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Interlaminar resistive heating behavior of woven carbon fiber composite laminates modified with ZnO nanorods

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ABSTRACT

Thermal heating in the interlaminar region of ZnO/woven carbon fiber composite laminates was investigated. In ZnO/woven carbon fiber composite laminates, the interlaminar region, composed of ZnO nanostructured arrays embedded on woven carbon fiber sheets, interacts with the thermoset vinyl ester resin. ZnO nanostructured arrays were formed into nanorods (NRs) using a hydrothermal process. To investigate the electrical resistive heating behavior of the interlaminar region, we analyzed the temperature profile as a function of time in three zones: a heating zone, a maximum temperature zone, and a cooling zone. The morphology of the ZnO NRs was investigated using scanning electron microscopy, and X-ray diffraction analysis was used to characterize the crystallinity and ZnO concentration. Differential scanning calorimetry was employed to analyze the specific heat capacity of ZnO/woven carbon fiber composite laminates. Electrical resistive heating was achieved in the interlaminar region through multiple junctions formed between the intrinsic woven carbon fiber tows and among the ZnO NRs. The contribution of the ZnO NRs to the thermal heat gain was interconnected with the woven carbon fiber and resin in the interlaminar regions. The interlaminar resistance between the upper and lower laminas of ZnO/woven carbon fiber composites increased with incremental increases in the ZnO concentration up to 110 mM. This effect was due to the interlaminar interface and the high surface density of ZnO NRs, which inhibit electron transport into the woven carbon fibers. Resistance decreased following electrical resistive heating due to an increase in the density of free electrons at high temperatures.

1. Introduction

Over the past few decades, fiber-reinforced polymer (FRP) composites have been widely used in many industrial applications owing to their high specific strength and stiffness. In particular, polymer composites reinforced by carbon fiber (CF) have received considerable attention because of their excellent mechanical properties and lightweight characteristics. Recently, emerging interest in nanoscale carbon-based fillers, such as carbon nanotubes (CNTs) [1,2], graphene/graphite nanoplatelets [3,4], carbon nanofiber (CNF) [5,6] and carbon black [7,8], has become extremely attractive due to their thermal stability, electrical conductivity, and enhanced mechanical properties. However, difficulties exist in preparing uniform dispersions of these nanoscale carbon-based fillers due to the strong intermolecular van-der Walls interactions between CNTs and graphene, and the tendency for CNFs and carbon black to form bundles and branches; as a consequence, these materials may aggregate in the composites. To address these problems, whiskerization has been used to obtain the desired interfacial reinforcement, which is the dominant factor in terms of the performance of composites, by growing a secondary reinforcement directly onto the surface of the fiber. In particular, ZnO nanostructures have been identified as one of the most promising whiskerization materials due to their favorable piezoelectric [9], optical [10–12], electrical [13,14], mechanical [15–17], dielectric [18], and microwave absorption [19,20] properties. ZnO nanostructure arrays enhance the load transfer capacity from the fiber to the matrix, but do not negatively impact on the mechanical properties of the fiber; they reduce stress concentration and increase the surface area for bonding with the polymer matrix [21].

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The electrical properties of carbon-based composites can be exploited for electrical resistive heating. In particular, electrical resistive [22–24] and magnetic induction [25] heating in vinyl ester-based composites reinforced with CF have been investigated for applications as heating elements [26,27]. Fosbury et al. investigated the electrical properties of the interlaminar interface of a CF/polymer matrix composite and showed that this interface can function as an effective resistive heating element [28]. Takahashi and Hahn used the electrical properties of CF/polymer matrix composites for automatic thermal management of graphite–fiber–polymer composite structures [29]. They showed that the temperature of the composite can be controlled by adjusting the conductivity in the directions both parallel and perpendicular to the axis of the fiber [29].

Rudolf et al. studied magnetic induction heating of continuous CF-reinforced thermoplastic composites [25]. They discovered that heat is generated only when closed fiber loops exist through which current can flow. For example, unidirectional fiber laminates cannot be heated because the laminates do not contain fiber junctions. However, no such reports of interlaminar region characterization for the electrical resistive heating of ZnO/woven CF composite laminates have been published.

Here, we investigate the electrical resistive heating of the interlaminar regions in composite laminates formed of woven CF sheets coated with a ZnO secondary reinforcement in a vinyl ester matrix. The junctions between ZnO/woven CF plies are expected to exhibit electrical resistive heating, and the ZnO nanostructures are expected to increase the mechanical stability of the interfacial region between the carbon fiber and vinyl ester resin. The hydrothermal method was used to synthesize the ZnO nanostructures, which is a low-temperature process (90 °C) that proceeds in an aqueous solution and entirely preserves the mechanical strength of the fibers. Significant enhancement of the interfacial properties is expected because of the bonding between ZnO and the hydroxyl, carbonyl, and carboxylic acid groups on the carbon fiber [21]. Aligned ZnO nanorod arrays were grown on the woven CFs using various ZnO concentrations. Scanning electron microscope (SEM) images were used to examine the morphology of the ZnO NRs grown on the surface of the woven CFs, and X-ray diffraction (XRD) patterns were analyzed to characterize the crystallinity of the ZnO NRs. Differential scanning calorimetry (DSC) was used to analyze the specific heat capacity of the ZnO/woven carbon fiber composite laminates.

