Mechanical Properties of MWNT-Loaded Plain-Weave Glass/Epoxy Composites

Myung-Sub Kim, **Sang-Eui Lee**, **Won-Jun Lee and Chun-Gon Kim** [*]

Department of Aerospace Engineering, School of Mechanical Aerospace and Systems Engineering, KAIST, 371-1, Kuseong-dong, Yuseong-Gu, Daejeon, 305-701, South Korea

Abstract
Carbon nanotubes (CNTs) have shown great potential for the reinforcement of polymers or fiber-reinforced composites. In this study, mechanical properties of multi-walled carbon nanotube (MWNT)-filled plain-weave glass/epoxy composites intended for use in radar absorbing structures were evaluated with regard to filler loading, microstructure, and fiber volume fraction. The plain-weave composites containing MWNTs exhibited improved matrix-dominant and interlaminar fracture-related properties, that is, compressive and interlaminar shear strength. This is attributed to strengthening of the matrix rich region and the interface between glass yarns by the MWNTs. However, tensile properties were only slightly affected by the addition of MWNTs, as they are fiber-dominant properties.
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Keywords
Multi-walled carbon nanotube, mechanical property, plain-weave composite, interlaminar fracture

1. Introduction

Since carbon nanotubes (CNTs) were discovered by Iijima [1] in 1991, a variety of studies have revealed that CNTs-added composites offer not only excellent mechanical properties but also improved electrical and thermal conductivity compared to polymer or fiber-reinforced composites containing no CNT [2–5]. The capacity of CNTs to serve as reinforcement for the improvement of mechanical properties and as filler for the induction of electrical conductivity or permittivity has opened up new perspectives for multifunctional composites, e.g., microwave absorbing materials with improved mechanical performance.

In general, the electromagnetic absorbers are made by mixing electrical or magnetic loss particles such as carbon black, metallic powder, carbonyl iron, and ferrite with various polymers [6]. However, few studies on electromagnetic absorbers con-

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[*] To whom correspondence should be addressed. E-mail: cgkim@kaist.ac.kr
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sidered their mechanical properties, despite that the addition of the particles has a direct effect on the mechanical properties of the composites; a positive effect as reinforcements, or a negative effect as impurities. Furthermore, the addition of the particles increases the viscosity of matrix, leading to difficulties in the fabrication process. Thus, the mechanical properties of the absorbers should be evaluated, as well as the electromagnetic properties, so as to confirm whether they are suitable for load-bearing radar absorbing structures (RASs).

RASs consist of fiber-reinforced composites and the functional particles, so they can be treated as treated as fiber-reinforced composites with the particles dispersed in the matrix. However, there have been few studies on the mechanical properties of the composites. It is known that the properties are highly dependent on the filler content, the degree of dispersion, impregnation with matrix, and interfacial adhesion. Oh [7] measured the mechanical properties of carbon black-added glass/epoxy composites that were used as RAS material. He observed that in-plane shear and compressive properties increased, while tensile property and inter-laminar shear strength (ILSS) decreased. Hussain *et al.* [8] added Al_2O_3 powders into composites in order to investigate mechanical and interfacial properties under normal and cryogenic temperatures. Timmerman *et al.* [9] modified carbon fiber/epoxy composites with layered inorganic clays to determine the effects of particle reinforcement on the response to cryogenic cycling. Iwahori *et al.* [10] observed the increase of tensile and compressive properties of carbon nanofiber (CNF)-added carbon fiber composites; the increases of 45% in tensile stiffness and 22% in tensile strength through 10 wt% addition of CNF were noted. To our knowledge, there has been almost no investigation into both mechanical and electromagnetic properties of fiber-reinforced composites.

In this study, the mechanical properties of MWNT-added plain-weave glass/epoxy composites designed for the material of RASs [5] were investigated, and the microstructures of the composites were observed to investigate the mechanism underlying the observed changes in the material characteristics.

2. Fabrication of MWNT-Filled Glass/Epoxy Composites

MWNTs and glass/epoxy plain-weave fabrics used in this study were identical to those used in the previous study about microwave properties [5]. The MWNTs, purchased from ILJIN Nanotech Co. (South Korea), were synthesized *via* a chemical vapor deposition method with a carbon mass fraction of about 95%. The MWNTs were 10–15 nm in diameter and 10–20 μm in length.

Plain-weave glass/epoxy composites, K618, were supplied by Hankuk Fiber Co. (South Korea). First, the MWNTs were dispersed in an epoxy matrix. The fabric composites were impregnated by a mixture of the matrix and the MWNTs. The MWNT-filled fabric composites were then dried for 5–7 min at 100°C. Drying times increased with MWNT contents. As the viscosity of the pre-mixture increased rapidly beyond the 3.0 weight percent (wt%), it was difficult to maintain the unifor-

mity of the MWNTs in the matrix. The weight percent of MWNTs is defined as the ratio of the weight of MWNTs to the total weight of the composite including the dry glass fabric, the epoxy system, and the MWNTs. The weights percent in use were 0.0, 0.4, 0.7, 1.0, 1.3, 1.6, 3.0, and 5.0 wt%. For example, MWNT 0.0 and MWNT 1.6 denote the MWNT-added fabrics with no and 1.6 wt% MWNTs, respectively. Specimens were cured and vacuum-bagged in an autoclave for 30 min at 80°C and then for 2 h at 130°C. The pressure was stabilized at 3 atm. while the specimens were being cured.

3. Microstructure of MWNT-Filled Glass/Epoxy Composites

3.1. Microstructure

The microstructure of the fabricated composites was captured by scanning electron microscopy (SEM). Figures 1 and 2 show SEM images of MWNT 1.0. Most of the MWNTs were dispersed in the matrix rich region and the interface between glass yarns, as shown in the enlarged image of Fig. 2(a). Figure 2(b) shows that the MWNTs did not penetrate far into the interior of the glass yarns due to the physical contact between the glass fibers. The matrix rich region and the interface region of the fabrics consist of only the matrix without MWNTs.

MWNT 3.0 and MWNT 5.0 were also fabricated. The microstructures of MWNT 3.0 and MWNT 5.0 are shown in Fig. 3. MWNT 3.0 and MWNT 5.0 had more pores than the other composites due to the increase of viscosity caused by high MWNT content. A comparison between Figs 1 and 3 reveals that the porosity increased as the weight fraction of the MWNT increased. Furthermore, although the loose parts of the yarns of MWNT 3.0 and MWNT 5.0 could contain more MWNTs,
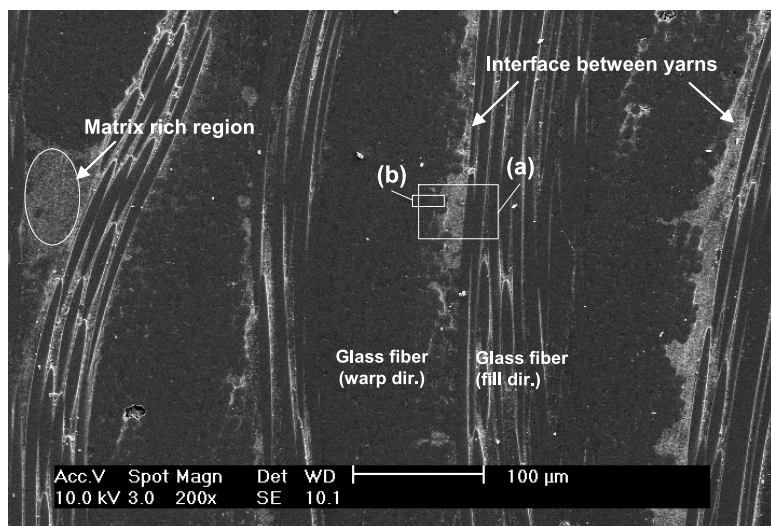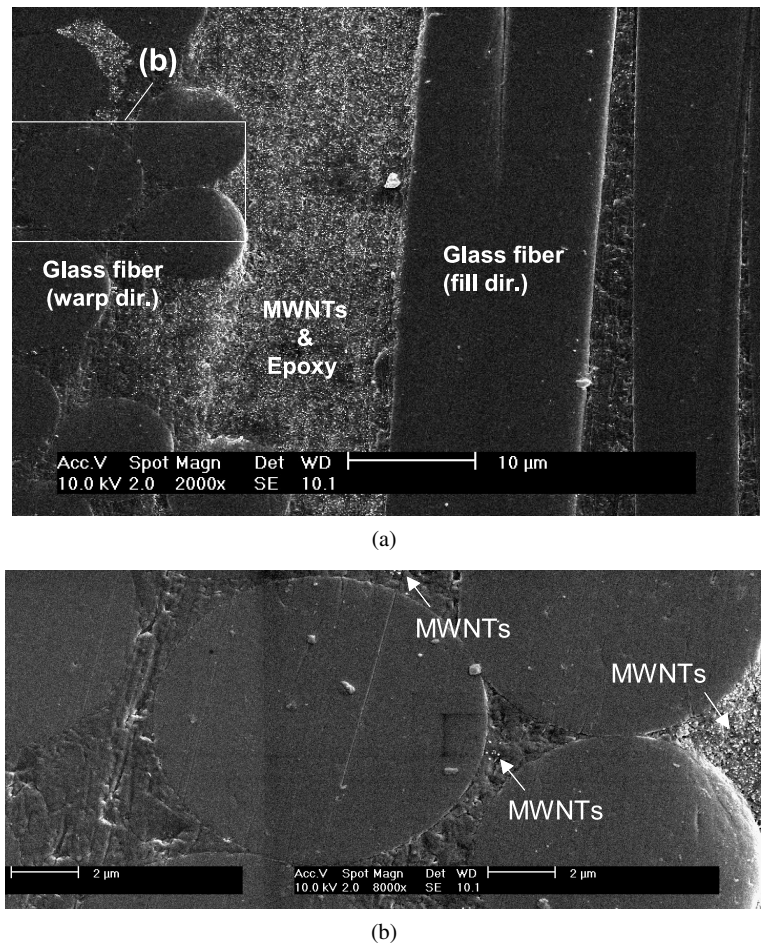

