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Modification of surface functionality of multi-walled carbon nanotubes on fracture toughness of basalt fiber-reinforced composites

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ABSTRACT

In this work, we studied the influence of surface functionality of multi-walled carbon nanotubes (MWCNTs) on the mechanical properties of basalt fiber-reinforced composites. Acid and base values of the MWCNTs were determined by Boehm's titration technique. The surface properties of the MWCNTs were determined FT-IR, and XPS. The mechanical properties of the composites were assessed by measuring the interlaminar shear stress, fracture toughness, fracture energy, and impact strength. The chemical treatments led to a change of the surface characteristics of the MWCNTs and of the mechanical interfacial properties of MWCNTs/basalt fibers/epoxy composites. Especially the acid-treated MWCNTs/basalt fibers/epoxy composites had improved mechanical properties compared to the base-treated and non-treated MWCNTs/basalt fibers/epoxy composites. These results can probably be attributed to the improved interfacial bonding strength resulting from the improved dispersion and interfacial adhesion between the epoxy resin and the MWCNTs.

1. Introduction

Fiber-reinforced polymer (FRP) composites are used in a wide range of industrial applications where high performances are required, such as for automotive parts, aerospace applications, and electrical insulators [1–3]. FRP materials are basically characterized by low specific weight, high strength, strong chemical resistance against corrosion. The polymers are traditionally reinforced by carbon, glass, and aramid fibers, but recently, basalt fibers have emerged as promising candidates for the reinforcement of composite materials [4–8]. Basalt fibers are made from basalt rocks through melting and the simple production process adds special benefit in cost. Basalt fibers have higher working temperature and better tensile strength than E-glass fibers, as well as good resistance against chemical attack, impact load, and fire with less poisonous fumes. They can also be used in a wide range of temperatures, from −265 °C to 700 °C, and environmentally harmless and free from carcinogens and other health hazards [9–12]. Mechanically, strength of basalt fibers is assumed to be closely associated with the existence of topographic non-uniformities like surface and structural defects and impurities [13]. These, non-uniformities help in lowering the calculated mechanical properties remarkably to their counterpart theoretical values. An another advantageous attribute of these fibers is their good compatibility with the host polymer matrix materials which not only helps the composite improve its mechanical property but also its surface wettability [14,15]. Several other good features like resistance and non-reactivity towards corrosive solvents/liquids, moisture, high degree of durability and applicability has led the use of basalt fibers as promising filler in the polymer composites by several industries over the years since its inception [16]. Basalt is reputed for its inherent thermal properties. It is highly used in the fabrication of fire retarding materials specially designed for personal upholstery (mattresses) and public transit systems for preventing accidental fires [12,17–20] when incorporated with other heat resistant polymers. For these reasons, a number of studies have been performed on the mechanical properties of basalt fiber-reinforced composites since the late 1990s. Russell et al. studied the influence of surface treatments on the mechanical properties of basalt/epoxy composites and found that sol/gel epoxy-silane surface treatments gave the largest improvement [21]. Friedrich et al. reported on the investigation of

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chemically treated basalt and glass fibers and showed a better alkaline resistance of basalt than of glass fibers [22].

Carbon nanotubes (CNTs) are a typically nanofillers and were discovered as fullerene-related structures by Iijima at NEC laboratory of Tsukuba in 1991 [23]. Since its discovery, CNTs also have been considered as a multi-functional reinforcement material within a polymer matrix due to their superior mechanical, electrical, and thermal properties [24–26]. Well-dispersed CNTs in a polymer matrix can improve the mechanical interfacial properties of FRP at low filler loadings [27]. The mixture of basalt fibers with CNT-reinforced epoxy resin may lead to a greater synergetic effect on the material properties. A pre-treatment of the nanotubes is needed to increase the interfacial adhesion between nanotubes and matrix. It is very important that the surface morphology and the specific surface area (SSA) of the CNTs be modified accordingly, so that the additives adapt with their surrounding polymeric matrixes well which helps the CNTs with improved chemistry and wettability [28]. Since wettability is primarily dependent upon the interfacial energy between the CNT and polymeric matrix, this helps in creating more bonds within the composite. Care should also be taken during the pre-treatment processes so that the crucial C–C covalent bonds of the CNTs do not get denatured/ruptured [29]. In carbon FRP composites, CNT-matrix adhesion plays a crucial role in contributing to good mechanical properties. Modern theory also states that at microscopic levels, the behavior of adhesion exists at interface with variable degree based on the interaction of fibers and matrix [30–33]. However, the primary demerit of CNTs during the fabrication of composite is their tendency to aggregate due to the presence of Vander Waals forces and also smooth surfaces. Due to these two properties, mechanical, electrical and chemical properties of the FRP composites are limited to larger extent [34]. Hence, several approaches are devised to increase their interfacial interaction within the matrix. Few promising approaches developed for treating the surface of CNTs are acid treatment, redo-ox reaction and use of surfactants, which helps in the release of COOH, C=O and OH groups [35]. These groups then help in altering the surface reactivity with increased (improved) dispersion, stability and host (polymer) interactions [36]. Kim et al. studied the flexural and fracture behaviors of silane-modified CNTs and its reinforced CNTs/basalt/epoxy composites. Their results showed that the flexure and fracture properties of the CNTs/basalt/epoxy composites were improved by the modification of CNTs [37].

