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Noncovalently functionalized carbon fiber by grafted self-assembled graphene oxide and the synergistic effect on polymeric shape memory nanocomposites

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ABSTRACT: This paper presents an effective approach to significantly improve the electrical properties and recovery performance of shape memory polymer (SMP) nanocomposites that are able for Joule heating triggered shape recovery. Reduced graphene oxide (GO) is self-assembled and grafted onto the carbon fibers to enhance the interfacial bonding with the SMP matrix via van der Waals and covalent crosslink, respectively. Experimental results verify that the electrical properties of SMP nanocomposites are significantly improved via a synergistic effect of GO and carbon fiber. The morphology and porous structure of GO on the carbon fiber are characterized by electron microscope and optical microscopes, respectively. Furthermore, the behavior of electro-activated recovery and the resultant temperature distribution within SMP nanocomposite are monitored and characterized. We demonstrate that this simple way is able to produce electro-activated SMP nanocomposites which are applicable for Joule heating at a lower electrical voltage.

Keywords: A: Polymer-matrix composites (PMCs), B: Electrical properties, B. Interface/interphase, E. Assembly
1. Introduction

Shape memory polymers (SMPs) are fascinating due to the feature of the shape memory effect (SME) [1,2]. Most likely this feature was firstly termed in 1932 after such an effect was discovered in an AuCd alloy [3]. After years of intensive research and development thereafter, recently SMPs have started to attract great attention as a promising candidate for many engineering applications in biomedicine, automobile, aerospace and textiles, etc, due to their high elastic strain, tailorable transition temperature, ease in manufacturing and variable in mechanical and physical properties within a wide range [4-9]. Consequently, they are now considered as an important part in smart materials and structures [10,11]. Remarkable progress in synthesis, characterization/analysis, modeling/simulation and structural design has been made in a knowledge based approach [12-17]. While the SME in SMPs has been achieved by applying a few different stimuli, via such as photoactive effect, magnetic-active effect, water (or solvent)-active effect and electroactive effect, utilization of Joule heating to drive the SME is desirable and convenient to apply in some practices, especially when direct heating is not easily achievable. A variety of conductive fillers from zero dimensional particles, one dimensional chains to two dimensional films, such as carbon nanotubes (CNTs) [18,19], carbon nanofibers (CNFs) [20,21], carbon black [22], magnetic particles [23], short carbon fibers [24,25], CNT alignment [26,27], CNF mat [28], nanopaper [29,30] etc have been used as conductive fillers not only to enhance the electrical conductivity for Joule heating, but also to improve the thermal conductivity [31-33].

Graphene, a one-atom-thick sheet of sp²-bonded carbon, has attracted enormous interest because it has superior physical properties: an electrical conductivity of 10⁶ S/cm, a thermal conductivity of 5000 W/m·K, and a large specific surface area, and a high aspect ratio [34,35]. Bulk quantities of graphene can be produced effectively by the thermal exfoliation of graphite oxide of which the sheets are reduced and exfoliated simultaneously upon rapid heating [36]. In order to turn graphite oxide into graphene oxide (GO), the most common techniques are
sonication, stirring, or a combination of both. Thermally-exfoliated graphene is normally comprised of few-layer graphene sheets with specific surface areas approximate to 1500 m$^2$/g [37-39]. Besides oxygen epoxide groups (bridging oxygen atoms), other functional groups experimentally found are: carbonyl (=CO) and hydroxyl (-OH) prepared using sulphuric acid (e.g. Hummers method) [40,41]. It is expected that GO should be able to fulfil its roles as a fixed structure as well as a filler for reinforcement in epoxy-based polymer due to the potential covalent bonds. Larger specific surface area provides a stronger connection between CF and polymer. On the other hand, the uniform distribution of GO on CF surfaces enables good dispersion of GO in the polymer around CF. Even at low volume fractions, the vast interfacial area created by well-dispersed GO could affect the behavior of the surrounding polymer matrix and create a co-continuous network to fundamentally change the physical properties of the polymer matrix [42-44]. In this study, a synergistic effect of GO and carbon fiber is introduced. The GO is self-assembled and grafted onto the carbon fibers to enhance the reliability in bonding between carbon fiber and SMP matrix via van der Waals and covalent crosslink, respectively. A combination of GO and carbon fibers is consequently utilized to significantly improve the electrical properties to achieve actuation of SMP composites at a low electrical voltage. A schematic illustration of the working mechanism of the self-assembled GO grafted onto carbon fiber to improve the interfacial bonding with epoxy-based SMP is shown in Figure 1.