2. Experimental

2.1. Materials

We used a bisphenol-A epoxy-based vinyl ester, together with a methyl ethyl ketone peroxide initiator. Dimethyl aniline was used as an accelerating agent to reduce the curing time and temperature of the vinyl ester resin. These reagents were purchased from Kukdo Chemical Co. Ltd., Korea. T-300 woven CFs were provided by Toray Industries Inc. (Japan), and analytical grade zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), NaOH, zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), and hexamethylenetetramine ($C_6H_{12}N_4$, HMTA) were purchased from Sigma–Aldrich (U.S.A.) and used to prepare ZnO NRs. Ethanol (reagent grade, J.T. Baker, U.S.A.) was used as a solvent together with zinc acetate dehydrate to obtain a stable colloidal suspension, which was used to seed the growth of the ZnO NRs.

2.2. Preparation of ZnO/woven CF/vinyl ester resin composite laminates

Hexagonal arrays of ZnO NRs were synthesized using the hydrothermal method, which is known for its simplicity, low temperature, and low environmental impact [30]. ZnO seed precursors were deposited onto the woven CFs via four soaking and annealing cycles, whereby in each 10-min cycle, the woven CF sheets were soaked in the colloidal suspension of ZnO nanoparticles. The seed-treated woven CF sheets were then placed in an aqueous solution of 1 M zinc nitrate hexahydrate and 1 M HMTA. The pH of the aqueous solution for ZnO growth was maintained between 6 and 8. The growth of the ZnO NRs was carried out at 90 °C for 5 h, and the reaction was as follows:

$$\mathrm{HMTA} + 6\mathrm{H_2O} \leftrightarrow 6\mathrm{HCHO} + 4\mathrm{NH_3} \quad (1)$$

$$\mathrm{NH_3} + \mathrm{H_2O} \leftrightarrow \mathrm{NH_4^+} + \mathrm{OH^-} \quad (2)$$

$$2\mathrm{OH^-} + \mathrm{Zn^{2+}} \leftrightarrow \mathrm{ZnO(s)} + \mathrm{H_2O} \quad (3)$$

Reaction (3) illustrates that ZnO growth was favored by high concentrations of OH^- anions.

Each woven CF sheet was 80×80 mm^2, cleaned using ethanol, and dried in an oven at 100 °C for 10 min. Further details of the synthesis can be found in the primary literature [17]. ZnO/woven CF composite laminates were formed using a vacuum-assisted resin transfer molding (VARTM) process and infiltrated with the vinyl ester resin, initiator, and accelerating agent, which were mixed at a ratio of 100:1:1 by weight. The molar concentration of ZnO was varied during the ZnO NR growth to study the effect on the surface morphology, crystallinity, electrical resistive heating behavior, and specific heat capacity of the resulting composite.

2.3. Experimental setup for electrical resistive heating and characterization

The electrical resistive heating was characterized using the experimental apparatus shown schematically in Fig. 1A. The sample was connected to an electrical power supply, and the temperature distribution at the surface was monitored using an infrared camera (H2640, Joowon Industrial Co., Ltd., Korea). The output from thermocouples placed on the surface was obtained and infrared thermographic analysis was performed; the difference in these measured temperature data were used to compensate for the temperature gap. The electrical resistance was measured using a two-probe method. The electrodes were placed on the samples with conducting silver paste. This ensured that the contact resistance between the electrodes and the composite laminas was much lower than that of interlaminar region. The inter-probe resistance of the sample was monitored using a digital multimeter (81/2-digit Model 2002, Keithley, U.S.A.).

The surface resistance and the interlaminar resistance were analyzed separately. The surface resistance was measured by an electrode connection method, which is discussed in the following section. The interlaminar resistance at the ZnO/woven CF composite interface is illustrated in Fig. 1B and is associated with current flow through the material thickness from the upper to the lower lamina of the CF plies. Since CF is regarded as a conducting material, the major resistance between the two probes was referred to as the interlaminar resistance, which was assumed to originate from inside the laminas. The interlaminar region is characterized by multiple contacts of the ZnO NRs on the two woven CF plies with the thermoset vinyl ester resin.

To investigate the electrical resistive heating behavior, silver wires were integrated on the surface of ZnO NRs grown on the CF sheets prior to the VARTM process. The ends of the silver wires were connected to the electrical power supply, and the temperature distribution between the two electrodes was monitored.