In this work, modifications of the surface functionality of multi-walled carbon nanotubes (MWCNTs) were performed in order to obtain MWCNTs/basalt fibers/epoxy composites with strong interfacial adhesion and high impact resistance. The effect of the modification on the relationship between interfacial adhesion and impact resistance was investigated.

2. Experimental

2.1. Material

The fibers used in this study were untreated basalt fibers. A commercial roving-type basalt fibers (12 K) manufactured by YJC Co., Ltd. of Korea. The average diameter of these basalt fibers was approximately 13 μm, and the typical tensile modulus and strength were about 90 and 4.8 GPa, respectively. MWCNTs were obtained from KUMHO PETROCHEMICAL Co., Korea. The epoxy was diglycidyl ether of bisphenol A (DGEBA, YD-128, Kukdo Chemical, Korea), and the curing agent was diaminodiphenylmethane (DDM, purchased from TCI Co. Japan). Methylethylketone (MEK, purchased from OCI Company. Ltd., Korea) was used to reduce the high viscosity of DGEBA.

2.2. Surface treatment of MWCNTs

MWCNTs were dispersed in 5 M HNO_3 and in 5 M NaOH at room temperature for 24 h, each. Prior to the following analyses, residual chemicals were removed by Soxhlet extraction, specifically by boiling with acetone at 80 °C for 24 h. Then, acid and base-treated MWCNTs were filtered with distilled water and dried in vacuum at 80 °C for 12 h.

2.3. Fabrication of multi-scale MWCNTs/basalt fibers/epoxy composites

The epoxy resin was mixed with 1 wt% of non-treated MWCNTs (N-MWCNTs), acid-treated MWCNTs (A-MWCNTs), and base-treated MWCNTs (B-MWCNTs). To get a homogeneous mixture, high-energy sonication was performed for 3 h at 60 °C. Then, the curing agent and MEK were added to the MWCNTs/epoxy mixture and stirred thoroughly. Basalt fibers/epoxy laminates were made by the drum-winding technique for manufacturing prepregs with subsequent hot pressing. Laminates with 18 plies of prepregs were made in a hot press at 10 MPa and 150 °C for 150 min employing the vacuum-bagging method [38].

2.4. Measurements

The acid/base values at the surface of the MWCNTs were determined by Boehm's titration technique [39]. In case of an acid value, about 1.0 g of the sample was added to 100 ml of 0.1 N NaOH solution and shaken for 24 h. Then, the solution was filtered through membrane paper and titrated with 0.1 N HCl standard solutions. The acid value was calculated by the following equation:

$$\text{Acid value}\left(\text{meq}^{-1}\right) = [(a-b)\times f \times N]\times\frac{1000}{M} \tag{1}$$

where, a is the titration amount (ml) of 0.1 N HCl if 20 ml of 0.1 N NaOH solution is titrated with 0.1 N HCl standard solutions without sample, b is the titration amount (ml) of 0.1 N HCl after adding the sample, f is the concentration of 0.1 N HCl solution, and M is the mass of the sample (g). Likewise, the base value was determined by converse titration.

Infrared spectra of the chemically treated MWCNTs were measured with FT-IR spectroscopy (FT-IR 4200, JASCO, USA). X-ray photoelectron spectroscopy (XPS) measurements of the MWCNTs surfaces were performed using a VG Scientific ESCA LAB MK-II spectrometer equipped with a Mg-Kα X-ray source.

The interlaminar shear strength (ILSS) was determined by the three-point short-beam bending test, According to ASTM D-2344. The crosshead speed was fixed at 2.0 mm min^{-1}. ILSS of the composites was determined using the following equation:

$$\text{ILSS} = \frac{3P}{4bd} \tag{2}$$

where, P is the load at the moment of break (N), b the width of the specimen (mm), and d the thickness of the specimen (mm).

An analytical expression for critical stress intensity factor (K_{IC}) of composites may be characterized by the single edge notched bending (SENB) test in three-point flexural mode. Notches were cut using a diamond-coated saw to a depth of approximately half of the thickness of the specimen. The three-point bending test was conducted using a universal test machine (LR5K plus, Lloyd, UK), according to ASTM E-399. The crosshead speed was fixed at 1 mm min^{-1}. K_{IC} is determined using the following relationship: