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Fluorination effects of MWCNT additives for EMI shielding efficiency by developed conductive network in epoxy complex

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ABSTRACT

To improve the efficiency in shielding electromagnetic interference in electronic devices, multi-walled carbon nanotubes were used, due to their excellent electric and magnetic properties at high aspect ratios, and were added to an epoxy matrix. Fluorination was carried out to achieve excellent dispersion and adhesion of the additives in the epoxy matrix. The improved dispersion was confirmed by UV spectra. The permittivity and permeability were also significantly improved based on the effects of the additives and the fluorination treatment. The efficiency of shielding electromagnetic interference increased up to 28 dB. This improved efficiency of shielding electromagnetic interference may be caused by a well-organized conductive network of additives in epoxy.

1. Introduction

Recently, electronic devices and components have been rapidly developing and advancing. Thus, with increased usage of electronic devices, electromagnetic waves generated by electronic systems can potentially create serious problems such as malfunctions of medical apparatus and industry robots and can even cause harm to the human body. Therefore, electromagnetic interference (EMI) shielding materials have been investigated [1–3].

EMI can be shielded by the reflection and adsorption of electromagnetic radiation. In the past, metals have been primarily applied for EMI shielding by the reflection of electromagnetic radiation. However, metals have several disadvantages, including high density, proneness to corrosion and physical rigidity. As an alternative, composites with conducting fillers such as metal particles, carbon black, carbon fibers and carbon nanotubes (CNTs) have been extensively employed for EMI shielding [4–6].

Before selecting conducting fillers, three primary conditions have to be addressed. The first is that the material must have excellent electrical conductivity and magnetic properties. The second requirement is a high aspect ratio, which can provide a continuously conductive network via interconnection. The last one is excellent dispersion and adhesion in a matrix, which is a highly investigated topic that has not yet been met with a real solution [7]. Among the above three requirements, the first and second can be solved by the appropriate selection of additive materials; however, the last one remains a problem for the use of conducting fillers.

To address this problem, fluorination surface treatment of carbon materials has been recently investigated based on functional groups, which can change the properties of the surface [8,9]. The direct fluorination method under a gas reaction has received especially large amounts of attention due to its potential for uniform modification, efficiency, short reaction times and low cost.

In our study, we attempted dispersion by direct fluorination treatment on the surface of CNTs, which have excellent electrical conductivity and magnetic properties, low density and a high aspect ratio [10–12]. We also investigated fluorination effects on multi-walled CNT (MWCNT) additives with respect to the EMI shielding efficiency by the developed conductive network in epoxy.

2. Materials and methods

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) (YD128, viscosity: 11,500–13,500 cps, Kukdo Chemical Co Ltd., Korea) was used as the epoxy monomer. Triarylsulfonium hexafluoro-phosphate (mixed, 50% in propylene carbonate, Aldrich Chemical Co.) was used as the photo-initiator. Multi-walled carbon nanotubes (MWCNTs, inner

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diameter: 2–15 nm, length: 1–10 μm, Aldrich Co.) were used as the conducting filler. Fluorine (Messer Grieheim GmbH, 99.8%) and argon (99.999%) gas were used for surface treatment.

2.2. Fluorination of MWCNTs

Fluorination of the surface of MWCNTs was carried out by a fluorination apparatus, which consists of a reactor, a vacuum pump and buffer-tank-connected gas cylinders. The conditions for fluorination were determined by trial and error to create fluorinated MWCNTs with a hydrophobicity similar to that of the epoxy. The contact angle of the epoxy was 65.5°. The fluorination conditions of the MWCNTs were then determined to obtain a similar contact angle. MWCNTs were loaded onto a nickel boat in the reactor and were degassed at 473 K for 2 h. Fluorination treatment was carried out at 303 K for 5 min at 0.5 and a total pressure of 1 bar by using mixed gas (fluorine:argon = 1:1, vol%). More details can be found in our previous work [13]. Non-treated MWCNTs and fluorinated MWCNTs treated at different pressures are referred to as follows: R-MWCNTs, F05-MWCNTs and F10-MWCNTs, respectively.

2.3. Blend preparation

A certain amount of MWCNTs (0.02 g) was dispersed in ethanol (50 ml). In order to release the bundles, the MWCNT and ethanol mixture was sonicated for 3 h. Next, the epoxy monomer (20 g) was added into the mixture and stirred at 2000 rpm for 4 h. After stirring, in order to remove the ethanol, the mixture was kept at 80 °C in an oven for 6 h.

2.4. Procedure of irradiation curing

The photo-initiator (1 g) was added into the prepared blend and then stirred at 2000 rpm and 70 °C for 5 h. The blend was poured into a 150 mm × 150 mm × 2 mm aluminum mold that was treated with a release agent. The mold was then placed under an E-beam accelerator (ELV-4, EB Tech Co., Korea) (energy: 2.5 MeV, current: 7.5 mA). E-beams were irradiated at a dose rate of 300 kGy/h in atmosphere for 10 min.

