Synergistic effect of Ag nanoparticle-decorated graphene oxide and carbon fiber on electrical actuation of polymeric shape memory nanocomposites

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Abstract

This study reports an effective approach of significantly improving electrical properties and recovery performance of shape memory polymer (SMP) nanocomposite, of which its shape recovery was triggered by electrically resistive Joule heating. Reduced graphene oxide (GOs) self-assembled and grafted onto carbon fiber, were used to enhance the interfacial bonding with the SMP matrix via van der Waals force and covalent bond, respectively. A layer of Ag nanoparticles was synthesized from Ag⁺ solution and chemically deposited onto GO assemblies. These Ag nanoparticles were expected to bridge the gap between GO and improve the electrical conductivity. The experimental results reveal that the electrical conductivity of the SMP nanocomposite was significantly improved via the synergistic effect between Ag nanoparticle-decorated GO and carbon fiber. Finally, the electrically induced shape memory effect of the SMP nanocomposite was achieved, and the temperature distribution in the SMP nanocomposites was recorded and monitored. An effective approach was demonstrated to produce the electro-activated SMP nanocomposites and the resistive Joule heating was viable at a low electrical voltage below 10 V.

Keywords: shape memory polymer, electrical properties, graphene oxide

(Some figures may appear in colour only in the online journal)

Introduction

Shape memory polymers (SMPs) are fascinating materials featured with a shape memory effect (SME) that traditional polymers do not have [1–3]. This unique behavior was first discovered in 1984 [4, 5]. SMPs have attracted significant attention as a promising candidate for a number of potential applications in biomedicine, automobile, aerospace or textiles due to their high elastic strain, tailorable transition temperature, ease in manufacturing and wide range of mechanical and physical properties [6–12]. Furthermore, they are now being investigated as a hot topic in the research field of smart materials and structures [13, 14]. Tremendous progress in synthesis, analysis, characterization, structural design, modeling and simulation promotes to the development SMPs in a knowledge based approach [15–18]. The thermally stimuli-responsive SME in SMPs have been achieved by a photoactive effect, magnetic-active effect, water (or solvent)-active effect and electro-active effect
The utilization of electrically resistive Joule heating to drive SME is desirable and convenient to apply in a number of real-life applications, especially where direct heating is not easily achieved. A variety of conductive fillers from zero dimensional particles, one dimensional chains to two dimensional films, such as carbon nanotubes (CNTs) [22], carbon black [23], carbon nanofibers (CNFs) [24, 25], magnetic particles [26], short carbon fibers [27, 28], conductive alignment [29, 30], CNF mat [31] and nanopaper [32] have been used in the SMP nanocomposites. These conductive fillers not only enable remote actuation of shape transitions but also enhance the thermal conductivity [33–35]. Graphene, a one-atom-thick sheet of sp²-bonded carbon, has triggered enormous interest due to its superior physical properties. It has the electrical conductivity of 10⁶ S cm⁻¹, thermal conductivity of 5000 W m⁻¹ K⁻¹, a large specific surface area, and high aspect ratio [36, 37]. 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 [38]. In order to turn graphite oxide into graphene oxide (GO), the most common techniques are sonication, stirring, or the combination of these two. Thermally-exfoliated graphene is normally comprised of few-layer graphene sheets with specific surface area approximately to 1500 m² g⁻¹ [39–41]. 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) [42, 43]. It is expected that GO is able to fulfill its role as a fixed structure as well as a reinforcement in an epoxy-based polymer due to their potentially covalent bonds. Larger specific surface area supplies stronger connection between CF and polymer. On the other hand, the uniform distribution of GO on CF surfaces enables a 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 [44–46]. In this study, a synergistic effect of GO and carbon fiber was investigated. The GO was 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 crosslinking, respectively. The combination of GO and carbon fibers was consequently used to significantly improve the electrical properties to achieve the actuation at a low electrical voltage for the SMP composites.

