH) and NR was made of smaller and flattened particles, which was not efficient for the growth and proliferation of normal human fibroblasts. However, no effort in the preparation of graphene/rubber composites by using LBL self-assembly strategy has been made. This strategy allows the assembly of different organic and inorganic building blocks into well-defined composite films with precise control of the film thickness and desired architecture.

In this article, we first demonstrated the successful fabrication of the free-standing multilayer films of alternating negatively charged GO sheets, positively charged polyethyleneimine (PEI), and negatively charged carboxylic acrylonitrile butadiene rubber (XNBR) latex by electrostatic LBL self-assembly. Then, the obtained multilayer films were transformed from insulation state to conductive state by thermal reduction. The growths, morphology, mechanical and electrical behaviors of the multilayer films were investigated in detail.

2. Experimental section

2.1. Materials

Polyethyleneimine (PEI) (branched, Mw = 50,000, 50%) was purchased from Sigma. P-type polished single-crystal silicon (111) wafers were procured from Huayan Silicon Materials Company (Zhejiang, China). The quartz slides were produced by Hongjun Optical Instrument Company (Jiangsu, China). Potassium permanganate ($KMnO_4$, 99.5%), sulfuric acid (H_2SO_4, 98%), sodium nitrate ($NaNO_3$, 99.0%), hydrogen peroxide (H_2O_2, 30%), hydrochloric acid (HCl, 37%), and methanol (CH_3OH, 99.5%), which were all used for the preparation of graphene oxide (GO), were supplied by Beijing Chemical Reagents Co., Ltd. (China). Carboxylic acrylonitrile butadiene rubber (XNBR) latex (NipolLX550L, acrylonitrile content ~27%, total solid ~45%) was provided by Nippon Zeon Corporation (Japan). Natural graphite flakes were supplied by Huadong Graphite Factory (China).

2.2. Synthesis of GO

Graphite oxide was prepared by oxidation of natural graphite power according to a modified Hummers' method [47]. Briefly, 50 mL of H_2SO_4 was put into a 500 mL three-neck flask in an ice-water bath, meanwhile 1.5 g natural graphite and 1.5 g $NaNO_3$ were added into the flask under stirring. Then, 6 g $KMnO_4$ was slowly added into the mixture in order to keep its temperature below 20 °C. Afterward, the mixture was heated to 35 °C and maintained for 40 min. Then, 69 mL deionized water was slowly added to avoid a high temperature of the solution above 98 °C. The mixture was further stirred for 20 min at 98 °C, then 170 mL deionized water and 35 mL H_2O_2 (30%) were put into the mixture. Later, the outcome was filtered, washed with 5% of HCl solution and methanol several times, and then dried in vacuum oven. Finally, graphite oxide was dispersed in deionized water under sonication for 40 min to prepare 0.5 mg/mL solution of exfoliated GO for LBL self-assembly.

2.3. Fabrication of GO/XNBR film

Firstly, the substrates of glass slides and silicon wafers were cleaned in “Piranha” solution (7:3 v/v of concentrated H_2SO_4:30% H_2O_2) for half an hour and washed with generous water, then dried in a steam of nitrogen. The multilayer films were constructed on the substrates by sequential adsorption of the positively charged PEI and the negatively charged GO and XNBR latex. The substrates were immersed in a PEI aqueous solution (2 mg/mL) for 5 min to get a positively charged surface, then rinsed with deionized water and dried by blowing N_2 gas. Then, the PEI-precoated substrates were then immersed in XNBR latex aqueous solution (2 mg/mL) for 5 min. Then, the substrates were heated at 120 °C for 2 min to make the water vapor rapidly so latex articles gradually contacted and fused to a successive film layer. Afterward, the substrates were re-immersed in PEI solution for 5 min, then rinsed and dried. After that, the substrates were immersed in the as-prepared GO dispersion for 5 min and rinsed with deionized water and dried again. Desired multilayered films of $(PEI/XNBR/PEI/GO)_n$ (n represents the number of deposition cycles) were obtained by repeated deposition cycles of the above mentioned alternating of XNBR latex, PEI and GO dispersion. The free standing films were got by immersing the substrates in 0.5% HF aqueous solution and rinsed by deionized water. Then, the resulting films were dried in room temperature for 24 h before characterization. The simple schematic representation of the assembling process and the target multilayer film structure were schematically indicated in Fig. 1. During the LBL electrostatic self-assembly process, negatively charged carboxyl groups of XNBR latex and GO sheets can be adsorbed by positively charged amino groups from PEI molecules through electrostatic attraction. After the assembled films heated by hot plate, part of the ionic bonds between XNBR latex, PEI and GO changed into covalent amide bonds. Finally, the multilayered rubber/graphene oxide films were fabricated with the structure of alternating GO sheets and XNBR latex layer.

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