



Aligned carbon nanotubes stabilized liquid phase exfoliated graphene hybrid and their polyurethane dielectric elastomers



Suting Liu^a, Haibin Sun^b, Nanying Ning^{a, b, **}, Liqun Zhang^{a, b}, Ming Tian^{a, b, *},
Wenjun Zhu^b, Tung W. Chan^c

^a State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, 100029, China

^b Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing, 100029, China

^c Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA, 24061, United States

ARTICLE INFO

Article history:

Received 25 December 2015

Received in revised form

22 January 2016

Accepted 26 January 2016

Available online 29 January 2016

Keywords:

Liquid phase exfoliation

Concentration

Hybrid

Dielectric elastomer

Graphene

ABSTRACT

The liquid phase exfoliation (LPE) method, as a cheap, easily scalable, and eco-friendly method, was used to produce defect-free, unoxidized graphene. A surfactant-free technique was used to concentrate the graphene dispersion through stabilization by carbon nanotubes (CNTs) without functionalization. A special kind of aligned CNT bundles, which can be well dissociated into single CNTs in *N*-methyl-pyrrolidone by sonication, was used and fabricate Gr-CNT hybrid by π - π interaction. A redispersed stable Gr-CNT dispersion at a concentration of 2 mg mL⁻¹ was used for preparing Gr-CNT/thermoplastic polyurethane (TPU) dielectric composite. The results show that the addition of 3.0 vol.% of hybrid improves the dielectric constant of the TPU greatly. As a result, a 10 times increase in electromechanical sensitivity (β) at 1000 Hz and 3.4 times increase in actuated strain at a low electric field (7.5 kV/mm) was achieved. The breakdown strengths of the Gr-CNT/TPU composites with 0.25 vol.% and 1.0 vol.% of hybrid are much higher than that of the pure TPU. As a result, the maximum actuated strain increases greatly from 4.8% for the pure TPU to 7% for the composite with 0.25 vol.% of the hybrid. Meanwhile, the energy density increases from 18 kJ/L for the pure TPU to 25 kJ/L and 48 kJ/L for the composites with 0.25 and 1.0 vol.% of hybrid, respectively.

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1. Introduction

Graphene is a two-dimensional (2D) nanostructured sp²-bonded carbon material with excellent mechanical, electrical, and thermal properties. Graphene is a promising candidate as a component in polymer composites [1,2]. The most commonly used method to produce graphene is the oxidation of graphite to graphene oxide (GO) followed by thermal or chemical reduction. The as-prepared product is reduced graphene oxide (rGO). The oxidation and the reduction process not only introduces toxic or corrosive chemicals but also results in numerous structural defects. Alternatively, the liquid phase exfoliation (LPE) method prepares

graphene in the liquid phase without the oxidation and the reduction step, that is, the direct dispersion and exfoliation of graphite in suitable organic solvents such as *N*-methyl-pyrrolidone (NMP), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) [3]. The LPE method produces dispersions of defect free, few-layer, unoxidized graphene flakes, which can be used to effectively improve the mechanical [4], electrical [5] or tribological [6] properties of polymers. More importantly, the LPE method is cheap, easily available, and eco-friendly.

However, the LPE method has three disadvantages: (1) the graphene can only be obtained at relatively low efficiencies and low concentrations (typically < 0.2 mg mL⁻¹), (2) the residual solvents are always difficult to remove due to the high boiling points (for example, 204 °C for NMP), which make many applications impractical, and (3) after desolventizing, the graphene is difficult to redisperse in solvents. So it is important to increase the concentration while maintaining the quality of the graphene flakes. Coleman et al. prepared graphene dispersions with high concentrations, up to 1.2 mg mL⁻¹, by sonication for long times (up to

* Corresponding author. State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, 100029, China.

** Corresponding author. State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, 100029, China.

E-mail addresses: ningny@mail.buct.edu.cn (N. Ning), tianm@mail.buct.edu.cn (M. Tian).

460 h) in NMP [7]. But the size of graphene decreases with increasing sonication time, and a long sonication time discourages industrial applications. Another method to get a concentrated graphene dispersion is the filtered-redissolved technique using surfactants [8]. Various polymers and surfactants such as polyvinyl pyrrolidone (PVP) and 1-pyrenesulfonic acid sodium salt (PSA) have been used to increase the concentration of graphene dispersion. However, the residual surfactants may limit the practical applications of graphene. Recently, some researchers reported that GO can effectively improve the dispersion of graphene in water [9,10]. Georgakilas et al. [11] reported that hydrophilic functionalized carbon nanotubes (CNTs) can stabilize graphene flakes in pure water at concentrations as high as 15 mg mL⁻¹ without the assistance of surfactants or hydrophilic polymers. However, the preparations of GO and hydrophilic functionalized CNTs are complicated, and the introduction of GO and hydrophilic functionalized CNTs decreases the electrical conductivity of graphene. Thus, it is still a great challenge to seek proper materials to form hybrid with the graphene flakes for achieving high concentrations of graphene dispersion. Such materials should prevent the restacking of graphene, stabilize the graphene flakes in solvents, or even endow the graphene flakes with additional performance.

Previous studies showed that carbon-based materials can prevent graphene from aggregating and improve graphene's redispersibility through $\pi - \pi$ interactions [10,11]. The filtered-redissolved technique can be used to concentrate graphene dispersions stabilized by CNTs. In addition, recent studies demonstrated that there are many pores in graphene-CNT (Gr-CNT) filtered films [12,13]. Compared with the "smooth" structure of graphene films [12], these pores allow the permeation of organic solvents into the hybrid films to facilitate the re-dispersion of graphene.

