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Electrical thermal heating and piezoresistive characteristics of hybrid CuO–woven carbon fiber/vinyl ester composite laminates

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ABSTRACT

The electric heating and piezoresistive characteristics of CuO–woven carbon fiber (CuO–WCF) composite laminates were experimentally evaluated. Hybrid CuO–WCF composites were fabricated via a two-step seed-mediated hydrothermal method. The interlaminar interface between two plies of hybrid CuO–WCF/vinyl ester composite laminae was influenced by interlocked fiber–fiber cross-linking structures with CuO NRs and acted as electric heating and resistance elements. The contribution of CuO NRs (10–110 mM) to the interlaminar interface was determined by measuring the temperature profile, in order to investigate the electrical resistive heating behavior. At higher concentration of CuO NRs growth in the interlaminar region applied by 3 A, the average temperature reached to 83.55 °C at the interface area $50 \times 50\ mm^2$ and the heating efficiency was 0.133 W/°C owing to radiation and convection given by 10.5 W (3 A, 3.5 V). To investigate the piezoresistive response, the through-thickness gauge factor was observed at 0.312 during Joule heating applied by 2 A, compared with 0.639 at an ambient air temperature for CuO 110 mM concentration. The morphology and crystallinity of CuO NRs were investigated using scanning electron microscopy and X-ray diffraction analyses, respectively. The temperature dependence of hybrid CuO–WCF composite laminates' storage moduli were analyzed using a dynamic mechanical analyzer. These characterizations showed that the interlaminar interface, combined with the high specific surface area of CuO NRs, provided the electron traps for electrical conduction around multiple WCF junctions and adjacent cross-linked laminae.

1. Introduction

In recent years, multifunctional materials and composite structures have drawn considerable interest for use in both structural and non-structural applications. Most of the mechanical development in structural functionalized materials aims to increase the specific strength, specific stiffness, and fracture toughness of a given material. In contrast, non-structural functionalized materials often require diverse properties such as electrical or thermal conductivity, sensing capabilities, energy harvesting/storage abilities, self-healing capabilities, electromagnetic interference shielding, recyclability, and biodegradability [1,2].

Polymer–matrix composites with carbon fibers boast both structural and non-structural functions and are used in various commodity and engineering applications requiring high specific strength, stiffness, light weight, and high thermal and electrical conductivities [3–5]. However, attaining desirable non-structural functions while maintaining the desired structural properties depends strongly on the interfacial interactions within the fiber–matrix interface, which govern the overall performance of a composite material [6]. Several researchers have reported various strategies to obtain desired non-structural functions in composite materials.

Whiskerization, a representative technique used to tailor interfacial interactions, results in a graded interface that reduces stress between the fiber and matrix phases. In composites, whiskerization is normally deposited in an array of whiskers onto the fiber and yields improvement of cohesion between fiber and matrix. Hence, the interphase properties are enhanced due to interlocking the matrix–fiber interface. CuO-grafted on the surface of fiber, one of the whiskerization tailored on the fiber, has been reported to get higher mechanical properties of composites because of the cross-linked network acting as the enhanced load-bearing capacity due

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to the higher specific surface area of CuO [7]. Metal oxide nanomaterials can be processed in this way and have been reported in unique sensor applications, such as piezoelectrics, chemical sensing, and photodetection [8]. CuO whiskers are promising in this regard due to their typical p-type semiconductor structure with a narrow band gap of ~1.2 eV. CuO whiskers also exhibit non-structural functions that have been shown useful in various applications including gas sensors, lithium-copper oxide electrochemical cells, magnetic storage media, and solar energy transformers [9–12].

Carbon fibers have drawn considerable attention as the heat transfer science and applications, particularly in the aircraft and automobile industries owing to flexible heating elements for complex aviation components with carbon fiber patches in aeronautics [13]. Carbon fiber resistive heating (Joule heating) has been also used to de-ice aircraft propellers specifically. This same strategy may be applied to prevent ice build-up on wings and other aerodynamic surfaces or deicing applications in the carbon fiber reinforced concrete slab [13,14]. In addition, carbon fibers exhibit strain-induced electrical resistance changes, *i.e.*, piezoresistivity [15–17]. Previous studies have characterized the electrical properties of carbon fiber polymer matrix composites [18–21]. Furthermore, the interlaminar interface of a carbon fiber epoxy–matrix composites can operate as an effective resistive heating element [22]. CuO-grafted WCF composite laminates can be expected for better electronic excitation or current pathway due to copper ions acting as subsidiary conducting fillers on carbon fibers surrounded in the interlaminar interface than pristine CF composites. However, in this regard, there has been no report so far.

