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Improved mechanical and electromagnetic interference shielding properties of epoxy composites through the introduction of oxyfluorinated multiwalled carbon nanotubes

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ABSTRACT

To improve the mechanical properties of epoxy composites, multiwalled carbon nanotubes (MWCNTs) were oxyfluorinated and used as reinforcement in an epoxy matrix. A comparison of various oxyfluorinated MWCNTs and neat epoxy revealed that the tensile strength of the epoxy composites with oxyfluorinated MWCNTs increased by approximately 24%. The maximum impact strength of these epoxy composites were improved by 43% compared to that of neat epoxy. The electromagnetic interference shielding efficiency (EMI-SE) of the epoxy composites with oxyfluorinated MWCNTs was enhanced, where the highest oxygen concentration. The composites resulted in the maximum EMI-SE increase of 18% compared to that of the neat epoxy. These results were attributed to the oxyfluorination effects of MWCNTs, which form an interface with stronger adhesion as a consequence of the presence of oxygen and fluorine functional groups on the surface of the MWCNTs.

Introduction

Recently, electromagnetic interference (EMI) has raised important issues, including the faulty operation of industrial apparatuses. Given the increasing number of electronic devices and instruments, the human body could also be adversely affected. The source of these problems is the interference effect of current induced by the magnetic and electric fields emitted from various electrical circuitry in close proximity. Accordingly, investigations of the attenuation of EMI have been conducted to protect devices potentially affected by spurious electromagnetic noise [1–4].

Metals and metallic materials are widely used as EMI shielding materials due to their high shielding effect, which is a consequence of their excellent electrical conductivity [5]. However, they suffer several disadvantages, such as high density, easy corrosion, easy oxidation, poor chemical resistance, and difficult and costly processing; these disadvantages restrict the wide application of these materials [6,7]. For example, metal-based materials mostly reflect radiation and cannot be used in diverse applications like stealth technology. Also, their mechanical properties and handling procedures should be considered. An approach for resolving these problems is the development of polymer composites [8–11].

Polymer composites have numerous advantages over metals, including toughness, hardness strength, stiffness and a high heat-distortion temperature. However, their low thermal and electrical conductivity represent disadvantages. To overcome these disadvantages, conductive particles such as carbon nanotubes (CNTs), graphene oxide, and carbon black have been used to enhance the properties of polymer composites [12–15]. CNTs have been widely applied as a reinforcement because of their remarkable mechanical, thermal, and electrical properties [16–18]. Extensive research has resulted in remarkable property improvements of CNT-reinforced epoxy composites [15,19,20]. For example, dispersing 0.2–10 wt.% CNTs into an epoxy matrix results in modulus improvements as high as 50% and strength improvements as high as 18% [21]. However, considering the properties of the CNTs, the improvements in these properties are smaller than expected. The poor dispersion and weak interfacial adhesion of CNTs are serious challenges to the satisfactory improvement of CNT/polymer composite properties. Their large surface-to-volume ratio leads to agglomerate due to the strong inter-tube attraction caused by van der Waals forces and by weak interfacial bonding [15,19–22].

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Chemical modification and functionalization have been shown to improve the dispersion of CNTs. In addition, the surface bonds of the functionalized CNTs facilitate the transfer of stress between the CNTs and the polymer matrix, which brings about enhanced interfacial interactions [19–22]. Youn et al. investigated changing the functional groups of CNT by acid, amine, and plasma treatment. Tensile stress of epoxy composites reinforced these CNT are 5, 12, and 38% higher than epoxy composites reinforced raw CNT [23].

Fluorination of CNTs has recently been investigated because fluorination is a simple and fast method. Previous research on fluorinated carbon materials such as CNTs has been used to interpret the interactions between the carbon surface and fluorine atoms. These include diverse interactions such as C–F covalent, semi-ionic, ionic and van der Waals interactions [24]. Therefore, the introduction of fluorinated CNTs has already been observed to result in increased dispersion in polymer composites [25,26].

Here, we studied the improved properties of epoxy composites with oxyfluorinated multiwalled carbon nanotubes (MWCNTs) with many different functional groups on their surface. The presence of functional groups on the MWCNTs is expected to enhance the interfacial interaction between treated MWCNTs and the epoxy matrix and to prevent agglomeration of MWCNT bundles in the epoxy matrix. The results of this study can therefore help us understand how the functional groups influence the mechanical and electrical properties of the composites. The mechanical properties of the epoxy composites with oxyfluorinated MWCNTs were evaluated by tensile and impact tests. Additionally, the effect of oxyfluorination on the EMI shielding effect (EMI-SE) of the MWCNTs, as indicated by the developed network structure in the epoxy composites, is reported.

