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Effect of heat treatment on ZrO_2-embedded electrospun carbon fibers used for efficient electromagnetic interference shielding

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ABSTRACT

ZrO_2-embedded carbon fibers were prepared for use as an electromagnetic interference (EMI) shielding material by electrospinning and heat treatment methods. Structural changes were observed in the ZrO_2 and in the carbon structures by XRD and Raman spectroscopy, respectively. During heat treatment, XRD analysis results revealed a transition from a monoclinic structure to a tetragonal structure in ZrO_2 and a graphitization in the structural formation of carbon fibers was observed by Raman spectroscopy. It was observed that these structural changes in the ZrO_2 and the carbon fibers improved the real and imaginary permittivities by a factor of more than 3.5. The EMI shielding efficiency (SE) improved along with the permittivity with higher treatment temperatures and greater amounts of embedded ZrO_2; the highest average EMI SE achieved was 31.79 dB in 800–8500 MHz. The heat treatment played an important role in the improvements in the permittivity and in the EMI SE because of the heat-induced structural changes of the ZrO_2-embedded electrospun carbon fibers. We suggest that the EMI shielding of the fibers is primarily due to the absorption of electromagnetic waves, which prevents secondary EMI by reflection of electromagnetic waves.

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1. Introduction

With the widespread use of electronic devices, electromagnetic interference (EMI) has become a serious problem. EMI can cause operational malfunctions of electric devices, such as medical apparatuses and industry robots, which lead to significant losses in time, energy, resources, and money. EMI can also harm our bodies by causing diseases such as leukemia and breast cancer. Thus, the search for materials that have effective EMI shielding properties has been the focus of recent research [1–3].

EMI shielding materials must have a high permittivity and a high permeability. When interacting with electromagnetic waves, the electronic and magnetic states of materials that have high permittivities and permeabilities can be changed significantly. For example, electrons have movement in those molecules that has a high permittivity. The electromagnetic waves are attenuated by this electron attraction effect. In short, electromagnetic waves are absorbed or reflected by the shielding material. By summing the EMI shielding efficiency (SE) by absorption and reflection, the total EMI SE is obtained. When electromagnetic waves are reflected by the shielding material the reflected waves can interfere with signals from other electronic devices in the vicinity, causing secondary EMI that can result in severe electronic malfunctions [4–6].

Traditionally, metals and metal oxides have been used as EMI shielding materials; unfortunately these materials provide EMI shielding by reflection of the electromagnetic waves [7,8]. Recently, carbon nanotubes (CNTs) have been of much interest as it is an electromagnetic wave-absorbing material. CNTs possess high permittivity, therefore yielding a high EMI SE. CNTs′ high permittivity is attributed to the well-organized carbon-graphite structure. However, CNTs are expensive and are prone to extreme aggregation. Thus, their application in industry is lower than expected [9–11].

In this study, we studied graphite-structured carbon nanofibers as an alternative EMI shielding material. ZrO_2 was used as an additive because it also has high permittivity. As an additive ZrO_2 has many advantages, such as low thermal conductivity (20% that of alumina), chemical inertness, and high hardness [12,13]. ZrO_2-embedded graphite-structured carbon nanofibers were prepared by electrospinning and heat treatment. The EMI shielding properties were analyzed using *S*-parameters based on the absorption of electromagnetic waves in relation to the permittivities of graphite-structured carbon and the tetragonal-structured ZrO_2.

2. Materials and methods

2.1. Materials

Polyacrylonitrile (PAN, M_W=150,000, Aldrich) was used as the carbon fiber source. N,N-dimethyl formamide (DMF, 99.995%

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Acros) was used as the solvent for the polymer because of its high boiling point (153 °C) and excellent conductivity (conductivity = 10.90 μS/cm, dipole moment = 3.82 D), both of which are important factors for electrospinning [14]. ZrO_2 (zirconium(IV) oxide, < 100 nm, monoclinic structure, Aldrich) was used as an additive. Y_2O_3 was used as a stabilizer agent to prevent the formation of cracks when the system experienced a volumetric increase during the transition from monoclinic ZrO_2 to tetragonal-structured ZrO_2 [15,16].

2.2. Methods

2.2.1. Preparation of solution for electrospinning

A polymer solution (12 wt%) was prepared by stirring PAN and DMF at 130 °C for 8 h. Then, 0.5, 1.0, or 1.5 g of ZrO_2 was added to 30 ml of the PAN-based polymer solution along with Y_2O_3 (4 mol% of Y_2O_3/ZrO_2) as the stabilizer agent. The resulting solution was sonicated at 30 °C for 2 h to disperse the additional reagents.

2.2.2. Preparation of electrospun carbon fibers (ECFs)

Each prepared polymer solution was loaded into a 30 ml syringe with a capillary tip (18G, inner diameter: 1.27 mm), and the syringe was placed in a KD scientific syringe pump (Model 100). The details of our experimental conditions have been previously described [17–19]. Briefly, the polymer solution was ejected from the syringe tip onto an aluminum foil-covered collector using an electrospinning apparatus. Electric power was applied with a high-voltage power supply (NT-PS-25K, NTSEE Co., Korea) at 18 kV. The tip-to-collector distance was 10 cm, and the feed rate of the polymer solution was 1.5 ml/h.