The present report describes the characterization of electrical contributions to the interlaminar interface in CuO-grafted WCF-reinforced composites. A two-step seed-mediated hydrothermal method, in which CuO nanostructures were grown on the WCF surface, was used to obtain hybrid CuO–WCF. Composite laminates of CuO–WCF were obtained using a conventional vacuum-assisted resin transfer molding (VARTM) process. The main goal of this study was to investigate the effects of the interlaminar interface composed of carbon fibers modified with CuO NRs. The electrical resistive heating and piezoresistive response of electrified composite laminates were evaluated. Scanning electron microscopy (SEM) was used to examine the morphology of CuO NRs grown on the surface of the WCF. X-ray diffraction (XRD) studies were performed to characterize CuO NRs' crystallinity. Dynamic mechanical analyses (DMA) were also performed to assess the thermal stability and thermal–mechanical behavior of the composites.

2. Experimental

2.1. Materials

T-300 grade plain WCFs were obtained from Toray Industries Inc. (Japan). To prepare hybrid CuO–WCFs, analytical grade chemicals for seed and growth solutions were provided by Sigma–Aldrich (U.S.A.). These included copper acetate monohydrate ($Cu(CH_3COO)_2{\cdot}H_2O$), sodium hydroxide (NaOH), copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), and hexamethylenetetramine ($C_6H_{12}N_4$, HMTA). Ethanol was obtained from J.T. Baker, Philipsburg, NJ, U.S.A. and was used as a solvent for copper acetate monohydrate to obtain a stable colloidal suspension of CuO seeds on WCFs.

2.2. Preparation of hybrid CuO–WCF composite laminates

Fig. 1 shows a two-step seed-mediated hydrothermal process used to synthesize the hybrid CuO–WCF. This method is relatively simple and allows low-temperature processing of nano-structured components. The seed solution was prepared from a solution of $Cu(CH_3COO)_2{\cdot}H_2O$ and NaOH. The CuO seed layer on WCF was prepared by soaking the WCF in the seed solution for 10 min and then annealing the seed-coated WCF in a hot furnace at 150 °C for 10 min. This process was repeated five times. Equimolar concentrations of $Cu(NO_3)_2{\cdot}3H_2O$ and HMTA were mixed in a deionized water solution to obtain a range of concentrations of CuO NRs from 10 mM to 110 mM. The growth of CuO NRs was carried out at 120 °C for 12 h according to the chemical reactions

$$C_6H_{12}N_4 + 6H_2O \leftrightarrow 6HCHO + 4NH_3 \quad (1)$$

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

$$2OH^- + Cu^{2+} \leftrightarrow Cu(OH)_2 \quad (3)$$

$$Cu(OH)_2 \underset{\rightarrow}{\Delta} CuO + H_2O \quad (4)$$

Reaction (4) shows that CuO was grown from OH^- and Cu^{2+} [23]. Further details of these synthetic routes can be found in the literature [24]. Hybrid CuO–WCF/vinyl ester composite laminates were formed using the VARTM process and infiltrated with vinyl ester resin, initiator, and an accelerating agent at a ratio of 100:1:1 by weight. The contributions of CuO NRs in the interlaminar interface were investigated by studying the surface morphology, crystallinity, dynamic mechanical properties, electric heating behavior, and piezoresistive response of the composite material under flexural tests during thermal heating and at ambient air temperature.

2.3. Evaluation of the electrical and piezoresistive properties of the interlaminar interface

To determine the electrical resistive heating behavior of the composites, infrared thermographic analyses were performed using an infrared camera (H2640, Joowon Industrial Co., Ltd., Korea). The temperature gap was controlled by thermocouples placed on the sample. Two current (outer) and two voltage (inner) electrodes were attached to each upper and lower lamina, respectively, so current flow orthogonal to the laminae generated resistive heating at the interlaminar interface (between two laminae). The sample size was 80×80 mm^2 and the distance between the voltage electrodes was 50 mm. The specific experimental configuration is shown for an equivalent circuit in Fig. 2A.

The piezoresistivity of the hybrid CuO–WCF composite laminates was analyzed *in situ* using a digital multimeter (81/2-digit Model 2002, Keithley, U.S.A.) during a three-point bending test with the universal material testing system (Instron 5982, USA), as shown in Fig. 2B. Upon the flexure, the interlaminar interface of the prepared composite laminates was subjected to the two-dimensional array of fiber junctions with CuO NRs of two adjacent laminae with negligible microstructural damages due to reversible elastic deformation. The degree of contact for CuO grafted on a WCF lamina increases around the polymer resin along the longitudinal (fiber) direction due to the multi-junctions of accumulated CuO NRs in the interface region between the fiber and matrix during flexural loading pressure. Flexural strain on the hybrid CuO–WCF composite laminates was applied at a strain rate of 1.6% min^{-1} under cyclic flexural loading for five cycles. The initial interlaminar resistance (R_0) was collected for 30 s to guarantee stability of the readings prior to cyclic loading. The piezoresistive effect of the hybrid CuO–WCF composite laminates was quantified by the gauge factor (GF, k), as shown in below [25]

$$k = \frac{\Delta R/R_0}{\varepsilon} \quad (5)$$

where k is the calculated resistance change ($\Delta R/R_0$) in response to an applied strain (ε) at a given temperature. In this study, the gauge