Experimental details

The polymer matrix used in this study is an epoxy-based fully formable thermoset SMP resin, which is composed of a mixture of epoxy resin and curing agent. Cured epoxy-based SMP has a unique shape memory effect, with a glass transition temperature \( T_g \) of 110°C. When heated above or approximate to \( T_g \), it could change from a rigid plastic to an elastic rubber. Natural graphite was received with an average diameter of 10 μm, 98% sulfuric acid (H₂SO₄), 30% hydrogen peroxide (H₂O₂) and potassium permanganate (KMnO₄) were used for synthesizing GOs. The distilled water was used in all experiments. The prepared GO of 0.02, 0.03, 0.04, 0.05 and 0.06 g were respectively mixed into 60 mL distilled water to form a suspension. GO suspension was then sonicated with a high-intensity sonicator (MISONIX Sonicator 4000, Qsonica, LLC, Newtown, Connecticut, USA) for 30 min. After the initial sonication, the GO suspension was then filtered through a carbon fiber mat and an 0.4 μm hydrophilic polycarbonate membrane under a negative pressure to self-assemble and being grafted onto the virgin carbon fibers. And then, the carbon fiber mat grafted with GO was further dried in an oven at 120°C for 2 h to remove the remaining water and surfactant. This heat treatment also could help to increase the bonding strength between carbon fiber and GO that has been demonstrated in the experiments. Consequently, Ag paste mixture was coated on the carbon fiber substrate to form a layer of Ag nanoparticles onto the GO. 0.02 g Ag nanoparticles was used to decorate the GO. The carbon fiber mat grafted with Ag nanoparticle-decorated GO was further heat treated at 200 °C for 30 min. Figure 1 presents the final carbon fiber mat grafted with Ag nanoparticle-decorated GO (on the left) in comparison with the carbon fiber mat grafted with GO (on the right). Finally, 0.14 g of carbon fibers with different weight ratio of Ag: GO (namely, 0.02: 0.02, 0.02: 0.03, 0.02: 0.04, 0.02: 0.05 and 0.02: 0.06) were placed on the bottom of the metallic mold. A resin transfer molding technique was applied to construct the SMP nanocomposites. The SMP mixture was then injected into the mold. The relative pressure of the resin transfer molding was kept at approximately 6 bars. After filling the mold, the mixture was cured at a ramp of approximately 1 °C min⁻¹ from room temperature to 100 °C and held 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. Furthermore, a schematic illustration of the working mechanism of the Ag nanoparticle-decorated GO grafted onto carbon fiber is presented in figure 2.
Results and discussion

Morphology of GO assemblies onto carbon fibers and Ag nanoparticles

Scanning electron microscopy (SEM) was used to study the morphology and structure of GO functionalized carbon fibers, as shown in figures 1(a) and (b). The morphology and structure of self-assembled GO where 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. With an increase in the weight fraction of GO, GO sheets can homogeneously cover the entire surface of carbon fibers. The GO appeared to be tightly associated with the carbon fiber surface. Furthermore, the morphology and structure of the GO assemblies decorated by the Ag nanoparticles are presented in figures 1(c) and (d) at a scale of 10 μm and 50 μm, respectively. The bright lines correspond to individual Ag nanoparticle aggregate. The Ag nanoparticle aggregates have a diameter ranging from 100 to 500 nm, and are uniformly deposited onto the GO assemblies. No large aggregates of Ag nanoparticles were observed. And it is confirmed that a continuously conductive network has been made from these Ag nanoparticles or their aggregates.

X-ray diffraction (XRD) studies

Analysis through x-ray diffraction (XRD) was carried out to confirm the effect of Ag nanoparticle on the GO, and the XRD pattern showed numbers of Bragg reflections that may be indexed on the basis of the face centered cubic structure of Ag nanoparticles. The XRD pattern of the Ag nanoparticle-decorated GO obtained by mulberry leaves extract is shown in figure 4. It is found that the Ag nanoparticles were evidenced by the peaks at 2θ values of 26.42° and 21.68° corresponding to (002) and (311) Bragg reflections of Ag and GO, respectively. The x-ray diffraction results show that the Ag nanoparticles formed by the reduction of Ag+ ions by the mulberry leaves extract are crystalline in nature. The narrow diffraction peak indicates a layer-to-layer distance (d-spacing) of 0.85 nm for the GO assembly. The increased d-spacing (>0.6 nm) may be caused by intercalated water molecules in its p–p stacked structure [47, 48]. The weak and broad peak at 26.42° in Ag modified GO assembly corresponds to a d-spacing of 0.34 nm, which suggests the removal of the intercalated water on the neighboring GO layers [49].

