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Effects of moisture absorption and surface modification using 3-aminopropyltriethoxysilane on the tensile and fracture characteristics of MWCNT/epoxy nanocomposites

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ABSTRACT

In this study, we examined the tensile and fracture behaviors of multi-walled carbon nanotube (MWCNT) reinforced epoxy nanocomposites with and without moisture absorption. The MWCNT/epoxy nanocomposites were fabricated using 0.1 wt.% unmodified, oxidized, and silanized MWCNTs and were kept in seawater for over 15 weeks. Silane-modified specimens demonstrated greater tensile strength, elastic modulus, and transmittance than unmodified or acid-modified specimens, irrespective of moisture absorption. Compared to dry nanocomposites, moisture absorption decreased the tensile strength and elastic modulus for each surface modification. Fracture behavior showed similar tendencies as tensile test results. However, the fracture toughnesses of oxidized and silanized MWCNT/epoxy nanocomposites were not notably different, whereas unmodified specimens had much lower fracture toughnesses, irrespective of moisture absorption. Moisture absorption may have caused degradation resulting in weak interfacial bonding due to epoxy swelling.

1. Introduction

Carbon nanotubes (CNTs) have unique molecular structures and outstanding thermal, electronic, optical, and mechanical properties [1–5]. Furthermore, they are potentially useful as reinforcement agents in nanocomposites with polymers, metals, and ceramics [6–9]. For these reasons, CNTs have been studied in the fields of physics, chemistry, and mechanics for more than a decade. However, the fabrication of CNT-reinforced nanocomposites is characterized by two main problems: agglomeration of CNTs and weak interfacial interactions between the CNTs and matrix. To address these problems, many studies have proposed methods to uniformly disperse CNTs and enhance the interfacial interactions in the polymer matrix.

Chemical functionalization of CNTs, which generates functional groups on surfaces, has been used to enhance interfacial adhesion between nanotubes and matrix [10,11]. Functional groups react with other chemicals or the polymer matrix and thus improve interfacial interactions between CNTs and matrix [12–14]. Silanization is an effective approach for chemical functionalization of CNTs that produces functional groups and improves dispersion. Kathi et al. [15] silanized MWCNTs and demonstrated that the structures of silanized MWCNTs remained largely intact, indicating that no real damage occurred to the MWCNTs during the silanzation process. Additionally, the MWCNTs retained their external average diameters even after oxidation and silanization. Ma et al. [16] reported similar results after examining MWCNTs silanized using 3-glycidoxypropyltrimethoxysilane.

Moisture absorption of epoxy causes plasticization and swelling, which weakens the interfacial strength between the epoxy and reinforcing materials [17]. Therefore, many studies have been performed to investigate the effects of moisture absorption on the mechanical behaviors of glass fiber or carbon fiber reinforced epoxy composites [18–20]. However, only limited studies have been conducted to investigate the effects of moisture absorption on the mechanical properties of CNT reinforced polymer nanocomposites.

In this study, we examined the effects of moisture absorption and silane treatment of MWCNTs on the tensile and fracture characteristics of MWCNT/epoxy nanocomposites. Moisture content, tensile strength, elastic modulus, fracture toughness, and transmittance were determined for unmodified, acid-modified, and silane-modified MWCNT reinforced epoxy nanocomposites. Following tensile and fracture tests, scanning electron microscope (SEM) and transmission electron microscope (TEM) examinations of fracture surfaces were performed to evaluate fracture

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mechanisms as a function of moisture absorption and surface modification.

2. Experimental

2.1. Materials

The carbon nanotubes used in this study were multi-walled carbon nanotubes (MWCNTs, CM-95) purchased from Hanhwa Nanotech Co., Ltd., Korea. The MWCNTs were prepared by a chemical vapor deposition method. The MWCNTs had diameters of 10–15 nm, tube lengths of 10–20 μm, and a purity greater than 95%. 3-Aminopropyltriethoxysilane (3-APTES) with a purity of 99% (Sigma–Aldrich, USA) was used as the silane functionalization agent. The reagents used for the acid treatment were nitric acid (60–62%, Junsei Chemical, Japan), sulfuric acid (95%, Junsei Chemical, Japan), distilled water (99.5%, Dae Jung Chemical, Korea), acetone (99.5%, Dae Jung Chemical, Korea), and ethanol (99.5%, Sigma–Aldrich). The epoxy used in this study was 118.2 g/equiv. of diglycidyl ether of bisphenol A (YD-115, Kukdo Chemical, Korea) and the hardener was 60 g/equiv. of polyamidoamine (G-A0533, Kukdo Chemical, Korea).

2.2. Functionalization of MWCNTs

In this study, surface modification of MWCNTs was performed via two methods: oxidation and silanization. Three grams of unmodified MWCNTs (U-MWCNTs) were dispersed in 300 mL of an acid solution consisting of 180 mL of H_2SO_4 and 120 mL of HNO_3, and were refluxed for 20 h at 50 °C. After refluxing, the solution was filtered with distilled water and acetone until the pH reached 6–7. The resulting oxidized MWCNTs (O-MWCNTs) were then dried in a vacuum at 80 °C for 12 h. For silanization, 1.8 g of the oxidized MWCNTs were dispersed in a 2% silane solution consisting of 2 mL of 3-APTES and 98 mL of distilled water, which was then added to 300 mL of an ethanol:water (95:5) solution. The mixture was stirred at 70 °C for 4 h. The silanized MWCNTs (S-MWCNTs) were separated by filtration using distilled water and acetone followed by drying at 80 °C for 12 h. A schematic illustration of the silanization process used for the multi-walled carbon nanotubes is shown in Fig. 1.

2.3. Fabrication of MWCNT/epoxy nanocomposites

To fabricate the MWCNT/epoxy nanocomposites, the U-MWCNTs, O-MWCNTs, and S-MWCNTs were mixed with ethanol at 0.1 wt.%. Ultrasonication was performed for 5 min to improve dispersion. After sonication, the U-MWCNTs, O-MWCNTs, and S-MWCNTs were mixed with the epoxy resin and stirred for approximately 2 h at 80 °C to completely evaporate the ethanol. After removing the ethanol, hardener was added (epoxy:hardener at 2:1 ratio) and the mixture was then poured into a Teflon mold. The mixture was de-gassed in a vacuum oven at 760 mmHg for 30 min and hardened in an oven at 60 °C for 6 h. A secondary curing process was performed under the same conditions to perfectly cure the epoxy. In addition, a pure epoxy specimen without MWCNTs was fabricated using the same method in order to compare transparencies.

2.4. Preparation of tensile and fracture specimens

The fabricated nanocomposite plates were machined as tensile specimens, and the dimensions in the gauge section were 5 mm thick × 80 mm long × 15 mm wide, following the ASTM D638 regulations [21]. A single edge notched tension (SENT) specimen 5 mm thick × 76 mm long × 15 mm wide with a 4.5 mm initial crack was prepared for fracture strength and fracture toughness measurements.

2.5. Moisture absorption measurement

Machined specimens were kept separate in sterile filtered seawater (Sigma–Aldrich, S-9148, USA) for up to 15 weeks. The specimens were periodically removed from the seawater and weighed using an electronic balance accurate to ±0.001 g. After wiping the surfaces dry, the weights of the seawater-absorbed specimens were measured quickly to minimize evaporation losses. The weight gain was reported as a percentage of the composite weight.

2.6. Characterization

Fourier transform infrared (FT-IR) spectra of the unmodified and surface-modified MWCNTs were recorded on a JASCO FT-IR

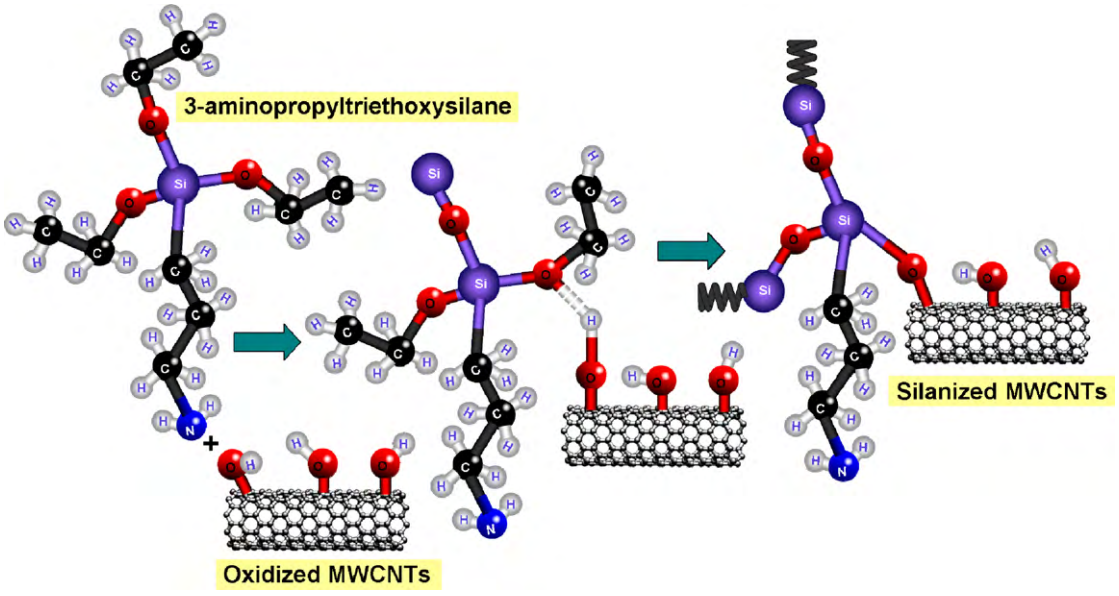

Fig. 1. Schematic illustration of the silanization process of multi-walled carbon nanotubes.