Experimental

Materials

Diglycidyl ether of bisphenol A (YD-128, Kukdo Chemical Co., Ltd., Korea), an epoxy monomer, and polyamide resin as a hardener (G-640, Kukdo Chemical Co., Ltd., Korea) were used. MWCNTs (internal diameter: 2–15 nm, external diameter: 50 nm, length: 1–10 mm, Hanhwa Chemical Co., Korea) were used as a reinforcement material.

Oxyfluorination of MWCNTs

The surfaces of the MWCNTs were modified via oxyfluorination using fluorine and oxygen gases. First, to remove impurities such as water, the MWCNTs were pretreated at 100 °C for 2 h; these MWCNTs were named raw-CNT. Oxyfluorination was conducted for 10 min with oxygen gas:fluorine gas mixture ratios of 2:8, 4:6, 6:4, and 8:2, named OF28, OF46, OF64, and OF82, respectively.

Fig. 1 presents the oxyfluorination surface treatment mechanism of the MWCNTs. When fluorine gas was injected in reactor, fluorine attacks the surface of MWCNTs, forming carbon radicals. After that, these carbon radicals react with oxygen or fluorine gas and form many oxygen and fluorine functional groups on the carbon surface. Therefore, these oxygen or fluorine functional group contributed to enhanced interfacial adhesion in the polymer composites [27,28].

Fabrication of epoxy composites with oxyfluorinated MWCNTs

The raw-CNT/epoxy and oxyfluorinated MWCNTs/epoxy mixtures were combined in a weight ratio of 100:0.3 (epoxy matrix: MWCNTs). The mixtures were dispersed by an impeller for 20 min and ultra-sonicated for 3 h. The MWCNTs/epoxy mixtures were cured with a hardener, which was blended with an epoxy: hardener weight ratio of 100:50. The sample was defoamed at 25 °C for 30 min using a vacuum pump. This process removed air bubbles from the epoxy mixtures that formed during their mixing; these air bubbles can adversely affect the properties of the epoxy composites by forming voids [29]. The epoxy mixtures with oxyfluorinated MWCNTs were poured into a mold for processing and were cured at 100 °C for 2 h. Neat epoxy, raw-CNT/epoxy composites and oxyfluorinated MWCNTs/epoxy composites prepared under oxygen gas:fluorine gas mixture ratios of 2:8, 4:6, 6:4, and 8:2 were denoted as neat epoxy, raw-CNT/E, OF28/E, OF46/E, OF64/E, and OF82/E, respectively.

Characterization of epoxy composites with oxyfluorinated MWCNTs

Surface chemical properties of MWCNTs

The oriented and defective carbon structures were evaluated using Raman spectroscopy (RM 1000-InVia, Renishaw) to determine the effects of oxyfluorination. The Raman spectra were collected using an excitation power of 10 mW at 514 nm.

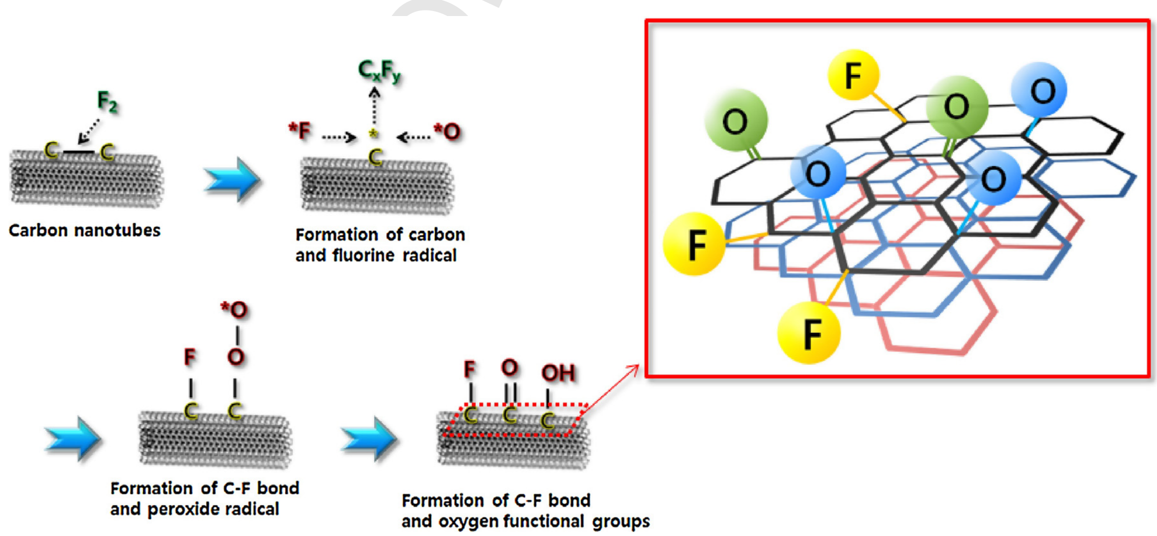

Fig. 1. Diagram of the oxyfluorination surface treatment mechanism of MWCNTs.

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