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Effects of mixed carbon filler composition on electric heating behavior of thermally-cured epoxy-based composite films

Young Gyu Jeong [a,*], Ji-Eun An [b]

[a] Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon 305-764, Republic of Korea
[b] Department of Materials Design Engineering, Kumoh National Institute of Technology, Gumi, Gyeongbuk 730-701, Republic of Korea

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ABSTRACT

Epoxy-based composite films are fabricated by film-casting and thermal-curing of epoxy resin/hardener mixtures with 5.0 wt% mixed carbon fillers of different compositions of graphene and MWCNT. The electrical resistivity of the composite films decreases from $\sim 10^3$ to $\sim 10^2\ \Omega$ cm with increasing the MWCNT composition in the mixed carbon fillers, which results from the bridge effect of MWCNTs among graphene sheets. Accordingly, maximum temperature of the composite films attained at an applied voltage increases with the MWCNT composition in the hybrid carbon fillers. The composite films exhibit excellent electric heating performance in terms of temperature response rapidity and electric power efficiency.

1. Introduction

Epoxy resins, which are also referred to as polyepoxides, are a class of reactive prepolymers and polymers which contain epoxide groups [1,2]. They can be cross-linked either with themselves through catalytic homopolymerization, or with a wide range of hardeners such as multi-functional amines, acids, acid anhydrides, phenols, alcohols, and thiols. The cross-linking reaction, commonly known as curing, forms a thermosetting polymer with high mechanical properties, temperature and chemical resistance. Therefore, epoxy resins have a wide range of applications including metal coatings, electronics/electrical components, electrical insulators, fiber-reinforced plastic materials, textile finishing, and structural adhesives [3].

For last few decades, the inclusion of nanoscale carbon-based fillers such as carbon nanofibers (CNFs) [4–8], carbon nanotubes (CNTs) [9–12], graphene/graphite nanoplatelets [13–16], and carbon blacks [17–20] into insulating epoxy resins have allowed to obtain electrically conductive nanocomposites in accompanying with unique mechanical and multi-functional properties. Accordingly, epoxy-based composites reinforced with carbon-based nanofillers have been extensively investigated for the uses in advanced areas such as electromagnetic shielding, electronic components, capacitors, electrodes for rechargeable batteries, sensors and actuators. Recently, epoxy-based composites including mixed or hybrid carbon fillers of two-dimensional graphene and one-dimensional CNT have been also investigated [21–25]. Yu et al. have reported the effective synergistic effects of graphene nanoplatelets and CNTs on enhanced thermal conductivity of epoxy composites, which is ascribed to the formation of a more efficient percolating nanoparticle network [21]. Chatterjee et al. have reported the improvement of mechanical properties of epoxy composites owing to the synergistic effects of mixed fillers based on CNTs and graphene nanoplatelets on [24]. Li et al. have investigated that the embedding of hybrids of CNTs and graphene nanoplatelets into pristine epoxy resins endows optimum dispersion of CNTs and graphene nanoplatelets as well as better interfacial adhesion between the carbon fillers and matrix, which leads to a significant improvement in load transfer effectiveness [25]. On the other hand, electric heating performance of epoxy-based composites including hybrid carbon fillers of graphene and CNT has not been investigated up to present. Since the electrical properties of the epoxy/graphene/CNT composites may be finely adjusted by controlling the relative content of graphene and CNT in hybrid carbon fillers, the thermosetting composites with improved electrical conductivity are considered to be utilized for electric heating materials in advanced areas such as floor heating, road deicing, and heating textiles without emitting electromagnetic waves that is harmful to human.

In this study, we have fabricated a series of epoxy-based hybrid composite films by using an efficient film-casting and thermal-curing technique for liquid mixtures of bisphenol-A diglycidyl ether (DGEBA) and amine-functionalized harder including 5.0 wt% mixed carbon fillers of different compositions of graphene and multi-walled carbon nanotube (MWCNT), and have characterized the microstructure and electrical properties of the composite films

* Corresponding author. Tel.: +82 42 821 6617; fax: +82 42 821 8870.
E-mail address: ygjeong@cnu.ac.kr (Y.G. Jeong).

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as a function of the graphene/MWCNT composition in 5.0 wt% mixed carbon fillers. In addition, electric heating behavior of the epoxy/graphene/MWCNT composite films has been investigated by considering temperature response rapidity, maximum temperature, and electric power efficiency at different applied voltages.

2. Experimental part

2.1. Materials

Diglycidyl ether of bisphenol-A (DGEBA, YD-128, Kukdo Chemical Com.) and (E)-8,8′-(3-(dec-2-enyl)-4-hexylcyclohexa-2,5-diene-1,2-diyl)bis(N-(2-aminoethyl)octanamide (G-0331, Kukdo Chemical Com.) are used as an epoxy compound and an amine-functionalized hardener for the thermosetting epoxy resin matrix, respectively. Natural graphite (flake type, average diameter of ~500 μm) was purchased from Sigma–Aldrich Inc. and it was used for preparing conductive graphene nanoplatelets. Sulfuric acid (95%, Junsei Chemical Co., Ltd.), nitric acid (60%, Junsei Chemical Co., Ltd.), and potassium chlorate (99.5%, Kanto Chemical Co., Inc.) are used for the oxidation of the natural graphite. Graphene nanoplatelets were prepared by acid-treatment of the natural graphite and following rapid thermal expansion of graphite oxide [26–28]. MWCNT (HANOS CM-250) with average diameter of 10–15 nm and length of ~100 μm was purchased from Hanwha Nanotech Inc.

