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Enhanced interfacial, electrical, and flexural properties of polyphenylene sulfide composites filled with carbon fibers modified by electrophoretic surface deposition of multi-walled carbon nanotubes

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ABSTRACT

Electrophoresis can be an effective approach for depositing carbon nanotubes (CNTs) on the surface of carbon fiber (CF). Nevertheless, it has been rarely reported on polyphenylene sulfide (PPS) composites filled with CFs surface-modified by CNTs based on electrophoresis. In this study, we investigated the electrophoresis process conditions that can completely coat CF with multi-walled CNTs (MWCNTs) using self-manufactured electrophoresis equipment, and the enhancement of interfacial, electrical and flexural properties of PPS composites by introducing CFs coated with MWCNTs based on electrophoresis. In particular, interfacial shear strength (IFSS) of the PPS composites was measured by microbond tests and improved by about 41.7% due to the MWCNTs introduced on the surface of CFs. These enhancements were theoretically explained by an interface-modified CF-based micromechanical model. Introducing MWCNTs on the CF surface based on electrophoresis was demonstrated to be an effective method for improving the interfacial, electrical and flexural properties of PPS composites.

1. Introduction

Polyphenylene sulfide (PPS) is one of the most widely used engineering plastics in the aerospace and automotive industries due to its excellent heat resistance, flame retardancy, chemical resistance, dimensional stability and processability [1,2]. However, PPS resins, which are a type of semi-crystalline polymer, have been otherwise limited in application by their relatively low mechanical strength and fragile characteristics [1,2]. The mechanical properties of PPS resin can be improved by incorporating fiber and/or filler [1,3]. In particular, carbon fiber (CF) has been employed as a reinforcing fiber material in PPS resin because it provides excellent reinforcing effect and heat characteristics [1,3]. As a result, CF reinforced PPS composites are considered high-performance engineering materials, not only because they exhibit beneficial physical properties, but also excellent processability [1,3].

The physical properties of CF reinforced composite materials are known to depend on the properties of the matrix and filler, the shape and volume fraction of the fibers, and the chemical and physical interactions between the fibers and the matrix [2]. In order to fabricate a CF reinforced PPS composite with excellent mechanical properties, good interfacial adhesion between the fiber and the matrix is required [4–9]. CF is a highly crystallized graphite based material with a non-polar surface and an inert structure, and interacts poorly with most polymer resins [2,10]. Therefore, it is necessary to control the interface between CF and PPS to improve mechanical properties.

A method has been proposed for growing or adhering a nanoscale whisker, which is characterized by a high aspect ratio and surface to volume ratio, on the surface of CFs to improve fiber-matrix interactions and interfacial properties [11]. The nanoscale whiskers have been demonstrated to significantly increase the load transfer area between the fibers and the matrix, thus effectively enhancing fiber-matrix interactions and interfacial properties [12]. Also, Chen et al. reported that graphene or carbon nanotubes (CNTs) based interface layers could improve load transfer from the matrix to the filler and reduce interfacial stress concentration [13,14]. Several studies have been proposed over the last few years to develop effective CNT/CF hybridization methods. These can be broadly divided into two categories [11]: the first involves the direct growth of CNTs on a CF surface by chemical vapor deposition (CVD) and the second is accomplished by coating CNTs on the CF surface, by spraying or electrophoresis.

Electrophoresis can be an effective approach to coat CNTs on a CF

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surface, and the technique can be easily automated and utilized in industrial applications [15]. Nevertheless, it has been rarely reported on polyphenylene sulfide (PPS) composites filled with CFs surface-modified by CNTs based on electrophoresis. In this study, we investigated the electrophoresis process conditions that can completely coat CF with multiwall CNTs (MWCNTs) using self-manufactured electrophoresis equipment. PPS composites filled with CNTs-coated CF were fabricated to evaluate the interfacial, electrical and flexural properties of the composites. In particular, interfacial shear strength (IFSS) of the fabricated composites was evaluated based on the microbond test and a modeling method based on control of the interfacial properties was proposed to theoretically understand the properties of the composites.

2. Experimental

2.1. Materials

PPS powders (W316 grade) supplied by Kureha Chemical Industry Co., Ltd (Tokyo, Japan) were used as the matrix. The density and molecular weight of the material were 1.35 g/cm^3 and 35,000 g/mol, respectively. CF (Granoc XN-80-A2S) was supplied by Nippon Graphite Fiber Corporation (Tokyo, Japan). The diameter and length of the CF was 10 μm and 6 mm, respectively. Desizing of the CFs was performed by immersing them in 40% nitric acid for 2 h because the sizing agents on the CF surface can act as an insulating gap that prevents the movement of electrons during electrophoresis. MWCNTs (Hanwha Nanotech Ltd., Seoul, Korea) manufactured by the CVD method were used for electrophoresis.

