Electrically and thermally conductive elastomer/graphene nanocomposites by solution mixing

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ABSTRACT

The greatest challenge in developing polymer/graphene nanocomposites is to prevent graphene layers stacking; in this respect, we found effective solution-mixing polymers with cost-effective graphene of hydrophobic surface. Since graphene oxide is hydrophilic and in need of reduction, highly conducing graphene platelets (GnPs) of ∼3 nm in thickness were selected to solution-mix with a commonly used elastomer — styrene–butadiene rubber (SBR). A percolation threshold of electrical conductivity was observed at 5.3 vol% of GnPs, and the SBR thermal conductivity enhanced three times at 24 vol%. Tensile strength, Young's modulus and tear strength were improved by 413%, 782% and 709%, respectively, at 16.7 vol%. Payne effect, an important design criteria for elastomers used in dynamic loading environment, was also investigated. The comparison of solution mixing with melt compounding, where the same starting materials were used, demonstrated that solution mixing is more effective in promoting the reinforcing effect of GnPs, since it provides more interlayer spacing for elastomer molecules intercalating and retains the high aspect ratio of GnPs leading to filler–filler network at a low volume fraction. We also compared the reinforcing effect of GnPs with those of carbon black and carbon nanotubes.

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1. Introduction

Graphene, a new star arising over the horizon of materials science, consists of sp^2 hybridized carbon atoms arranged in honeycomb structure with one atom thickness and plate-like structure [1–4]. So now the family of carbon allotropes is completed: 0-dimensional fullerenes, 1-D nanotubes, 2-D graphene and 3-D graphite [2]. Graphene is considered as the strongest material since it possesses a Young's modulus of 1 TPa and an ultimate strength of 130 GPa, and can elongate to a quarter of its original length. Moreover, it has unique electrical and thermal conductivities, up to 6000 S cm^{-1} and 5000 W m^{-1} K^{-1}, respectively, higher than the copper's. In addition, chirality is not a matter to its electrical conductivity — another advantage over carbon nanotubes (CNTs) [1–4].

Our group [5,6] has recently succeeded in producing graphene platelets (GnPs), each of which consists of 1–5 graphene layers, by thermally expanding a commercial graphite intercalated compound (GIC) in a common furnace and sonicating the expanded product. GnPs have advantages over graphene oxide (GnO), including (i) low production cost estimated at 10–20 US$/kg in comparison with 30 US$/kg for GnO excluding its reduction cost [5], (ii) high structural integrity as evidenced by a Raman I_D/I_G ratio of ∼0.07 [5,6] in comparison with ∼1.0 for reduced GnO [7], and (iii) maximum resemblance of the stiffness, strength and electrical and thermal conductivities of graphene [8]. More importantly, the GnP surface can be covalently modified by using amine-end, long-chain surfactants [6]; when the modified GnPs were in situ mixed with epoxy resin, a very low percolation threshold of electrical conductivity was observed at 0.25 vol%.

The high specific strength, low production cost and corrosion resistance of polymers make them favourable in industries. Adding nanofillers, such as carbon black, silica, layered silicates and carbon nanotubes, into polymers can dramatically improve their mechanical performance and functional properties. Although elastomers can elongate up to 1000% their original length, they are

limited by low strength, stiffness and thermal and electrical conductivities, which disadvantage the applications. Compounding nanofillers with elastomers is essential to address these limitations. Carbon black (CB) has been extensively used to reinforce elastomers. Because CB depends on petroleum, researchers during the last two decades developed alternatives including silica [9,10], layered silicates [11–13], starch [14,15] and CNTs [16,17]; of these, layered silicates have been extensively studied, because they are inexpensive and provide a high barrier property, albeit of their silicon oxide-based composition with very low electrical and thermal conductivities. Nevertheless, the cost of conductive, robust CNTs prohibits their applications. By contrast, graphene combining the advantages of layered silicates and CNTs are inexpensive since both GnO and GnPs are fabricated from graphite.

Cost-effective, high-structural integrity graphene platelets (GnPs) of 2–4 nm in thickness are proposed in this study as a class of nanofiller to develop functional elastomer nanocomposites by solution mixing as most elastomers are synthesized by solution polymerization. It is a daunting challenge to prevent graphene stacking in polymer matrixes; and a well-known strategy is to use solution mixing. Ruoff et al. [18] has recently found that compounding methods could pose a significant effect on the morphology and properties of natural rubber/reduced graphene oxide nanocomposites which were fabricated at below 5 wt% of reduced graphene oxide— such a low fraction was chosen possibly due to the fabrication process of graphene and its chemical reduction.