2.5. Characterization of samples

UV spectrometry (Optizen 2120 UV, Mecasys, Korea) was used to investigate the dispersion of CNTs in ethanol. The measurement was carried out following the general method presented by other groups [14]. Measurements were acquired at 635 nm after sonication for 1 h.

In order to investigate fluorination effects on the MWCNTs, the change of surface morphology was investigated by field-emission transmission electron microscope apparatus (FE-TEM, JEM-2100F HR) at 200 kV.

The oriented and defected carbon structures were examined using Raman analysis to determine the effects of heat treatment temperature and fluorination. Raman spectral analysis was conducted with an excitation power of 10 mW at 514 nm (RM 1000-InVia, Renishaw).

The XPS spectra of the MWCNTs used in this study were obtained with a MultiLab 2000 spectrometer (Thermo Electron Co., England) to evaluate the changes of chemical species on the surface of the MWCNTs before and after fluorination. Al Kα (1485.6 eV) X-rays were used with a 14.9-keV anode voltage, a 4.6-A filament current and a 20-mA emission current. All samples were treated at 10^{-9} mbar to remove impurities. The survey spectra were obtained with a 50-eV pass energy and a 0.5-eV step size. Core level spectra were obtained at a 20-eV pass energy with a 0.05-eV step size.

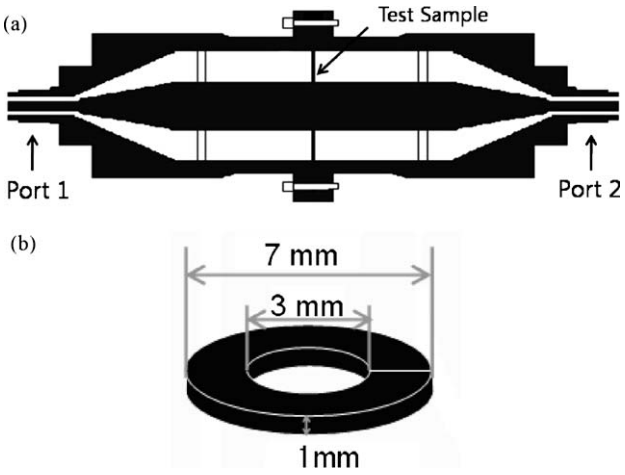

Fig. 1. Structure of the EMI SE holder (a) and the shape and dimensions of the EMI SE test specimen (b).

Permittivity, magnetic permeability and EMI shielding efficiency (SE) were obtained according to the ASTM D-4935-99 method using a network analyzer (Agilent, E5071A) equipped with an amplifier and a scattering parameter (*S*-parameter) test set over a frequency range of 800 MHz–4 GHz [15]. Annular disks were prepared with a punching machine and were installed into the test tool as shown in Fig. 1. The EMI SE was calculated using *S* parameters via equations found in the literature [16].

3. Results and discussion

3.1. Effects of fluorination on the dispersion of MWCNTs in ethanol

The dispersion stability of MWCNTs is an important factor in uniformly manufacturing MWCNTs dispersed in epoxy. The electrochemical properties of the resultant sample will be strongly influenced by the dispersion stability of the MWCNTs. The improved dispersion of the MWCNTs in ethanol can be observed from the UV spectra shown in Fig. 2. At all times, the transmitted intensity is lower with fluorination treatment, as seen by comparing the R-MWCNTs and F05-MWCNTs, indicating that the dispersion was improved by fluorinating the MWCNTs to match the hydrophobicity of ethanol Under higher fluorination pressure, more improved dispersion was observed in the

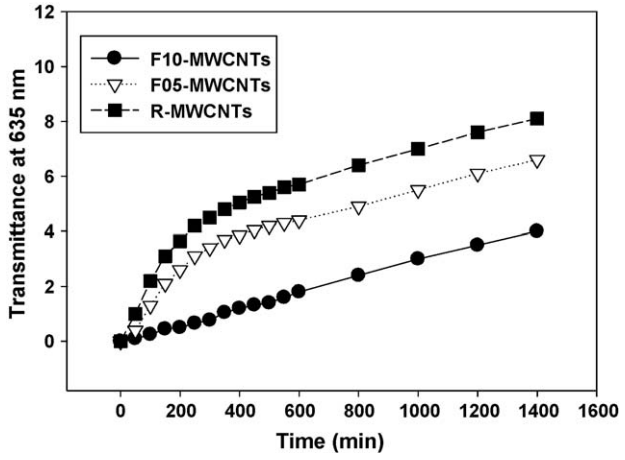

Fig. 2. Dispersion of fluorinated MWCNTs measured by IR.