Nanocomposites of epoxy-based shape memory polymer and thermally reduced graphite oxide: Mechanical, thermal and shape memory characterizations

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ABSTRACT

Low mechanical strength and low thermal stability of pristine epoxy-based shape memory polymer (ESMP) hinder its practical applications, and the usually used reinforcing fillers are expensive. In this study, thermally reduced graphite oxide (TrGO) was used as a low-cost but efficient reinforcement phase for ESMP. Compared with pristine ESMP, an increase of 41%–71% for Young's modulus and 44%–64% for tensile strength were observed for the TrGO/ESMP composites containing only 1–3 wt.% TrGO. Thermogravimetric analysis (TGA) showed that 2 wt.% TrGO can improve the thermal stability of ESMP significantly. The thermal conductivity of TrGO/ESMP composites increased almost linearly with increasing TrGO content. Moreover, The TrGO/ESMP composite containing 2 wt.% TrGO can decrease the shape recovery time of ESMP down to 1 min as a result of enhanced thermal conductivity. The TrGO/ESMP composites with such improved properties may have great potential in smart systems.

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1. Introduction

Shape-memory polymers (SMPs) have the ability to recover their original shape from a temporary shape with stimulus such as heat, light, magnetism, moisture, change in pH, or electricity [1]. The shape memory mechanism is based on reversible energy conversion in polymer chain movement. Typically, when SMP is subject to heat and deformation and then cooled below its switch transition temperature, large internal stress can be stored in the cross-linking structure; by heating the SMP above its switch transition temperature, the SMP recovers its permanent shape by releasing the internal stress [2]. SMPs have several advantages over shape memory alloys, such as light weight, low cost, high shape deformability and recoverability, and tailor-able switch temperatures [3]. Based on these advantages, SMPs have many potential applications including clothing manufacturing, automobile engineering, and medical treatment [4]. However, pristine SMP materials suffer from relatively low thermal stability, low strength and

stiffness, which hinder their applications as functional and structural materials [5,6]. At room temperature, epoxy-based SMP (ESMP) shows an elastic modulus of about 1 GPa [7], styrene-based SMP (SSMP) has an elastic modulus of less than 1 GPa [8], while the elastic modulus of shape-memory polyurethane (SMPU) is only around 200 MPa [9,10].

Therefore, some reinforcing fillers are tried to improve the mechanical strength and thermal stability, while maintaining shape memory properties of pristine SMPs. These fillers include particles (such as SiC [11] and Fe_3O_4 [12]), fibers (such as glass fibers [13], carbon fibers [6] and carbon nanotubes [14]), and sheets (such as graphene [15]). However, some of these fillers are expensive which limits their use in SMP composites (such as carbon nanotubes and graphene); while some additives need high weight fractions in the composites, but the improvements in some key properties of the SMP are not significant. For example, the recovery force of ESMP was increased by only 50% with 20 wt.% SiC [7], and that of SMPU was increased by only 20% with 1 wt.% nanoclay [10]. The mechanical, thermal and shape memory properties of SMP composites are determined by dispersion states of fillers and filler–polymer interactions [14]. Uniform dispersion of fillers and strong filler–polymer interactions result in improved thermal stabilization, mechanical and shape memory properties of the SMP

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composites [14]. For ESMP, SMPU and shape-memory polyvinyl alcohol based composites, some polar groups (such as hydroxyl, carbonyl, and epoxy) on fillers can enhance the filler-matrix interfacial bonding, leading to significant improvements in mechanical properties [16,17], glass transition temperatures [18], and shape memory performances [19,20] of the SMP composites.

Thermally reduced graphite oxide (TrGO) is a kind of porous graphite material, which is synthesized by heating graphite oxide (GO) to 200–1100 °C [21,22] or treating GO with microwave [18]. Due to its high specific surface area (>100 m^2/g) and large pore volume (>0.5 cm^3/g) [23], high thermal [24] and electrical conductivity [25], strong mechanical property [26], polar surface [27] and fine compatibility with many polymers [28], TrGO has been widely used as reinforcement phase for high-performance polymer nanocomposites. The TrGO can significantly enhance the mechanical properties (such as tensile strength, Young's modulus, storage modulus, and hardness) of polyethylene [29], poly (methyl methacrylate) [30], polyvinyl alcohol [31], thermoplastic polyurethane [32], poly (ethylene oxide) [33], natural rubber [34], and many others [28]. Moreover, TrGO can improve thermal stability [32] and thermal conductivity [35] of polymers.

Because of the enormous surface area and surface polarity of TrGO, TrGO is believed to improve mechanical and thermal properties of ESMP. And some studies show that exfoliated GO materials, which have abundant oxygen-containing groups, show a good interfacial bonding with ESMP matrix [36,37]. In our previous study [38], 1 wt.% TrGO was incorporated into ESMP by three-roll mill (TRM), and the obtained TrGO/ESMP composite exhibited better mechanical property, higher thermal stability, and improved recovery force, compared with unfilled ESMP. Herein, different weight fractions of TrGO (1–3 wt.%) is incorporated into ESMP by TRM. The micro-structure, static mechanical property, glass transition, thermal stability and conductivity, and shape memory behavior of the TrGO/ESMP composites are systematically investigated as a function of TrGO content, and the optimized TrGO weight fraction in the TrGO/ESMP composites is discovered.

