Polymer 54 (2013) 3663–3670

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

A novel approach to electrically and thermally conductive elastomers using graphene

Sherif Araby [a,d], Liqun Zhang [b], Hsu-Chiang Kuan [c], Jia-Bin Dai [a], Peter Majewski [a], Jun Ma [a,b,*]

[a] School of Engineering, University of South Australia, SA 5095, Australia
[b] Key Laboratory for Nanomaterials, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China
[c] Department of Energy Application Engineering, Far East University, Tainan County 744, Taiwan
[d] Department of Mechanical Engineering, Faculty of Engineering, Benha University, Egypt

ARTICLE INFO

Article history:
Received 16 December 2012
Received in revised form
28 February 2013
Accepted 6 May 2013
Available online 13 May 2013

Keywords:
Graphene
Elastomers
Composites

ABSTRACT

Electrically and thermally conductive elastomers are highly desired in industries, since they can prevent static electricity accumulation and reduce internal heat build-up. Previous methodologies using carbon black, metal nanoparticles and carbon nanotubes are either ineffective or expensive. By contrast, we in this study developed electrically and thermally conductive, high-mechanical performance elastomers, by adopting cost-effective, high-structural integrity graphene platelets (GnPs) of 3.55 ± 0.32 nm in thickness and employing an industrial compatible method. A percolation threshold of electrical conductivity was observed at 16.5 vol% GnPs, and the elastomer thermal conductivity improved 240% at 41.6 vol%. At 24 vol%, tensile strength, Young's modulus, and tear strength improved 230%, 506% and 445%, respectively. By comparing the reinforcement effect of GnPs with those of carbon black, multi-walled carbon nanotubes and silicate layers, we found that GnPs are a promising candidate for developing cost-effective, functional, high-mechanical performance elastomers.

1. Introduction

Graphene is a well-known rising star in science, since it features higher electrical and thermal conductivities than copper, is the stiffest, strongest material ever measured, and upon loading, is able to elongate 25% of its original length [1,2]. In spite of the extensive research conducted for graphene in electronic and energy industries, the research for graphene/polymer composites has not been so progressive, due to the following reasons: (i) graphene fabricated by micromechanical exfoliation [3,4], chemical vapour deposition [5,6] and epitaxial growth [7,8] is not suitable for polymers owing to its large lateral dimension; and (ii) graphene oxide (GnO) prepared by harsh oxidation of graphite provides suitable size and rich surface functional groups, but it is disadvantaged by the low structural integrity, leading to highly reduced strength one-fourth of typical graphene with no or little conductivities [9]. The integrity can be more or less improved by reduction that unfortunately poses an add-on cost.

Cost-effective fabrication of graphene plays a critical role in promoting polymer/graphene research. Sonication of graphite was proved workable in producing graphene, but this method cannot scale up due to its low yield [10,11] although the yield is actually higher than the micromechanical exfoliation method [12]. During sonication, expansion or exfoliation of graphite occurs owing to cavitation (growth and collapse of micron-sized bubbles) and shear forces that grow with sonication time. A recent progress is to combine acidified graphite with sonication [13,14]. Chen et al. [10] obtained graphite oxide platelets of 52 nm in thickness by exposing graphite oxide to 1050 °C for 15 s and sonicating the expanded product in a mixture of water and alcohol for 10 h. Recently we developed graphene platelets (GnPs) of 2–4 nm in thickness [11,12] by combining the thermal expansion of a commercial graphite intercalation compound (GIC) in a common-purpose furnace with sonication of the expanded product in solvent. Fig. 1 summarizes this fabrication procedure. GnPs have a number of advantages over GnO, including (i) a low fabrication cost at 10–20 US\$/kg, (ii) high-structural integrity, as shown by its low Raman I_D/I_G ratio at ~0.07 in comparison with ~1.0 for the reduced GnO [13], which means a maximum retainment of stiffness, strength and electrical and thermal conductivities from its sister graphene, and (iii) modifiable surface due to the reaction between GnP's epoxide groups and amine-end molecules [11].

---

* Corresponding author. School of Advanced Manufacturing & Mechanical Engineering, University of South Australia, Mawson Lakes, SA 5095, Australia. Tel.: +61 8 830 25117 (office), +61 8 830 23771 (lab); fax: +61 8 830 23380.
E-mail address: Jun.Ma@unisa.edu.au (J. Ma).
URL: http://people.unisa.edu.au/jun.ma

0032-3861/\$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2013.05.014

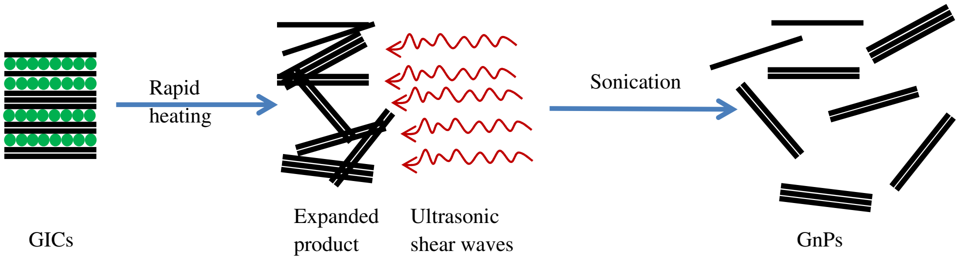

Fig. 1. Schematic of the fabrication of graphene platelets (GnPs).