2.2. Preparation of composite films

Epoxy-based composite films containing 5.0 wt% mixed carbon fillers of different graphene/MWCNT compositions were prepared by a sequential process of ultrasonication-assisted mixing, film-casting, and thermal-curing. Firstly, liquid mixtures of DGEBA with the predetermined amount of mixed carbon fillers with different graphene/MWCNT compositions were sonicated in a bath-type sonicator (50–60 Hz) for 1 h and then were again sonicated for 5 min with a horn-type sonicator (20 kHz). The amine-functionalized harder was then added in the mixtures. The ratio of DGEBA to the hardener was adjusted to be 70:30 by wt%. The mixtures of DGEBA/hardener/graphene/MWCNT were sonicated in a bath-type sonicator for 10 min and were casted on a polyimide film. Finally, the mixtures were thermally cured at 60 °C for 1 h, 100 °C for 1 h, and 120 °C for 1 h to obtain final epoxy/graphene/MWCNT composite films. The content of mixed carbon filler in the composite films of ~100 μm in thickness was set to be 5.0 wt%, in which the relative compositions of graphene and MWCNT in the mixed filler were controlled to be 5.0/0.0, 4.5/0.5, 3.5/1.5, 2.5/2.5, and 1.5/3.5 by weight ratio, as summarized in Table 1.

2.3. Characterization

The structural order of the epoxy-based composite films with 5.0 wt% mixed carbon fillers of different graphene/MWCNT compositions was examined by using a X-ray Diffractometer (X-MAX/2000-PC, Rigaku) with Ni-filtered Cu Kα radiation (40 kV and 150 mA). X-ray diffraction patterns were obtained at a scanning rate of 2°/min in the 2θ range of 3–50°. The dispersion state and morphological feature of the mixed carbon fillers in cross-section of the composites films was characterized with aid of a transmission electron microscope (TEM, JEM 2100, JEOL Ltd.). 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.).

Changes of electric current (I) and electric power (P) with applied voltage for the composite films were measured by employing multiple sourcemeters and ohmmeters (6517A, 2400, 2182A, Keithley Instruments Inc.). Electric heating behavior of the composite films under a variety of applied voltages of 1–60 V was characterized with an Infrared camera (SE/A325, FLIR Systems Inc.) and a sourcemeter (2400, Keithley Instruments Inc.). For electrical experiments, composite film samples with 5.0 mm width and 20.0 mm length were prepared and the distance between electrical test probes was controlled to be 10.0 mm.

Table 1
Sample code and composition of epoxy-based composite films containing 5.0 wt% mixed carbon fillers of different graphene/MWCNT compositions.

Sample code	Epoxy resin (wt%)	Composition of 5.0 wt% mixed carbon filler	
		Graphene (wt%)	MWCNT (wt%)
E/G	95.0	5.0	0.0
E/G/M-9/1	95.0	4.5	0.5
E/G/M-7/3	95.0	3.5	1.5
E/G/M-5/5	95.0	2.5	2.5
E/G/M-3/7	95.0	1.5	3.5

3. Results and discussion

3.1. Structural characterization

In order to identified the structural order and packing state of hybrid carbon fillers in the thermally-cured epoxy matrix, X-ray diffraction patterns of MWCNT, exfoliated graphene sheets, the composite films with 5.0 wt% hybrid carbon fillers of different graphene/MWCNT compositions are obtained, as shown in Fig. 1. For the neat MWCNT, a broad X-ray diffraction peak was detected at 2θ ~26.4°, which corresponds to the d-spacing of 0.337 nm. This peak is caused by the fact that the neat MWCNT has relatively well-ordered and layered structure among cylindrical graphene sheets. Fig. 1B shows the TEM image of MWCNT used in this study. On the other hand, graphene sheets do not show any diffraction peak. It demonstrates that fully exfoliated graphene sheets were successfully obtained by the oxidation of the natural graphite and following rapid thermal expansion of the graphite oxide flakes, which can be confirmed by the SEM image shown in Fig. 1C. X-ray diffraction patterns of the epoxy-based composite films containing 5.0 wt% mixed carbon fillers show only broad amorphous hallo scattering without any noticeable diffraction peak associated with ordered crystalline structures. These results demonstrate that 5.0 wt% mixed carbon fillers of different graphene/MWCNT compositions were well dispersed in the epoxy matrix without forming any ordered aggregates.

The dispersion state of the 5.0 wt% mixed carbon fillers in the composite films was also characterized by using TEM images of the ultramicrotomed composite films, as presented in Fig. 2. In case of TEM image of the epoxy composite film containing only 5.0 wt% graphene sheets (i.e., E/G), the graphene sheets are found to be well dispersed and interconnected each other in the epoxy matrix, as can be seen in Fig. 2A. On the other hand, it should be noted that the epoxy composite films containing 5.0 wt% MWCNTs were not satisfactorily manufactured owing to the easy precipitation of the neat MWCNT in liquid mixtures of the epoxy compound and the hardener (not shown here). For all the composite films with 5.0 wt% mixed carbon fillers of different graphene/MWCNT compositions, TEM images display that the graphene sheets and MWCNTs are well dispersed in the epoxy matrix without forming any phase-separated aggregates (Fig. 2B–E). In addition, it is noticeable that the two-dimensional graphene sheets are interconnected with the bridging effect of one-dimensional MWCNTs. Overall, it is valid to contend that the epoxy/graphene/MWCNT composite films were