2. Experimental details

2.1 Raw materials

Commercially available carbon-fibers (12K, 1.80 g/cm$^3$), with an average diameter of 7 μm, were used as reinforcing fillers in this study. The matrix used in this study is an epoxy-based fully formable thermoset SMP resin, which was composed of a mixture of epoxy resin and curing agent. After mixing and curing, this polymer has the thermo-responsive SME, in addition to high toughness and strength. Its glass transition temperature is 110$^\circ$C. Natural
graphite flakes were received with an average diameter of 10μm. Sulfuric acid and hydrochloric acid were supplied from Tianjin Chemical Factory, China. KMnO₄ was obtained from Sinopharm Chemical reagent Co., Ltd. (Shanghai, China).

2.2 Preparation of Graphene Oxide

GO was prepared and synthesized following a modified Hummers’ method. The raw graphite, NaNO₃, and sulfuric acid were stirred together for 15 min below 5°C. A certain amount of KMnO₄ was slowly added into the mixture while stirring maintained to prevent the mixture temperature exceeding 20°C. And then the mixture was transferred into a 25°C water bath and stirred for 30 min to form a thick paste. Consequently, 200 mL deionized water was added into the mixture accompanied with strong mechanical stirring. Subsequently, the mixture was further treated in a 700 mL of deionized water and 60 mL of 30% H₂O₂ solution. The solution was then filtered and subjected to cyclic washing with deionized water. Finally, the resulting graphite oxide was dispersed in deionized water and sonicated for 1 h to obtain graphene oxide. Finally, the mixture was centrifuged at 7000 rpm for 15 min to get rid of the unexfoliated graphite oxide.

2.3 Fabrication of SMP nanocomposite

GO has been regarded as a hydrophilic material since it was discovered because of its excellent water solubility. Distilled water was used as the solvent. As prepared GO of 0.02, 0.03, 0.04, 0.05 and 0.06 g was mixed with 60 mL of distilled water to form suspension. GO suspension was then sonicated for 30 min. After that, the suspension was filtrated under a high pressure to enabled GO for self-assemble and subsequently grafted onto the virgin carbon fibers with the aid of a hydrophilic polycarbonate filter membrane. The suspension and 60 mL of distilled water were then filtered through the filter. In the next step, the carbon fibers grafted with GO were dried in an oven at 120 °C for 2 h to further remove the remaining water. Finally, six pieces of nanopaper with different weight ratio of GO: carbon fiber (namely, 0: 0.14, 0.02: 0.14, 0.03: 0.14, 0.04: 0.14, 0.05: 0.14 and 0.06: 0.14) were
obtained to prepare nanocomposite samples. These six pieces of mat were individually placed on the bottom of a metallic mold. Resin transfer molding technique was applied to make SMP nanocomposite. The relative pressure of the resin transfer molding was kept at a constant level of 6 bar. After the mold was filled, the mixture was cured at a ramp of approximately 1°C/min from room temperature (22°C) to 100°C and kept for 5 h before being ramped to 120°C at 20°C per 180 min. Finally, it was ramped to 150°C at 30°C per 120 min to produce the final SMP nanocomposites.

3. Results and discussion

3.1 Morphology of CNT assemblies onto carbon fibers

The surface morphologies and structure of GO functionalized carbon fibers were observed by field emission scanning electron microscopy (FESEM) at two scales of 2 µm and 10 µm, respectively, as shown in Figure 2. Figures 2(a), (b) and (c) reveal the surface morphology of self-assembled GO in which many wide and deep grooves are visible along the axial direction of carbon fiber. It is shown that different sized GO sheets are attached to the surface and stick to the carbon fibers along the outer edges of the grooves with different angles due to the high specific surface area of GO, forming a new hierarchical structure. The GO was grafted onto and uniformly deposited on the carbon fiber via the membrane filtration process. With an increase in the weight fraction of GO, GO sheets homogeneously cover the entire surface of carbon fibers (Figures 2(b) and (c)). Both images reveal that GO sheets can be easily introduced into the interfacial regions of carbon fiber.