Dielectric elastomers (DEs), as an attractive branch of electroactive polymers (EAPs), have been receiving more and more attention because they can easily be actuated by applying an electric field [14]. DEs are highly promising materials for actuators, strain sensors, and electrical generators due to their large strain, high energy density, high electromechanical coupling efficiency, high reliability, fast response, and ease of processing. Dielectric elastomer actuators (DEAs) consist of thin electrically insulating elastomeric membranes sandwiched between two compliant electrodes. When a voltage is applied across the thickness direction, the film shrinks in the thickness direction and expands in the plane direction. The thickness strain (S_z) is given by

$$S_z = -\left(\epsilon_0 \epsilon' E^2 / Y\right) = -\left(\epsilon_0 \epsilon' (V/d)^2 / Y\right) \quad (1)$$

where Y is the elastic modulus, ϵ_0 and ϵ' are the dielectric constants of free space and the polymer, respectively, E is the applied electric field, V is the applied voltage, and d is the thickness of the film.

It can be seen from the equation that a high electromechanical sensitivity ($\beta = \epsilon' / Y$) is required to obtain a high actuated strain. However, the ϵ' of common DEs is very low (lower than 8). Thus, a key issue is to increase the ϵ' of DEs, but maintain other excellent properties such as low dielectric loss and good flexibility. One common method to improve the ϵ' of DEs is to introduce high- ϵ' ceramics into the elastomer matrix. A high content (up to 50 vol.%) of ceramics is usually required to improve the ϵ' , resulting in high Y , low flexibility, and poor processability. Another effective method is to prepare percolative composites by adding conductive fillers such as silver particles, graphene [15] CNTs [16], and conductive carbon black into the matrix. As reported in previous studies, owing to its good conductivity and layered structure with a large aspect ratio, even a small amount of graphene can improve the ϵ' of DEs greatly,

and thus the flexibility of the elastomer is maintained [15].

Inspired by previous studies, we first prepared a graphene dispersion by the LPE method and then concentrate the graphene dispersion through stabilization by a special kind of aligned CNT bundles (CNTBs) prepared by electrostatic self-assembly [16]. These CNTBs can be well dissociated into many single CNTs in NMP after mechanical grinding and sonication. The as-prepared CNTs without functionalization were then used to concentrate the graphene dispersion and to fabricate Gr-CNT hybrid through $\pi - \pi$ interaction. During the whole concentration process by vacuum filtration, the restacking of graphene is effectively prevented by the steric hindrance effect of CNTs. A redispersed stable Gr-CNT dispersion at a concentration of 2 mg mL⁻¹ was used for preparing polymer composites by solution blending. A uniform dispersion of Gr-CNT hybrid in a TPU matrix and good interfacial adhesion between the Gr-CNT hybrid and TPU were obtained. The Gr-CNT hybrid with a large surface area and high electrical conductivity can greatly improve the dielectric properties and the actuated properties of the TPU. Our goals are to develop a simple and effective way to concentrate the graphene dispersion prepared by the LPE method, to prepare an all-carbon hybrid filler, and to study the effect of the as prepared Gr-CNT hybrid on the electromechanical properties of DEs for a wide range of applications.

2. Experimental

2.1. Materials

Natural graphite (1000 mesh, purity > 99%) was provided by Huadong Graphite Factory (China). Thermoplastic polyester-polyurethane (TPU, Elastollan Soft 45A, 1.18 g/cm³) was purchased from BASF Polyurethane Specialties (China) Co., Ltd., and dried at 60 °C for 5 h before use. Carbon nanotube bundles (CNTBs, FloTube™ 7000, purity > 93%) was supplied by Beijing CNano Technology Co., Ltd. (China). *N*-methyl-pyrrolidone (NMP, 99.5%) was supplied by Beijing Chemical Reagents Co., Ltd. (China). All the chemicals were used as received.

2.2. Preparation of graphene and Gr-CNT hybrid

Graphene was prepared from natural graphite by bath sonication [3]. In a typical process, 4.0 g of graphite that was dried thoroughly at 60 °C for 5 days were dispersed in 80 mL of NMP. The graphite was exfoliated by sonication for 6 h in a KQ218 bath (Kunshan Ultrasonic Instrument Co., Ltd., China). The mixture was taken out of the sonication bath every 30 min and stirred for 1 min to re-homogenize the graphite suspension. Subsequently, a gray liquid was obtained. The mixture was allowed to sediment overnight and then centrifuged at 4000 rpm for 10 min to remove the non-exfoliated graphite particles and other impurities.

A well-dispersed CNT/NMP dispersion is primarily to obtain a stable Gr-CNT dispersion. The detailed information is supplied in Supporting Information.

Gr-CNT hybrids were fabricated as demonstrated by the schematic representation in Fig. 1. The graphene dispersion and CNT dispersion were mixed directly in the mass ratio of graphene to CNT of 8:2. The mixture was subjected to ultrasonication by using a GA 98-III ultrasonic cell disruptor (Shangjia Biological Technology, China) at a power of 600 W for 30 min and then vacuum filtered onto a nylon membrane of pore size 0.22 μ m to obtain a moist Gr-CNT cake. Finally, a Gr-CNT hybrid dispersion with a concentration of 2 mg mL⁻¹ was obtained by redissolving the moist cake into NMP by sonication for 2 h.

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