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Carbon fibre/graphene foam/polymer composites with enhanced mechanical and thermal properties

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ABSTRACT

The effect of carbon fibre (CF) on the mechanical and thermal properties of graphene foam (GF)/polydimethylsiloxane (PDMS) composites was investigated. The CFs with different weight percentages (2, 4, 6, 8 and 10 wt%) were thoroughly dispersed in the PDMS matrix using a high-speed shearing and stirring method and then the GF was filled with the mixture. The CF/GF/PDMS composites were characterized in terms of microstructure, mechanical and thermal properties using various testing techniques. The results reveal that the addition of CF observably improved the mechanical and thermal properties of GF/PDMS composites. For 10 wt% CF/GF/PDMS composite, the tensile strength and Young's modulus are increased by 52% and 71% respectively compared with GF/PDMS composite. In addition, its thermal conductivity reaches 0.55 $Wm^{-1} K^{-1}$, i.e., an increase by about 41% and 162% compared to GF/PDMS composite and pure PDMS, respectively. SEM images show a strong interfacial bonding between CF and PDMS.

1. Introduction

During the past decade, graphene, a single-layered two-dimensional (2D) structure, has been studied widely due to its excellent mechanical, thermal and electrical properties [1–3]. Recently, graphene foam (GF) assembled from 2D graphene sheets (GSs), graphene oxide (GO) or reduced GO (rGO) has attracted a great attention because of its macroscopic three-dimensional (3D) structure [4–7]. Among these, the GF fabricated using the chemical vapour deposition (CVD) technique on a nickel foam template is regarded as a material that best exhibits the superior thermal and electrical properties of graphene. Pettes et al. [8] reported that the thermal conductivity of GF varied from 0.26 to 1.7 $Wm^{-1} K^{-1}$, being influenced by different etchants and low internal contact thermal resistance in the continuous GF structure. Zhang et al. [9] found that the thermal interfacial resistance of GF at the Si–Al interface was as low as 0.04 $cm^2 KW^{-1}$, which is one order of magnitude lower than conventional thermal interface materials (TIMs). Li et al. [10] discovered that this thermal property of GF was improved with rising temperature above room temperature, which is opposite to the prediction by Umklapp phonon scattering theory. Zhou et al. [11] fabricated a GF electrode with high sulphur loading, reaching 10.1 mg cm^{-2}, which presented an extremely high areal capacity of 13.4 mAh cm^{-2}.

Precisely because of its integrated 3D structure and superior properties, GF was chosen as a promising filler to greatly improve the performance of polymer composites, such as the mechanical, electrical and thermal properties [6,12,13]. In our previous work [14], the thermal conductivity of 0.7 wt% GF/PDMS composite reached 0.56 $Wm^{-1} K^{-1}$, which was about 300% and 20% higher than that of pure PDMS and graphene sheets/PDMS composite. From the above studies, the amount of GF in the composites is very limited by the CVD method and the density of Ni foam. Therefore, it is necessary to add another type of filler such as carbon black [15], etc. to further improve the properties of composites.

Carbon fibres (CFs) and their reinforced polymer composites have already been investigated and applied extensively because of their low weight, excellent mechanical properties, superior electrical properties and high thermal conductivity [16–22]. Jin et al. [23] introduced a model to predict the thermal conductivity of CF reinforced polytetrafluoroethylene composites. Patton et al. [24] prepared vapour grown carbon fibre (VGCF)/phenolic resin composites and found that the average thermal conductivity reached 0.7714 $Wm^{-1} K^{-1}$ at 40 wt% VGCF. Wu et al. [25] found that due to CF's highly crystallinity, CF reinforced polyamide-6/clay composites

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showed a higher heat distortion temperature than the same composite reinforced with glass fibre. Rezaei et al. [26] investigated the effect of fibre length on the thermal properties of short carbon fibre/polypropylene composites, and found that the longer CFs endowed the composites with better thermomechanical properties and thermal stability.

Due to the small size of graphene, its reinforcement effect on mechanical properties of polymer composites is very limited. Fortunately, carbon fibres can remedy this shortfall because of their rigid and straight nature. The thermal conductivity of graphene is much higher than that of carbon fibre. So, the combination of graphene and carbon fibre may afford the composite with both high thermal and mechanical properties, and find broad applications in industry. Using 3D graphene foam as a filler can avoid the agglomeration problem of 2D graphene sheets. Currently, composites composed of 3D graphene foam and carbon fibre do not exist and should be further investigated.

In this paper, a novel polymer matrix composite reinforced with 3D graphene foam and 1D carbon fibre was first prepared and characterized in terms of mechanical and thermal properties. It is expected to have better performance than single graphene and single carbon fibre reinforced composites. As a result, the study will provide a path for the development of new composite materials.

2. Materials and experimental methods

2.1. Preparation of the mixture of short CFs and PDMS

Nickel foam and CFs (T-300B) were supplied by Shanghai Zhongwei Materials Co. Ltd. and Torayca, respectively. Poly(methyl methacrylate) (PMMA) with molecular weight of 996,000 was purchased from Sigma Aldrich. Polydimethylsiloxane (PDMS, Sylgard184) used as polymer matrix was supplied by Dow Corning.

