



Exfoliation approach for preparing high conductive reduced graphite oxide and its application in natural rubber composites



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ABSTRACT

High conductivity reduced graphite oxide (RGO) was prepared by exfoliation of graphite waste from the metal smelting industry. To improve the surface properties of the RGO, the graphite oxide obtained based on Hummers' method was reduced by L-ascorbic acid to give RGOV, which was then subjected to thermal reduction to obtain RGOT. The residual oxygen-containing groups in RGOV were almost completely removed by the thermal reduction and the conjugated graphene networks were restored in RGOT. The effect of the RGOT content in natural rubber (NR) on the cure, electrical and mechanical properties of the NR-RGOT (NG) composites was evaluated. The electrical conductivity of NR was increased by the inclusion of RGOT at a percolation threshold of 5 phr, with an electrical conductivity of 8.71×10^{-6} S/m. The mechanical properties, i.e., the modulus, tensile strength and hardness, of NG were comparable with those of conductive carbon black filled NR ones.

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1. Introduction

Recently, conductive polymers have received increased attention due to their potential use in a number of applications, such as electronic devices [1–3], solar cells [4–6], supercapacitors [7–9], sensors [10,11], electromagnetic interference shielding [12,13] and biomedical applications [14,15]. This intense interest of applying polymers in electronic devices is due to their ease of processing, low cost, wide range of electrical properties and light-weight nature compared to metals. However, the limitation of polymers for most practical applications is their low conductivity. Accordingly, diverse methods have been used to induce electrical conductivity, such as mixing the polymer with a conjugated conducting polymer (polypyrrole [16] or polyacetylene [17]) or a conducting solid (metal [18,19], carbon black [11,20] or carbon nanotubes [21,22]). The difficulty in preparing polymer blends is the different polarity between the polymers, resulting in their phase incompatibility and inferior mechanical and electrical properties. Although the addition of a conductive metal solid into the polymer matrix is an alternative approach, it is rarely used because the metal component is easily oxidized. To improve the polymer conductivity, carbon black has been developed as an alternative

filler to metals. The carbon black is currently obtained from the incomplete combustion of hydrocarbon feedstock. However, graphene, a single-layer carbon sheet with a hexagonal packed lattice structure, has received increasing attention as a substitute for carbon black because it generally shows excellent mechanical, electrical and thermal properties [23–26].

Several methods have been used to synthesize graphene, such as chemical vapor deposition [27,28], unzipping of carbon nanotubes [29,30] and epitaxial growth on silicon carbide [31,32]. However, such methods are not suitable for polymer composites that require a large amount of graphene. For the large scale production of graphene, the chemical exfoliation of graphite is more suitable, where the graphite powder is first oxidized and then reduced using a strong reducing reagent, such as hydrazine [33,34], hydroquinone [35] and sodium borohydride [36,37]. However, under these conditions, the chemicals are highly toxic. In addition, the introduction of heteroatoms in the reduced products may prevent delocalized electrons on the carbon planes in graphene sheets [38]. Consequently, approaches that reduce the graphite oxide (GO) into a graphene sheet under mild conditions using environmentally friendly reducing agents, such as alcohols [39,40], reducing sugars [41], amino acids [42,43] or L-ascorbic acid [44] (LAA) need to be explored. From 2010 to 2015, the worldwide graphite mine production was approximately 1,000,000 metric tons [45] and the mined graphite was applied in a number of technologies, specifically refractories, foundries and metallurgy,

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resulting in a high increase in the amount of graphite waste. Accordingly, in this study, reduced graphite oxide (RGO) was prepared via an exfoliation of graphite waste from the metal smelting industry in order to avoid competition with graphite and to add value to this graphite waste. However, the RGO obtained by chemical reduction was of a low conductivity (range of 0.5–1.0 S/m) [37]. Thus, a thermal reduction process was introduced to yield a high-quality RGO sheet with a high conductivity. For practical application such as fuel hoses, conveyor belts or automotive belts, natural rubber (NR) was used as a polymer matrix to produce conductive rubber due to its excellent mechanical properties, in terms of a high strength, high elasticity and low heat build-up. The effect of the RGO content on the cure characteristic, conductivity and mechanical properties of the NR-RGO composites was studied. All the obtained results were compared to NR filled with conductive carbon black (PRINTEX® XE2-B) as a reference. A structure-orientated model of the conductive RGO sheets prepared via the oxidation and reduction processes was proposed. The electrical conductivity model of RGO filled NR composite materials based on the Mamunya equation was also presented.

2. Experimental

2.1. Materials

The NR (STR-5L) was manufactured by PI Industry Ltd., (Thailand). Graphite powder was provided by Mahamek Flow Innovation Co., Ltd., (Thailand). Sulfuric acid (H_2SO_4), sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), sodium carbonate (NaCO_3), tetrahydrofuran (THF) and LAA were purchased from QREC Chemical Co., Ltd. (Thailand). Active zinc oxide (ZnO) and stearic acid as an activator, *N*-cyclohexylbenzothiazole-2-sulfenamide (CBS) as an accelerator, and sulfur as a crosslinking agent were obtained from PI Industry Ltd., (Thailand). Conductive carbon black (PRINTEX® XE2-B with mean particle size of 35 nm, specific surface area of $\sim 980 \text{ m}^2/\text{g}$, dibutyl phthalate (DBP) absorption of 420 ml/100 g, electrical conductivity by four-pint probe of 106.72 S/m) was bought from Kij Paiboon Chemical Ltd., (Thailand). All chemicals were of analytical grade and used as received.