Fig. 1 illustrates the procedure of compounding GnPs with SBR in this study, which includes (i) using a common furnace with an ultrasonication bath, to produce cost-effectively GnPs, (ii) employing solution mixing to compound GnPs with a popularly used elastomer in industries – styrene-butadiene rubber (SBR), (iii) investigating the structure–property relations of these nanocomposites, and (iv) comparing solution mixing with our previous melt compounding [19] in terms of mechanical performance and functional properties of the prepared nanocomposites. Our investigation shows that the solution method takes more advantages of GnPs, as evidenced by the remarkable improvement in mechanical properties and the low electrical conductivity percolation threshold.

2. Experimental section

2.1. Materials

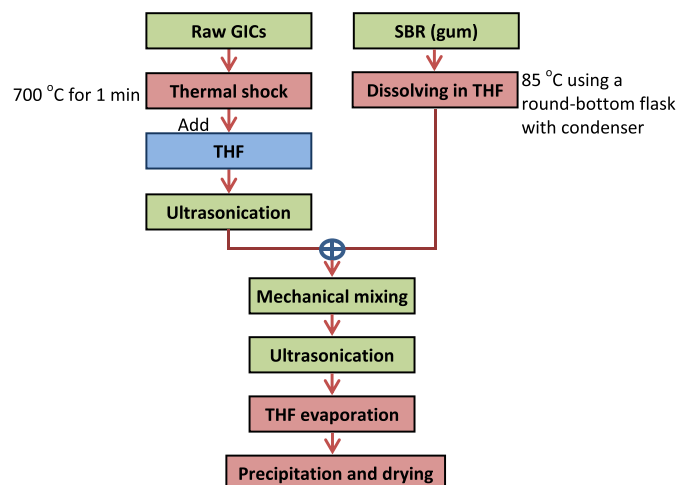Styrene–butadiene rubber (SBR 1502), consisting of 23.5% styrene and 76.5% butadiene with a Mooney viscosity of ML(1 + 4) at 100 °C = 52, was provided by Jilin Petrochemical Limited, China. Asbury Carbons (Asbury, NJ) kindly provided free samples of a commercial graphite intercalated compound (GIC, Asbury 3494). Curing chemicals were purchased from market, with the vulcanization recipe presented in Table 1. Tetrahydrofuran (THF) was purchased from Sigma–Aldrich (Australia). Curing chemicals and GICs were used as received without any purification. Other chemicals used in this study were brought from market.

2.2. Preparations

Graphene platelets (GnPs). 1 g of GIC was transferred into a crucible preheated in a common furnace at 700 °C and treated for 1 min. The expanded product was left to cool down. Safety procedures, such as placing the furnace in the fume cupboard to prevent nanospecies inhaling hazard and wearing safety glasses, respirator, and heat resistant gloves, are required in this process. A desired amount of the expanded product was immersed in THF (1 wt%) in a metallic container and treated in an ultrasonication bath (200 W at 42 kHz) for 1 h below 30 °C. Upon sonication, the expanded product in suspension was able to split into platelets of 2–4 nm in thickness, as evidenced in our previous works [6,20]. This suspension would be used for the following preparation of nanocomposites.

Elastomer/GnP nanocomposites. A given weight of styrene–butadiene rubber (SBR) was dissolved in tetrahydrofuran (THF, 4 wt%) and heated to 90 °C using an oil bath and a round-bottom flask equipped with a condenser. To prevent SBR sticking to the flask bottom, we split it into many small pieces, and added one by one with magnetic stirring. The SBR solution was mixed with the aforementioned suspension under mechanical stirring at 200 rpm, followed by 1 h sonication below 30 °C. Then 60% of THF was evaporated by heating up to 60 °C with mechanical stirring. Using ethanol, the nanocomposite was precipitated, collected, washed and dried at 60 °C using a ventilated oven for 12 h. The density of graphene was taken as that of graphite, 2.26 g/cm^3, and the matrix density was assumed to be 1.043 g/cm^3; thus we were able to convert wt% to vol%.

To produce samples for characterization and various measurements, a vulcanization process was performed on these mixtures. A laboratory size, two-roll mill with a nip clearance 1 mm and a friction ratio 1.3 was used to compound curing chemicals (the recipe described in Table 1) with the elastomer/GnP mixtures at room temperature. The vulcanization was conducted in an electrically heated compression-molding hydraulic press. Vulcanization conditions were determined and optimized according to a previous study [19], where samples were heated under 3 MPa at 150 °C for 23 min. The cured samples had been stored for 48 h before testing.

2.3. Graphene platelets and nanocomposite characterization

X-ray diffraction (XRD) spectra of GIC, expanded product, GnPs and nanocomposites were collected in a reflected mode using a Mini-Materials Analyzer (MMA) with a diffractometer equipped with curved graphite monochromators with CuKα radiation (wave

Fig. 1. Schematic of solution-mixing graphene platelets with elastomer.

Table 1
Recipe of elastomer/GnP nanocomposites.

Material	Weight (g)
SBR	100
Sulfur	2
Dibensothiazole disulfide (DM)	0.5
Diphenylguanidine (D)	0.5
Tetramethylthiuram disulfide (TT)	0.2
GnPs	Variable