On the other hand, optical microscope observation of self-assembled GO sheets was performed on using a three-dimensional optical-resolution photoacoustic microscopy (VHX-900) and Olympus stereomicroscope (OLS3100) equipped with a CCD camera. The maximum magnifications of the ocular and objective are 10× and 100×, respectively, and thus the overall magnification is 1000×. Optical microscope provides an effective approach to characterize and provide three-dimensional visualization of the internal morphology and
structure of GO sheets. The GO assembly structure has pores with an average size of around 50 µm, as shown in Figures 3(a) and (b). Therefore the polymer resin is able to penetrate into this porous structure to closely attach to the GO. It is expected and has been verified that the GO can significantly improve the interfacial shear strength and interlaminar shear strength of carbon fiber reinforced polymer composite [45]. A stereomicroscopic three-dimension observation was conducted on the self-assembled GO to further confirm the internal morphology and structure. In the testing, the thickness readings were taken from the back of the mat to determine the thickness of the GO grafted onto carbon fiber mat. The thickness distribution of the GO is shown in Figure 3(c). The three-dimensional graph reveals the thickness distribution of the GO on the carbon fiber mat within an area of 480 µm × 640 µm. It is concluded that the thickness is in a range of 0 to 178.3 µm due to the random layered structure. At the same time, it is shown that the self-assembled GO is uniformly dispersed on the carbon fiber.

3.2 Raman spectra characterization

Raman spectroscopy (Horiba HR 800 spectrometer) was used to characterize disorder and defects in GO. 632 nm radiation from a 20 mW air-cooled Argon ion laser was used as the exciting source. The graphene and GO could manifest themselves in Raman spectra by means of changing in relative intensity of two main peaks: D and G bands. Figure 4 shows the Raman spectra of graphene and GO. The D peak of graphene located at 1348 cm⁻¹ and at 1346 cm⁻¹ for GO streams from a defect-induced breathing mode of sp² rings. Here, Raman spectroscopy is shown to provide a powerful tool to differentiate sp² carbon nanostructures of graphene and GO which have many properties in common and others that differ. The intensity of D band is related to the size of the in-plane sp² domains [46,47]. The decrease of the D peak intensity indicates the formation of less sp² domains. The G bonding of C=C shifts from 1591 cm⁻¹ to 1593 cm⁻¹. All sp² carbon lattice arises from the stretching of C=C bond. The G peaks are at approximate 1593 cm⁻¹ for GO and at 1591 cm⁻¹ for graphene. The relative
intensity ratio of both peaks (I_D/I_G) is a measure of the degree of disorder and is inversely proportional to the average size of the sp² clusters [48]. The D/G intensity ratio for GO is of 0.95 that is larger than that of the graphene of 0.85. This suggest that more graphitic domains are formed and the sp² cluster number increases.

3.3 Electrical resistivity measurement

The electrical resistivity of the resultant composites was determined based on the measured data using a van der Pauw four-point probe apparatus. The apparatus has four probes with an adjustable inter-probe spacing. A constant current passed through two outer probes and an output voltage is measured across the inner probes with a voltmeter. In order to reduce experimental errors, a symmetrical tested sample is preferable. The specific resistivity and Hall effect of an electrically conductive material is measured by cutting a sample into a symmetrical shape [49]. Current contact points A and B and voltage contacts points C and D as shown in Figure 5(a). The electrical resistivity of the carbon fiber mats grafted with different GO contents (in weight) plotted in Figure 5(b). Figure 5(c) reveals the discrepancy of measured results. It was found that the average value of electrical resistivity decreases from 1.46, 1.28, 1.23 to 1.16 Ω·cm, as the weight content of GO increases from 0.03, 0.04, 0.05 to 0.06 g, while the weight of the carbon fiber is kept at a constant of 0.14 g. And the experimental error in the testing is limited to 4%. While the electrical resistivity of 0.05g reduced graphene oxide being reduced as measurement times increase is resulted from the more nonuniform dispersion of GOs. The electrical resistivity of tested samples is improved and lowered with an increase in the weight concentration of GO. It is expected that the more GO being assembled and invloved, both the amplitude of electric current and current carrying capability increase, resulted by a lower electrical resistivity. And it should be noted that the improved electrical properties are resulted by the synergite effect of GO and carbon fiber.
3.4 Electrically triggered shape recovery and temperature distribution