Polymers combining high-mechanical performance with satisfied electrical and thermal conductivities are highly desired in electronics, automotive and aerospace industries, because this combination creates rapid heat dissipation and thus long service life for (i) the polymers used in dynamic loading conditions and (ii) the polymers used in electronics which are desired to dissipate heat. The accumulation of static electric charges on a polymer surface can be reduced by improving its electrical conductivity. Elastomers have inherently poor thermal and electrical conductivities. The accumulated internal heat is the major ageing mechanism for the elastomers used in dynamic loading conditions: such as tyres, conveyor belts and rubber rollers [14]. The heat build-up usually comes from [15]: (i) the hysteresis loss of rubbery matrix and (ii) the internal friction between the molecular networks, such as elastomer chains and filler–filler and filler–elastomer networks.

Compounding with fillers is a dominant method to improve polymers' conductivities and strength — metallic nanoparticles [15,16], carbon nanotubes [17] and carbon black [18] have been developed. *In-situ* polymerization, solution compounding and melt compounding are the major fabrication methods for functional polymer nanocomposites; of these, melt compounding is highly desired, because it is the most compatible with industrial practice causing the lowest environment impact.

Taking advantage of the cost-effective, high-structural integrity GnPs developed recently, we in this study made the following hypotheses for elastomer/graphene nanocomposites: (i) interface modification may be unnecessary because both GnPs and elastomer are based on carbon, opposite to the hydrophilic silicate layers that need surface modification for compounding with most polymers; (ii) In comparison with stiff thermoplastics, elastomers often have far higher electrical conductivity percolation thresholds owing to their elastomeric nature. Cost-effective GnPs may suit this role better than the extensively studied carbon nanotubes and the reduced graphene oxide, and (iii) melt compounding features high shear, which may be able to uniformly disperse GnPs in elastomer.

In this study, we will adopt melt compounding to develop electrically and thermally conductive, high-mechanical performance elastomer/graphene nanocomposites. The reinforcing effect of GnPs will be compared with that of multi-walled carbon nanotubes. This is the first report to produce high graphene volume fractions (up to 43 vol%) of elastomeric nanocomposites by melt compounding towards high thermal conductivity.

2. Experimental part

2.1. Materials

The graphite intercalated compound (GIC, Asbury 3494) with a size of over 75 μm and a pure carbon content of over 80% was kindly provided by Asbury Carbons. More details are available online [19]. Styrene butadiene rubber (SBR, 1502 styrene content 23.5% with a Mooney viscosity of ML (1 + 4) at 100 °C = 52) was purchased from Jilin Petrochemical Limited China. Curing chemicals (Table 1) were purchased from market and used without further purification.

2.2. Preparation

2.2.1. Graphene platelets

1 g GIC was weighed, transferred to a preheated crucible at 700 °C in a common-purpose furnace, and treated for 1 min. The crucible was carefully moved out and allowed it to cool to room temperature. The volumetric expansion ratio was measured at around 200 times [11], which depends on the volume of GIC. The whole process should be conducted in a fume cupboard to prevent inhaling hazard. The cooled product was dispersed in 100 g acetone using a stainless container, and the container was covered and sonicated for 1 h under 30 °C to produce graphene platelets (GnPs), each of which contains single or multilayer graphene [20]. Acetone was removed from GnPs through filtration, followed by drying GnPs at 60 °C in a fanned oven for 12 h; this produced a densified product that can prevent much of the breathing hazard during the subsequent compounding process.

2.2.2. Elastomer/graphene nanocomposites

Compounding GnPs with styrene butadiene rubber (SBR) was conducted by a two-roll mill at room temperature. GnPs were gradually added to SBR sheet to avoid loss. Similarly, curing agents were added by a formula shown in Table 1. The ratio of curing chemicals to elastomer was carefully kept constant for neat elastomer and its nanocomposites. Vulcanization was carried out at 150 °C for 23 min under 3 MPa. This pressure was chosen since it produced similar results to those at high pressure, as shown in the supporting information (SI). The nanocomposites were prepared based on weight fractions that were converted to volume fractions using Eq. (1):

$$V_f = \frac{\rho_m W_f}{\rho_f \left(1 - W_f\right) + \rho_m W_f} \tag{1}$$

where ρ, W, m and f refer to density, weight fractions, matrix and filler, respectively. Density values of elastomer and GnPs were taken as 1.034 g/cm^3 and 2.26 g/cm^3, respectively.

Table 1
Formulations 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