Using a green method to develop graphene oxide/elastomers nanocomposites with combination of high barrier and mechanical performance

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ABSTRACT

Graphene oxide/carboxylated acrylonitrile butadiene rubber (GO/XNBR) nanocomposites with high mechanical and gas barrier properties were fabricated by using a simple and environment-friendly latex co-coagulation method. The oxygen-containing groups attached to the surface of GO generate strong interactions with the XNBR chains through hydrogen bonding (H-bonding), as confirmed by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimeter (DSC) results. The morphology of the nanocomposites was characterized by high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD), which show highly exfoliated and uniform dispersion of GO sheets in the matrix. The tensile strength and tear strength of the nanocomposite with 1.9 vol% of GO increased by 357% and 117%, respectively, over those of the matrix. The gas permeability of the nanocomposite is significantly lower than that of the matrix. The high mechanical properties and low gas permeability of the nanocomposite are correlated to the homogeneous dispersion of the GO sheets and strong interfacial interactions, which facilitate the load transfer from XNBR to the GO sheets.

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1. Introduction

Polymer nanocomposites based on carbon black, carbon nanotubes, and layered silicates have attracted extensive research and development in the past decades owing to their fascinating properties and numerous potential applications. Graphene, an atom-thick layer composed of sp²-hybridized carbons, has attracted interest due to its striking electrical, mechanical, thermal and gas barrier properties [1–5]. Thus, graphene is considered as a promising additive for development of functional polymer nanocomposites. However, pristine graphene cannot be used directly as fillers due to its high manufacturing cost and lack of functional groups for bonding with polymers. Therefore, most studies have focused on compounding polymers with graphene oxide (GO). GO, which is fabricated from natural graphite by oxidation, contains rich functional groups and can be readily dispersed in water to form a stable colloidal suspension [6]. GO has been compounded with various polymers, such as epoxy, polyamide, polyurethane, poly(vinyl alcohol), and polyester [7–11].

Three major methods have been used for fabrication of graphene/polymer nanocomposites: including melt compounding, solu-

tion mixing, and *in situ* polymerization [12]. Melt compounding is widely used in industry due to its compatibility with industrial facilities, but it is disadvantaged by a low degree of graphene dispersion and exfoliation, evidenced by a rather high percolation threshold of electrical conductivity [13]. Although solution mixing produces good dispersion and exfoliation [12], it is limited by (i) graphene stacking induced by slow solvent evaporation and (ii) the use of solvent posing an add-on cost and causing environmental pollution. *In situ* polymerization is the most effective in improving the dispersion and exfoliation of graphene in a matrix, and can create a covalent bonding interface between graphene and the matrix [8,11]; however, graphene's steric effect limits the growth of chains in polymerization, leading to poor mechanical properties. Few studies are focused on using latex co-coagulation technology to develop graphene/elastomers nanocomposites [13–16]. The latex co-coagulation method involves mixing the latex with other latices or fillers, and then the polymer blends can be co-precipitated by adding flocculants. Latex co-coagulation method is a simple and environment-friendly approach to obtain good dispersion of graphene in composites, since GO can be dispersed at the individual sheet level in water. Moreover, this method has been employed for the fabrication of carbon nanotubes and clay-based polymer composites [17,18].

Elastomers are a class of versatile polymers. Owing to their high elasticity, they are used in manufacturing tires, conveyors belts

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and hoses. As a polar elastomer, carboxylated acrylonitrile butadiene rubber (XNBR) features a high resistance to oil and oxidation. As XNBR suffers from insufficient mechanical properties in many applications, many kinds of reinforcements, including carbon black, clay, and expanded graphite have been explored for reinforcing XNBR [19,20]. For high performance polymer nanocomposites requires high interfacial adhesion between the filler and the polymer matrix, the so called effective load transfer. Hydrogen bonding (H-bonding) is identified as the strongest van der Waals interaction, which would produce a strong interface and promote stress transfer from the matrix to the dispersed phase effectively [21,22]. Recently, Wang et al. [23] have prepared GO/XNBR vulcanizates with improved mechanical properties and thermal conductivity. The relationship between structure and performance could help to interpret the enhancement of performances. However, this article put the emphasis only on the improved properties, and did not investigate the interaction between GO and XNBR. Hence, in this study we analyze and establish the relationship between structure and performance. The hypotheses made in this study include (i) since both XNBR and GO contain many oxygen-containing groups, H-bonding should occur and produce strong interfacial interactions, and (ii) the strong interfacial interactions would promote the dispersion of GO, transmit external loads to the GO sheets, and thus significantly improve the stiffness, strength, and gas barrier properties of XNBR.

Considering that GO can be readily exfoliated in water, we in this study adopted a simple and environment-friendly latex co-coagulation method to fabricate GO/XNBR nanocomposites. The interfacial interactions (H-bonding) were fully characterized. The morphology, mechanical properties and gas permeability of the nanocomposites were also investigated.