As experimentally demonstrated above, the electrical property of SMP nanocomposite is improved. Therefore, it is expected that these nanocomposites could show the electrically induced SME. The tested SMP nanocomposite had a permanent flat shape (60×6×1.5 mm³). After the nanocomposite was heated above 120°C, it was deformed into a “U” shape upon application of an external force. After cooling back to room temperature, the freestanding nanocomposite largely maintained the deformed shape. The synergistic effect of carbon fiber (0.14 g in weight) and self-assembled GO (0.03 g in weight) on the electrical actuation was investigated on SMP nanocomposites (1.2 g in weight). A constant 5.5 V DC voltage was applied to the SMP nanocomposite. While the applied electric current was 0.45 A. The electro-responsive shape recovery was recorded by a video camera. Snapshots of the shape recovery sequence are shown in Figure 6. Experimental results reveal that it took 80 s to complete the shape recovery. There was not much recovery during the first 20 s, but remarkable recovery was recorded at 60 s and virtually no more further recovery after that till 80 s. Finally, the SMP nanocomposite regained its permanent shape and the recovery ratio is close to 95%. Simultaneously, an infrared video camera was also used to record and monitor the shape recovery behavior and temperature distribution in the recovery process. Snap-shot of the tested SMP nanocomposite is presented in Figure 7. As we can see, higher temperature is observed where internal strain is higher during the shape recovery process, which is attributed to the higher local resistive heating loss. When an electrical current is passed through Joule heating effect results in temperature increased, and thus the shape recovery of SMP nanocomposite.

4. Conclusion

A series of experiments were conducted to study the synergistic effect of carbon fiber and GO on SMP nanocomposites, of which the actuation was triggered by means of Joule heating. The GO was grafted onto the carbon fiber to significantly enhance the reliability in bonding.
and further helped to transfer the resistive Joule heating between the carbon fiber and the SMP. As demonstrated, the electrically driven shape recovery was carried out by means of applying an electric voltage of 10 V and a power of 2.5 W. Furthermore, temperature distribution of the SMP nanocomposite was monitored during the recovery process to present the synergistic effect of carbon fiber and rGO on the shape recovery induced by Joule heating. We demonstrated a simple way to produce electro-activated SMP nanocomposites by application of deposition of rGO onto carbon fibers, and thus Joule heating was possible at a lower electrical voltage.

Notes
The authors declare no competing financial interest.

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References


Figure captions

Fig. 1. (a) Schematic illustration of the graphite stack is oxidized to separate the individual layers of GO. (b) The role of GO in the interfacial bonding between carbon fiber and epoxy-based SMP matrix via Van der Waals bonding and covalent crosslink, respectively.

Fig. 2. The typical surface profile of the GO grafted onto the carbon fibers at a scale of (a) 2 µm, (b) 10 µm and (c) 20 µm, respectively.

Fig. 3. (a) and (b) internal morphology and structure of self-assembled GO on the carbon fiber mat revealed by optical microscopies. (c) 3D graph of thickness distribution of GO.

Fig. 4. Raman spectra of graphene and GO were recorded with 632 nm laser and at a laser power of 20 mW.

Fig. 5. Electrical resistivity of carbon fiber mat with different weights of GO. (a) Schematic measurement mode. (b) Electrical resistivity as a function of measurement time for the carbon fiber mat with 0.03 g, 0.04 g, 0.05 g and 0.06 g of GO. (c) Deviation of measured results.

Fig. 6. Joule heating-induced shape recovery of SMP nanocomposite incorporated with 0.14 g of carbon fiber and 0.03 g of GO.

Fig. 7. Snapshot of Joule heating-induced shape recovery in SMP nanocomposite recorded by infrared video camera (VarioCAM HiResl, JENOPTIK Infra Tec.).
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