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Synergistic effect of hybrid carbon fillers on electric heating behavior of flexible polydimethylsiloxane-based composite films

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ABSTRACT

Flexible polydimethylsiloxane (PDMS)-based composite films containing 1.0 wt% hybrid carbon fillers composed of multiwalled carbon nanotube (MWCNT) and graphene sheet were manufactured by an efficient solution-casting and curing technique. Microstructures and electrical properties of the composite films were quite dependent on the MWCNT/graphene ratios in 1.0 wt% hybrid carbon filler content. The composite film containing MWCNT/graphene of 9/1 weight ratio exhibited the lowest electrical resistivity of ~73 Ω cm, which was even lower than the values of the composite films containing each single carbon filler, which resulted from the synergistic bridge effect of MWCNTs and graphene sheets that dispersed uniformly in the PDMS matrix. Accordingly, the electric heating behavior of the composite films was quite different, especially in the maximum temperatures attained at different applied voltages. The maximum temperatures of the composite films could be finely adjusted by tuning the hybrid carbon filler ratio as well as the associated electric power. In addition, the composite films, which were thermally stable up to ~250 °C, showed excellent electric heating performance in temperature response, electric energy efficiency, and heating–cooling cyclic operation at given applied voltages.

1. Introduction

Nanoscale carbon materials such as carbon nanotube (CNT) and graphene sheet have been widely used as multifunctional reinforcing fillers in composites due to their excellent physical and chemical properties including electrical conductivity of 10^4–10^6 S/cm, thermal conductivity of 3000–6600 W m^{-1} K^{-1}, and thermal stability up to ~700 °C in air [1–3]. The superlative properties also make them ideal for numerous applications of supercapacitors [4,5], Li-ion batteries [6,7], sensors [8,9], dye sensitized solar cells [10,11], field emitters [12], organic LEDs [13], and emerging heating devices [14,15].

The combination of 1D and 2D allotropes of carbon nanomaterials has attracted great interests with the properties expected to exceed the respective single one because of their synergistic effect. Xu et al. reported enhanced load transfer and mechanical strength of polydimethylsiloxane (PDMS)-based composites due to synergistic effects in binary mixtures of MWCNT and graphene, which was confirmed by a Raman spectroscopic analysis [16]. Chen et al. manufactured a highly conductive MWCNT/graphene/PDMS composite [17]. The MWCNT/graphene 3D conductive network was established and the junctions between the proximal nanofillers, liked a 'binder' and reduced the contact resistances among nanofillers. The electrical conductivity could thus reach 2.8 S/cm with only 1.3 wt% of MWCNT/graphene loading. Kong et al. fabricated PDMS hybrid composites consisting of exfoliated graphite nanoplatelets (xGnP) and MWCNT functionalized with hydroxyl groups (MWCNT–OH) [18]. With the total filler content fixed at 4.0 wt%, a hybrid composite consisting of 75% xGnP/25% MWCNT–OH showed the highest thermal conductivity of 0.392 W/mK and electrical conductivity of ~1.24×10^3 S/m, which attributed to the synergistic effect among the fillers that formed an interconnected hybrid network. Herein, PDMS, a kind of silicone elastomer, is an ideal candidate to provide soft and stretchable mechanical property and high thermal stability for composites and has been widely applied in many fields [19–22].

CNT and graphene have shown very effective conversion of electric energy to thermal energy due to Joule effect. And with ultra-light weight, flexibility, faster and more efficient heating, uniform temperature distribution, they have the potential to replace currently employed materials such as indium tin oxide (ITO), Ni–Cr (nichrome) or Fe–Cr–Al (Kanthal) in the foreseeable future [8]. Jeon and Jeong investigated the *m*-aramid and the epoxy composites containing various compositions of MWCNT and graphene fillers by an efficient solution-casting method [23]. The electrical

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resistivity of the composite films decreased with increasing the MWCNT composition in the mixed carbon fillers, resulting from the bridge effect of MWCNTs among graphene sheets and the maximum temperature attained at a given applied voltage for the composite films can be finely controlled by the MWCNT/graphene composition.

In this study, PDMS-based flexible composite films containing 1.0 wt% hybrid carbon filler contents of MWCNT/graphene were fabricated by a solution-casting and curing technique. Morphological features, thermal stability, and electrical property of the composite films were characterized using TEM, TGA, and multi-ohmmeter, respectively. Crucially, electric heating behavior of the composite films was discussed by considering temperature response rapidity, maximum temperature, and electric power efficiency at different applied voltages.

2. Experimental details

2.1. Materials

PDMS and curing agent (Sylgard 184 Silicone Elastomer Kit, Dow Corning) were used as elastomeric polymer matrix. Ethyl acetate (Sigma Aldrich Co.) was used as a solvent for preparing PDMS/carbon filler solutions. Hybrid carbon fillers used as conductive reinforcing components were composed of pristine MWCNT(CM-95, Hanwha Chemical) with 10–15 nm diameter and 10–20 μm length, produced by thermal chemical vapor deposition, and graphene sheets, obtained by acid-treatment and rapid thermal expansion of natural graphite flakes (Sigma–Aldrich). The detailed preparation and characterization of the graphene sheets was described in the previous report [15]. All the materials and chemicals were used as received without further purification.