2.2. Preparation of GO and RGO

The GO was synthesized from graphite waste via Hummers method [46]. Graphite (10 g) with a mixture of H_2SO_4 (230 ml) and NaNO_3 (5 g) was stirred and cooled in an ice-bath under 0–5 °C for 30 min. Then, KMnO_4 (30 g) was added gradually with stirring under an ice-bath. The temperature of the mixture was maintained below 20 ± 2 °C for 2 h. The mixture was then allowed to rise to room temperature for 30 min. Deionized water (460 ml) was slowly added to increase the reaction temperature up to 98 °C and the mixture was maintained at this temperature for 15 min. The reaction was terminated by adding deionized water (1.4 L) followed by 30% H_2O_2 solution (100 ml). The solid product was filtered with Whatman paper No. 40, washed by 10% HCl to remove the sulphate, washed by deionized water for several times and dried in an air oven at 60 °C for 12 h. The obtained GO (0.25 g) was dispersed in deionized water (100 ml) and sonicated in a portable ultrasonic cleaner (NXPC, KODO Technical Research, Korea) for 30 min in order to exfoliate the GO sheets by mechanical force. After sonication, samples were precipitated by a centrifuge (EBA 20, Hettich, UK) at 4000 rpm for 30 min and dried in air oven at 60 °C for 24 h.

Exfoliated GO (2 g) was added to 1 L deionized water. The pH of solution was adjusted to 9–10 by 5% Na_2CO_3 solution and then LAA

(8.8706 g) was added to the colloidal GO solution and stirred at 95 °C for 1 h. The reaction mixture was allowed to cool down to room temperature and filtered by Whatman paper No. 40. The solid product, referred to as “RGOV”, was washed by deionized water to remove residual ions and dried in an oven at 60 °C for 24 h. In order to remove residual oxygen-containing groups in the carbon planes, the RGOV was annealed under vacuum at 750 °C for 1 h to yield “RGOT”. The abbreviation of V and T means the reduction of GO by L-ascorbic acid and thermal, respectively.

2.3. Preparation of NR-RGO and NR-conductive carbon black composites

One hundred parts per hundred of rubber (phr) of NR was mixed with 4 phr ZnO, 2 phr stearic acid, 1 phr CBS, 2.5 phr sulfur and conductive fillers (RGOT or conductive carbon black at 5–25 phr) in an internal mixer (Barbender, Germany) at 50 °C and 40 rpm for 13 min. In order to achieve a good dispersion, the compounding was mixed again by a two-roll mill. The total mixing time was less than 20 min to avoid premature vulcanization from the excess heat generated during compounding. The cure characteristics of the NR compounding were determined by a Moving Die Rheometer (TECHPRO rheotech MD+, US) at 150 °C according to ASTM D5289. Subsequently, NR vulcanizates (NR-V) were performed by compression molding at 150 k/m² at 150 °C with the optimum cure time (t_{c90}). The composites are referred to as NC-x and NG-x for the NR composites with conductive carbon black and RGOT, respectively, where x is the amount of conductive carbon black or RGOT in phr.

2.4. Characterization of GO and RGO

The obtained RGO was characterized by fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM) and four-point probe.

The functional groups of the samples were determined by FTIR (PerkinElmer, Inc., Spectrum one, USA). The samples were evaluated using KBr pellets and examined in the attenuated total reflectance (ATR) mode. The scan was performed in the range of 500–4000 cm^{-1} with a spectral resolution of 0.5 cm^{-1} .

Elemental composition analysis and functional groups on surface of samples were measured using XPS (PerkinElmer, Inc., USA). The XPS spectra were taken at a working pressure under 10^{-7} Pa with a monochromatic AlK_α radiation source.

The structure of samples were characterized by XRD (Bruker, D8 advance X-ray diffractometer, Germany) with a CuK_α radiation source ($\lambda = 1.54 \text{ \AA}$). The X-ray was operated at 40 kV and 40 mA with a scanning rate of 5–50° changing at 0.1°/s.

The morphology of all samples was examined by TEM (JEOL JEM-2100, Japan). The sample (0.5 mg) in THF solvent was sonicated in a bath sonicator for 5 min and then the colloidal solution was drop cast on the TEM grid.

Surface area determination of samples was performed by the Brunauer-Emmett-Teller (BET) method (Autosorb-1, Quantachrome, Germany). The nitrogen (N_2) adsorption isotherm was recorded at 77 K. All samples were degassed at 250 °C for 3 h under vacuum before analysis.

The conductivity of sample powder was determined by four-point probe (RM3-AR, JENDEL, UK). The powder was compressed to from a pellet using a hydraulic press machine.

The surface energy and the wettability of the composite materials were investigated by water contact angle measurement (Raméhart, USA) at ambient temperature. The sample particles were ground to a powder and pasted onto a glass slide with adhesive tape. The water contact angle was measured by placing a 50 μl

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