Electrical resistivity measurement

The electrical resistivity was measured by the van der Pauw four-point probe method, as shown in figure 5. This approach is expected to accurately measure the electrical properties of a sample with an approximately two-dimensional shape. In order to reduce errors in the calculations, the tested sample is symmetrical. The specific resistivity and Hall effect of a conducting material is measured by cutting a sample in the form of a bar [50]. The electrical resistivity of the carbon fiber mats grafted with a variety of weight content of Ag nanoparticle-decorated GO was plotted in figure 5(a). According to experimental results, it was found that the average value of electrical resistivity decreased from 0.28, 0.24, to 0.23 Ω·cm, as the weight content of GO increased from 0.03, 0.04 to 0.05 g, while the weight of the carbon fiber is kept constant of 0.14 g. Meanwhile, figure 5(b) reveals a discrepancy of the each measurement result to the average value to examine the experimental error in the tests. And experimental error of the electrical resistivity in the testing is limited to 0.4%. The electrical resistivity of tested samples is increased with an increase in the weight concentration of GO. It is expected that the more GO being assembled and involved, the amplitude of electric current and current carrying capability both decrease due to the nature structure of reduced GO, of which the electrical conductivity in its thickness direction is smaller than that in the basal plane [51]. Although the electrically conducting properties of Ag nanoparticle-decorated GO is not as good as that of carbon fiber, resulting in the electrical resistivity increased with an increase of weight content of Ag
nanoparticle-decorated GO. And it is should be noted that the electrical properties resulted from the synergic effect of the Ag nanoparticle-decorated GO and carbon fiber that is expected to significantly improve the electrical actuation of SMP nanocomposites.

Electrically triggered shape recovery and temperature distribution

As experimentally demonstrated previously, the electrical property of SMP nanocomposite could be significantly improved with incorporating of the carbon fiber mat grafted with Ag nanoparticle-decorated GO. Therefore, it is expected that these nanocomposites could show an electrically induced SME upon applying a proper electric current. The tested SMP nanocomposite had an original flat shape (with a dimension of 60 × 6 × 1.5 mm$^3$) with a 'Π' shaped sample in the test. After the tested sample was heated above 120 °C, it had been deformed into a 'U' shape upon application of an external force. Cooling down below room temperature, the nanocomposite with a deformed shape was kept and fixed. The synergistic effect of carbon fiber (0.14 g in weight) and self-assembled Ag nanoparticle-decorated GO (0.05 g in weight and weight ratio of 0.02: 0.03 for Ag nanoparticle to GO) on the electrical actuation was investigated on the SMP nanocomposites (1.2 g in weight). A constant 8.6 V DC voltage was applied to the SMP nanocomposite, while the electric current is of 0.45 A. The electrically responsive shape recovery was recorded with an infrared video camera. And snapshots of the shape recovery sequence of the SMP nanocomposite sample is shown in figure 6. The experimental result presents the fact that the tested SMP nanocomposite...
The sample took 36 s to complete the shape recovery in response to electrical stimulus. It showed very little recovery ratio during the first 12 s, but then exhibited a faster recovery behavior until 33 s and no noticeable deformation could be further found. Finally, the SMP nanocomposite regained its permanent shape and the recovery ratio is approximate to 99% compared with its permanent shape. Simultaneously, the infrared video camera was also used to record and monitor the temperature distribution in the recovery process of the SMP nanocomposite. As images presented, higher temperature is observed where internal strain is higher during the shape recovery process, which is attributed to the higher local resistive heating loss. With electricity being applied, the resistive Joule heating resulted in the gradually increased temperature. At 36 s, the maximum temperature of the sample reached approximately 120 °C, and the external electricity was turned off to avoid thermal degradation of the polymer. Consequently, the temperature on the tested sample lowered to room temperature.

Conclusions

A series of experiments were conducted to study the synergistic effect of carbon fiber and GO on the SMP nanocomposites, of which the actuation was achieved by electrically resistive Joule heating. These GOs were grafted onto carbon fiber to significantly enhance the reliability in bonding, and further facilitated transferring the resistive Joule heating between carbon fiber and SMP. The electrically driven shape recovery was carried out by an electric voltage of 10 V and a power of 2.5 W. The temperature distribution of the SMP nanocomposite was monitored during the recovery process to indicate the synergistic effect of carbon fiber and GO on the SMP nanocomposites.
GO on the shape recovery induced by the resistive Joule heating. A simple way was demonstrated to produce electro-activated SMP nanocomposites through the deposition of GO onto carbon fibers and the Joule heating was viable at a low electrical voltage.

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