2.2. Preparation of MWCNT suspension for electrophoresis

1 g of MWCNTs and 200 ml of an acid mixture of nitric acid and sulfuric acid in a ratio of 1:3 were mixed, and the surfaces of the MWCNTs were modified at a low rotation speed of 200 rpm. After the surface modification, the MWCNTs were washed with distilled water of 2–3 MΩ to remove residual acid solution, until pH 7. The washed MWCNTs were then dried at 80 °C for 24 h. To overcome the phase separation, aggregation and low dispersion of the MWCNTs, cetyltrimethylammonium bromide (CTAB, Merck, Darmstadt, Germany), a cationic surfactant, was used to alter the electrical properties of the surface of the MWNTs. CTAB (20 times as much as MWCNTs) and the prepared MWCNTs were added to 300 ml of deionized water and dispersed by sonication for 5 min to prepare a positively charged MWCNTs solution.

2.3. Electrophoresis

Electrophoresis is a process in which very small particles or colloids dispersed in a liquid move under electric field in one direction toward a pole. In this study, the positively charged MWCNTs are moved toward the negatively charged CFs by the electrostatic attraction by the electric field, and are deposited. A device was constructed to transfer charge from the prepared suspension to the desized CFs using a copper film, which served as an electrode connected to an external direct current (DC) power source as shown in Fig. 1. Designed to provide continuous treatment to CFs, the system consisted of two power supplies capable of voltage regulation, a motor to control the speed of movement of the CFs, and an acrylic case for electrical safety. The electrophoresis conditions were controlled by adjusting the voltage of the power supply and deposition time.

2.4. Composite fabrication

PPS composites filled with desized CFs or with CFs coated with MWCNTs were fabricated with their respective target compositions as listed in Table 1, using a twin-screw extruder (TK-40, BauTech, Seoul, Korea). The screw rotation speed of the compounder was 300 rpm, and the temperature of the barrel was set at 295, 320, 320, 320, and 290 °C from the inlet of the raw material. The fabricated mixture was pelletized, and specimens for property measurements were prepared at 320 °C using a programmable hydraulic press (MTP-14, Tetrahedron Associates, Inc., San Diego, USA).

2.5. Characterization

2.5.1. Morphology

The morphology of the desized CFs and CF with MWCNTs introduced based on electrophoresis was observed, using a field emission scanning electron microscopy (FE-SEM, Nova NanoSEM 450, FEI Corp., OR, USA) and a transmission electron microscope (TEM, Tecnai F20, FEI Corp., OR, USA). The CF specimens for FE-SEM measurement were coated with platinum in a vacuum for 200 s using a sputter coating machine (Ion Sputter E-1030, Hitachi High Technologies Corp., Japan). The FE-SEM measurements were carried out at 15.0 kV. For the TEM sample preparation, the CFs coated with MWCNTs were dispersed in ethanol and sonicated for 5 min, and subsequently the dispersion was dropped onto a lacey-carbon coated film on a Cu grid. The TEM measurements were performed at 120 kV.

2.5.2. Microbond tests to measure IFSS

To investigate the interfacial properties between the fiber and matrix, the IFSS of the PPS composites filled with desized CFs or with CFs coated with MWCNTs was measured based on a microbond test, as shown in Fig. 2(a). The free fiber length of the prepared specimens in the microbond test was approximately 20 mm. Molten PPS resin droplets were placed on the CF monofilament and cooled, as shown in Fig. 2(b). The microbond test was performed using an interfacial microbond evaluation instrument (Model HM410) fabricated by TOHEI SANYOU CO. LTD (Tokyo, Japan). The prepared CF fiber with PPS droplets was loaded at a speed of 2 mm/min while the force was recorded against the displacement. The interfacial shear strength, τ, was determined using the following equation [16].

$$\tau = \frac{F_{max}}{\pi D L_e} \tag{1}$$

where F_{max} is the force at the moment when the interfacial debonding or sliding occurs, D is the CF diameter, and L_e is the embedded length of the CF in the PPS resin droplet.

2.5.3. Physical properties of the composites

Electrical conductivity measurements were performed on the PPS composite specimens, which had a length of 80 mm, width of 19.5 mm and thickness of 2.5 mm. The volume electrical resistivity of the prepared composite specimens was measured by standard four electrode method, based on the previous study [17]. A standard electrode assembly for the volume resistivity measurement based on the four electrode method was used with a distance between the knife-edged electrodes of 15 mm and a distance between the potential electrode and the current electrode of 20 mm, respectively. The flexural strength and modulus of the prepared PPS composite specimens were measured according to ASTM D790.

3. Theoretical model for composites containing interface-modified CF

A micromechanics-based theoretical model was adopted to theoretically calculate the electrical and mechanical behaviors of the interface-modified CF embedded composites. The characteristics of the interface was selected as a key parameter to describe the physical and chemical transformations in the complex material system. The theoretical scheme of the present model is represented in Fig. 3. To reflect the actual properties of the composite, the CF was assumed to be 3D