Short CFs of about 1 mm long were dispersed in acetone and sheared with high speed for 2 h. Then the base agent of PDMS was added and sheared for another 1 h. Next, the acetone was removed at 60 °C with continuous magnetic stirring. At last, the curing agent (base agent/curing agent = 10/1 in weight) was added and the mixture was stirred for 30 min.

2.2. Preparation of composites

The GF was fabricated by using the CVD method on a nickel foam template which was reported in detail in our previous work [15]. The mixture of CF and PDMS was poured into the mould filled with freestanding GF in advance. Then it was vacuumized, pressed mechanically under about 1.0 MPa and solidified at 80 °C for 4 h. For comparison, pure PDMS, GF/PDMS and CF/PDMS composites were also prepared in a similar way. The GF loading of both GF/PDMS and CF/GF/PDMS composites is 0.5 wt%, while CF's contents are 2, 4, 6, 8, 10 wt% for CF/PDMS and CF/GF/PDMS composites.

2.3. Characterization methods

The morphology of CF, GF and composites was observed by scanning electron microscope (SEM, S-4800, HITACHI). The length of short CF was measured with metalloscope (6XB-PC, Beijing Shangguang). The thickness of graphene sheet (GS) composing GF was identified by transmission electron microscope (TEM, JEM-2100F, JEOL). The samples for tensile tests are standard dumbbell pieces, 2 mm in thickness and 35 mm in length according to GB/T 528-92, and were tested on the MiniMat 2000 type tensile machine at a loading rate of 1.5 mm/min. The valid parallel part of the sample is 2 mm in width and 12 mm in length. The heat flux method (DRL-III, Hunan Xiangyi Instruments Co. Ltd.) was applied to measure the thermal conductivity with the sample dimension of 30 mm in diameter and 2 mm in thickness. Three samples of each composite were tested to get average values both for tensile strength and thermal conductivity measurements. Thermogravimetric analysis (TGA, Q600 SDT, TA) was utilized to evaluate the thermal stability from room temperature to 900 °C at a scan rate of 20 °C/min in a N_2 atmosphere.

3. Results and discussions

3.1. Morphology

SEM images in Fig. 1(a) and (b) present the morphology and length distribution of CF. The diameter is about 8 μm, and the length distribution proves the reduction from initial 1 mm to about 150 μm on average after the high-speed shearing and stirring. The surface shows deep or shallow rill-like folds rather than being smooth. Fig. 1(c) shows that the thickness of hollow arms and pore diameter of GF are about 40 μm and 300 μm, respectively. Fig. 1(d) and (e) show a small piece of graphene sheet (GS) taken from GF with thickness 3–4 nm.

Fig. 2 shows the SEM images of freeze-fractured surfaces of GF/PDMS and CF/GF/PDMS composites with different CF loadings. As shown in Fig. 2(a), the liquid PDMS not only filled the GF pores, but also penetrated into the GF arms without any obvious bubbles. It can be seen from Fig. 2(b)-(f) that the CF exists only in the space of the interconnected network. Due to its longer length compared to the arm thickness of GF, it could not penetrate into the interior of GF arms as shown in Fig. 2(c) (Fig. 2(d)-(f) are similar, but with different CF contents.). It is noted that the distribution of CF is uniform and random within the PDMS matrix, which can be attributed to the effect of high-speed shearing and stirring. Also, the interface between CF and PDMS is good without evident pulling out of CF by freeze fracture.

3.2. Mechanical properties in tension

To investigate the reinforcement effect of different CF loadings on the mechanical properties of CF/GF/PDMS composites, tensile tests were carried out. Typical stress–strain curves are shown in Fig. 3(a), from which values of Young's modulus, tensile strength and elongation at break can be obtained, as presented in Fig. 3(b)-(d). As can be seen in Fig. 3(b) and (c), both Young's modulus and tensile strength display an important increase with the addition of GF and CF. The Young's modulus and tensile strength of GF/PDMS composite increase by 66% and 7% respectively compared with pure PDMS. The adding of CF can further improve the mechanical properties of composites. At 10 wt% CF, Young's modulus and tensile strength reach 3.05 MPa and 2.50 MPa, i.e., an improvement of 71% and 52% respectively compared with the GF/PDMS composite, and by 185% and 63% respectively compared with pure PDMS.

According to Halpin-Tsai's equations [27,28], Young's modulus E of short fibre reinforced composite can be obtained by

$$\frac{E}{E_m} = \frac{3}{8}\left[\frac{1+\zeta\eta_L V_f}{1-\eta_L V_f}\right] + \frac{5}{8}\left[\frac{1+2\eta_T V_f}{1-\eta_T V_f}\right] \tag{1}$$

where

$$\zeta = 2l/D \tag{2}$$

$$\eta_L = \frac{E_f/E_m - 1}{E_f/E_m + \zeta} \tag{3}$$

and