2. Experimental details

2.1. Materials

The graphite supplied by Sigma Aldrich had a particle size less than 20 μm. Concentrated sulfuric acid (H$_2$SO$_4$), sodium nitrate (NaNO$_3$), potassium permanganate (KMnO$_4$), hydrogen peroxide (H$_2$O$_2$), and hydrochloric acid (HCl) were of analytical grade and purchased from Sinopharm Chemical Reagent (Shanghai, China). ESMP resin in this study is a thermoset crosslinked network, consisting of epoxy resin, hardener, and linear epoxy monomer [39]. For curing, the resin was cast into a flat glass mold and cured at 80 °C for 1 h, then 150 °C for 6 h.

2.2. Preparation of TrGO/ESMP composites

The synthesis of TrGO can refer to [38]. TrGO/ESMP mixture pastes with different TrGO contents (1 wt.%, 2 wt.% and 3 wt.%, respectively) were prepared by a TRM device (EXAKT 80E, EXAKT Advanced Technologies GmbH, Germany) with gradually smaller gaps (from 100 μm down to 5 μm) between the rollers. After the combination of TrGO and ESMP resin, the paste was cast into a flat glass mold and cured at 80 °C for 1 h, followed by 150 °C for 6 h.

2.3. Characterization methods

Scanning electron microscope (SEM) analyses were performed with an environmental microscope (FEI-Quanta 200F). Before SEM

analysis, the samples were vacuum coated with a thin gold layer using a precision etching coating system (Model 682, Gatan, USA) and the duration was 10 min. X-ray diffraction (XRD) experiments were performed in a D/max-rb rotating anode X-ray diffractometer (Japan). Samples were scanned in the reflection mode using the Cu Kα 1 radiation (wavelength: 1.5405 Å). The tensile properties of the materials at 25 °C were measured according to the ASTM D638 test method using a materials testing machine (Z050, Zwick/Roell) with the following conditions: gage length, 25 mm; crosshead speed, 5 mm/min; load cell, 50 kN; and preload, 8 N. For flexural tests at 25 °C, the specimens with a dimension of 65 mm × 12.7 mm × 3 mm (according to ASTM-D790) were loaded in three-point bending until 25 mm at a rate of 1 mm/min with a support span of 48 mm on a universal testing machine (Zwick/ Z010). For both tensile and flexural tests, more than five specimens were tested for each material. A dynamic mechanical analyzer (DMA/SDTA861, Mettler Toledo) in tension mode was used to measure the dynamic mechanical properties of pure ESMP and TrGO/ESMP composites. Scanning measurements were performed between 25 °C and 180 °C with 1 Hz at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was conducted from 25 °C to 600 °C at a rate of 10 °C/min under 50 ml/min air flow (TGA/DSC 1, Mettler Toledo). Thermal conductivity tests were carried out by DRL-III heat conduction modulus testing instrument (Xiangke).

Shape memory test included five steps [38]. First step, cured samples were cut into strips (dimension: 50 mm × 3 mm × 3 mm), and five strips were prepared for each material. Second step, these strips were heated to 130 °C using a hot plate (MODELKW-4AH, CHEMAT TECHNOLOGY, INC.) and kept for 5 min. Third step, the heated samples were bent into U shapes around a mandrel with a radius of 5 mm. The maximum bending angle (θ_{max}) was 180°. Fourth step, the U-shaped samples were cooled down to 18 °C under external force. Then this force was removed and the deformed specimens were stored at 18 °C for 24 h. Last step, the fixed bending angles (θ_f) of the specimens were measured and then they were put onto the hot plate at 130 °C. The bending angle (θ_i) was recorded as a function of time since the beginning of heating. Shape fixity ratio (R_f) was calculated by the equation:

$$R_f = \frac{\theta_f}{180^o} \times 100\% \tag{1}$$

Shape recovery ratio (R_r) was calculated by the equation:

$$R_r = \frac{180^o - \theta_i}{180^o} \times 100\% \tag{2}$$

3. Results and discussion

3.1. Micro-structure characterization

The micro-structures of TrGO, pure ESMP and TrGO/ESMP composites were characterized using SEM and XRD methods, respectively. Fig. 1a shows SEM image of TrGO. The TrGO are layered (indicated by arrows 1 and 2) and porous (indicated by arrow 3) as a result of GO exfoliation [40]. This unique structure gives the TrGO a high Brunauer–Emmett–Teller (BET) specific surface area of about 300 m^2/g, much higher than graphite [38]. The fracture surface of unfilled ESMP is very flat, as shown in Fig. 1b, which indicates a brittle fracture [41]. The particle on the fracture surface in Fig. 1b may come from specimen breakage, which reflects the smoothness of the fracture surface of pure ESMP. The fracture surfaces of TrGO/ ESMP composites are rather rough (see Fig. 1c, d, and e) and the direction of crack propagation varies due to the existence of TrGO.