Before carbonization of the electrospun fibers, a stabilization step (an oxidation process) was necessary to prevent the electrospun materials from losing their fiber form and softening/melting at high temperature [18,19]. This stabilization step was carried out at 260 °C for 5 h in air at a heating rate of 1 °C min^{-1}. After the oxidation step, the heat treatment was applied to carbonize or graphitize the oxidized fibers in an argon atmosphere with the following conditions: a heating rate of 10 °C/min, a holding time of 1 h, an argon gas (99.999%) feed rate of 60 ml/h, and a target temperature of 900, 1300, or 2100 °C. The treatment temperatures were set based on the conditions under which monoclinic ZrO_2 undergoes phase transitions to the tetragonal and cubic structures (1127 and 2297 °C, respectively); tetragonal-structured ZrO_2 has the highest permittivity among monoclinic-, tetragonal-, and cubic-structured ZrO_2 [20,21]. The prepared samples were named according to the conditions under which they were prepared, as listed in Table 1.

2.2.3. Characterization of samples

Field emission scanning electron microscopy (FE-SEM, Hitachi, S-5500) was used to investigate the surface morphology of the nanofibers. Images were taken without prior treatment (e.g., Pt coating) to ensure the acquisition of accurate images. The sizes of the electrospun carbon fibers and the embedded ZrO_2 clusters were measured using the software program installed on the FE-SEM apparatus. The X-ray diffraction (XRD) patterns of the samples were obtained using an XRD apparatus [D8 Discover, Bruker AXS, Germany] and analyzed to investigate the phases and crystal structures of ZrO_2.

The permittivity, magnetic permeability, and EMI shielding efficiency (SE) were measured by 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 800–8500 MHz [22–24]. Annular disks were prepared with a punching machine and were installed into the test tool, as described in the previous work [25]. The EMI SE was calculated using the S-parameters and equations found in the literature [22–24].

Table 1
Sample names and the conditions under which they were prepared.

Samples	Reaction temperature (°C)		
	900	1300	2100
Amount of embedded ZrO_2 (g)			
–	CF9	CF13	CF21
0.5	CF9-0.5Z	CF13-0.5Z	CF21-0.5Z
1.0	CF9-1.0Z	CF13-1.0Z	CF21-1.0Z
1.5	CF9-1.5Z	CF13-1.5Z	CF21-1.5Z

3. Results

3.1. Structural analysis of carbon fibers

Fig. 1 presents the Raman spectra of the thermally treated carbon fibers. These spectra show that the reaction temperature during heat treatment affected the frequency of defects in the graphitic lattice of the carbon fibers. In three samples, peaks related to defects and graphite structures (D and G peaks, respectively) were observed at 1356 and 1585 cm^{-1}, respectively [26]. The intensity of the G peaks increased with higher reaction temperatures, indicating that heat treatment promotes the development of the graphite structure of carbon fibers. The I_G/I_D ratios (the ratio of the intensity of the G peak to the intensity of the D peak) of the CF9, CF13, and CF21 samples were 1.12, 2.65, and 3.84, respectively. This result may be attributed to the change of orbital hybridization of the carbon sites in the carbon fibers after heat treatment, resulting in the development of graphite-structured carbon.

3.2. Effect of various treatment temperatures on the structural changes of ZrO_2

To investigate the structural changes in ZrO_2 during heat treatment, XRD was performed on the ZrO_2-embedded carbon fibers treated at different temperatures (900, 1300, and 2100 °C). The results are shown in Fig. 2. The CF9-1.5Z, CF13-1.5Z, and CF21-1.5Z samples were selected to investigate the structural

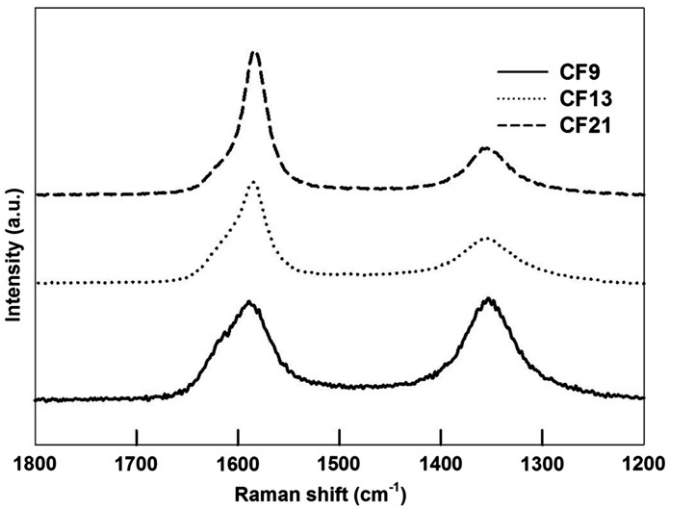

Fig. 1. Raman spectrum of electrospun carbon fibers treated at different temperatures.

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