2.2. Preparation

PDMS-based hybrid composite films were manufactured by a solution-casting and curing technique. Firstly, the ethyl acetate solutions with different ratios of MWCNT/graphene (0/10, 1/9, 3/7, 5/5, 7/3, 9/1, and 10/0 by weight ratio) fillers in 1.0 wt% hybrid carbon fillers were prepared by ultrasonication for 1 h using a bath-type ultrasonicator (50–60 Hz). After adding predetermined amounts of PDMS into the MWCNT/graphene/ethyl acetate solutions, another ultrasonication was applied for 1 h. Subsequently, the curing agent (1/10 of PDMS by weight) was added into the prepared solutions, which were casted onto glass petri-dishes and cured at room temperature for 24 h and at 70 °C for 2 h. During the curing process, the ethyl acetate solvent could be evaporated. Finally, the PDMS/carbon filler composite films were dried in a vacuum oven at 40 °C for 24 h. The final samples were named as PDMS/M/G_x/y, where x/y denotes the MWCNT/graphene weight ratio of 1.0 wt% hybrid carbon fillers in the composite films.

2.3. Characterization

The morphological feature and the dispersion state of hybrid carbon fillers in the composite films were examined by a transmission electron microscope (JEOL/JEM-2100). For TEM characterization, the composite films were cryo-sectioned to be ~60 nm in thickness by adopting an ultramicrotome (PT-PC&CR-X, Boeckeler Instruments, Inc.). The electrical current and power of the composite films with different MWCNT/grapheme ratios were measured as a function of applied voltage by using multiple sourcemeter and nanovoltmeter (2400, 2182A, Keithley Instruments). The electric heating behavior of the composite films under a variety of voltages of 1–100 V was characterized with an infrared camera (SE/A325, FLIR Systems) and a sourcemeter (2400, Keithley Instruments). For the electrical experiments, the distance between electrical test probes on the composite films (5.0 mm × 20.0 mm) was fixed at 10.0 mm. The thermal stability of the composite films were investigated under nitrogen atmosphere using a thermogravimetric analyzer (TGA/DSC 1, Mettler-Toledo) from 25 to 800 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Electrical property and microstructures

The electrical properties of PDMS-based composite films with different MWCNT/graphene ratio in 1.0 wt% hybrid carbon fillers were investigated as a function of the applied voltage of 0–100 V. The current–voltage (I–V) and the electric power–voltage (P–V) curves of the composite films are represented in Fig. 1A and B, respectively. In Fig. 1A, for all the composite films, the current increased linearly with the applied voltage by obeying the Ohm's law of $I = V/R$, where R denotes the electrical resistance. One striking phenomenon is that the slopes of the I–V curves became steeper with changing of the MWCNT/graphene ratio from 0/10 to 9/1 in 1.0 wt% hybrid carbon fillers, while PDMS/M/G_10/0 exhibits even lower slope than PDMS/M/G_5/5. The higher slope of the I–V curve is ascribed to the increased physical contacts among carbon fillers reducing tunneling gap and thus facilitating electron hopping [18,23]. The slightly negative deviation of the linear I–V curves for PDMS/M/G_9/1 at high applied voltages of 95–100 V was caused by the fact that the PDMS matrix is thermally damaged at too high temperature response owing to the electric heating effect, as will be discussed below. On the other hand, in Fig. 1B, the electric power of the composite films increased quadratically with the applied voltage, according to the equation of $P = IV = V^2/R$. In the same way, PDMS/M/G_9/1 showed the highest slope for P–V curves.

The electrical resistance R of the PDMS-based nanocomposite films was evaluated from the initial slopes of I–V curves in Fig. 1A and the value was plotted as a function of the relative MWCNT content in 1.0 wt% hybrid carbon fillers as can be seen in Fig. 2. In addition, the electrical resistivity ρ of the composite films could be calculated by using the equation $R = \rho(L/A)$, where L is the sample length between electrodes and A is the cross-sectional area of a film sample, and the result was also presented in Fig. 2. The electrical resistivity of PDMS/M/G_0/10 was measured to be $6.2 \times 10^2\ \Omega$ cm, while that for PDMS/M/G_10/0 was to be $2.3 \times 10^2\ \Omega$ cm. This is coincident with the reports in the literature that the electrical resistivity as well as the electrical percolation threshold of MWCNT/polymer composites is lower than that of graphene/polymer systems [24,25]. Meaningfully, for the composite films with hybrid carbon fillers, PDMS/M/G_9/1 achieved the lowest electrical resistivity of 73 Ω cm, which was far lower than that of PDMS/M/G_10/0. Even PDMS/M/G_5/5 and PMDS/M/G_7/3 present lower values than PDMS/M/G_10/0. These results declared that the hybrid carbon filler ratio has a great influence on the electrical property of the composite films owing to the synergistic effect.

For identifying the microstructures of the PDMS-based hybrid composite films associated with the dispersion of the carbon fillers, TEM images of PDMS/M/G_0/10, PDMS/M/G_5/5, PDMS/M/G_9/1, and PDMS/M/G_10/0 were obtained as illustrated in Fig. 3. For PDMS/M/G_0/10 and PDMS/M/G_10/0, respective MWCNTs and graphene sheets were uniformly dispersed in the PDMS matrix without any phase-separated aggregates (Fig. 3A and D). In cases of the composite films containing hybrid carbon fillers, 1D MWCNTs and 2D graphene sheets were connected to each other