2. Experimental

2.1. Materials

Carboxylated acrylonitrile butadiene rubber latex (NipolLX550L, acrylonitrile content ~27%, total solid ~45%) was supplied by Nippon Zeon Corporation (Japan). Natural graphite flakes were supplied by Huadong Graphite Factory (China). Sulfuric acid (H_2SO_4), hydrochloric acid (HCl), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), calcium chloride ($CaCl_2$), hydrogen peroxide (H_2O_2) (30%), methanol and ammonia (25–28%) of analytical grades were purchased from Beijing Chemical Factory (China). Dicumyl peroxide (DCP) was used as received.

2.2. Preparation of graphene oxide

Graphene oxide (GO) was prepared by oxidizing natural graphite flakes according to a modified Hummers method [6]. Briefly, 46 ml of H_2SO_4 was put into a 500-ml flask in an ice-water bath, and 2 g of graphite and 1 g of $NaNO_3$ were added to the flask under stirring. Then, 3 g of $KMnO_4$ was slowly added to the above mixture. Stirring below 20 °C was continued for 2 h. The mixture was then heated to ~35 °C and kept there for 30 min before 46 ml of deionized water was slowly added below 80 °C. The resulting mixture was further stirred for 30 min at 98 °C, and 140 ml of deionized water and 8 ml of H_2O_2 (30 wt%) were added. The product was filtered, washed with 5% of HCl solution and methanol several times, and then finally dried in a vacuum oven at 60 °C for 24 h.

2.3. Preparation of GO/XNBR composites

First, 0.1 wt% of GO suspension was formed by dispersed GO in deionized water under sonication. The GO suspension was added into XNBR latex and stirred for 1 h. The mixture was co-coagulated by adding $CaCl_2$ aqueous solution (1.0 wt%) and dried at 50 °C. Then the dried mixture was mixed with DCP (0.5 phr relative to the XNBR) on a two-roll mill before being compression molded at 150 °C for the optimum curing time T_{90} determined by a vulcameter. The volume fraction of GO was determined by using the densities of 2.2 g/cm³ for GO and 1.05 g/cm³ for neat XNBR.

2.4. Characterization

Atomic force microscopy (AFM) was conducted in the tapping mode on an Agilent-5500 microscope. The sample was prepared by suspending GO in water at 1×10^{-5} wt% under sonication for 30 min, dropping the suspension on a silicon wafer, and drying in a vacuum oven. Fourier transform infrared spectra were collected on a Bruker Tensor 27 spectrometer. All the spectra were obtained at a resolution of 4 cm⁻¹ in the wavenumber range of 600–4000 cm⁻¹. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250 XPS system (Thermo Electron Corporation, USA) with an Al Kα X-ray source (1486.6 eV).

The transition temperature (T_g) was investigated using a Mettler–Toledo differential scanning calorimeter. All samples were cooled to −100 °C at 10 °C/min and reheated up to 100 °C at 10 °C/min. The strain amplitude dependence of storage modulus was measured on a RPA 2000 rheometer (Alpha Technologies, USA) at 60 °C and 1 Hz. The morphology was investigated by field emission scanning electron microscopy (FESEM, Hitachi SEM 4800) and high resolution transmission electron microscopy (HRTEM, JEOL2100). A swelling test was performed by immersing the sample into toluene for 72 h. The sample was weighed before immersion to obtain m_1. After immersion, the soaked sample was wiped and weighed to obtain m_2. The sample was dried in vacuum at 40 °C for at least 24 h and then weighed to obtain m_3. The swelling ratio is determined by Eq. (1):

$$\zeta = \frac{m_2 - m_1}{m_1} \tag{1}$$

The crosslink density (v_e) is calculated by using the Flory–Rehner equation [24]:

$$v_e = -\frac{\ln(1 - v_2) + v_2 + \chi v_2^2}{V_s(\sqrt[3]{v_2} - 0.5v_2)} \tag{2}$$

where V_s, the molar volume of solvent, is 106.3 cm³/mol for toluene, and χ is the Flory–Huggins interaction parameter between toluene and the XNBR, which is taken as 0.43. The rubber volume fraction (v_2) after swelling was calculated according to the equation:

$$v_2 = \frac{(m_3 - m_1\phi)}{(m_3 - m_1\phi) + (m_2 - m_3)\eta} \tag{3}$$

where ϕ is volume fraction of filler, and η is ratio of the density of elastomer to that of toluene.

Tensile tests were performed with dumbbell-shaped specimens according to ASTM D412 by using a CMT 4104 electrical tensile instrument (Shenzhen SANS Test Machine Co., Ltd., China) with a crosshead speed of 500 mm/min at 23 °C. The tear strength was determined by the same machine with a right-angle tear die C according to ASTM D624. For each measurement, five specimens were tested and the average taken. Nitrogen permeation tests were conducted at 40 °C according to the ISO 2782 differential-pressure method with a home-made apparatus. The pressure on one face of the sample sheet was kept at 0.57 MPa with pure nitrogen gas, and the other face at 0.1 MPa with a carrier gas (pure hydrogen). The rate of transmission of nitrogen was determined by gas chromatography from which the nitrogen permeability was calculated.