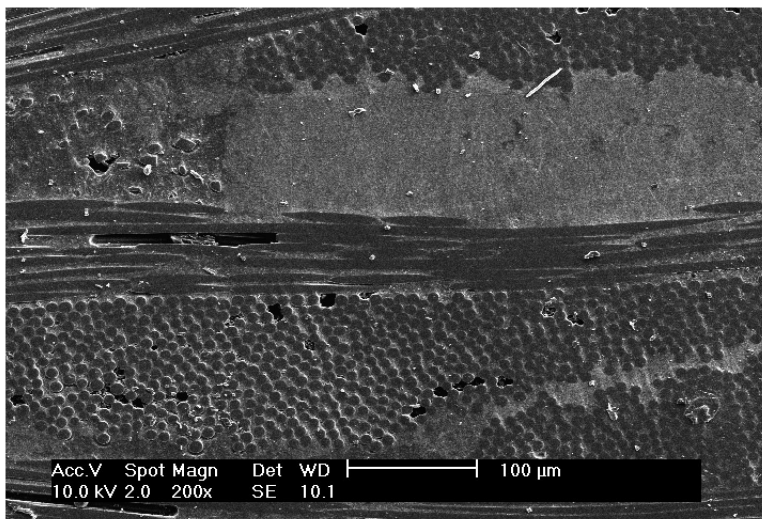**Figure 1.** SEM photograph of MWNT 1.0 [5].

(a)

(b)

Figure 2. Enlarged SEM photograph of MWNT 1.0. (a) Interface between yarns in warp and fill direction [5]; (b) MWNTs between glass fibers.

the amount of MWNTs in the interior and exterior of their yarns had an obvious distinction compared to the other MWNT loadings.

3.2. Glass Fiber Volume Fraction

The porosity can degrade the mechanical properties of fiber-reinforced composites. In addition, MWNTs can bear curing pressure which leads to the increase of ply thicknesses of the fabrics. Therefore, the variation of the volume fraction of glass fibers was inspected according to MWNT contents. The volume fraction was measured by the matrix digestion method of ASTM D3171-76. Five specimens for each MWNT content were employed in this measurement.

The measurement procedure was as follows. First, the weight and density of the specimens were measured down to the fourth decimal places, and the density was measured using Archimedes' principle. Second, each specimen was dipped in 62%

(a)
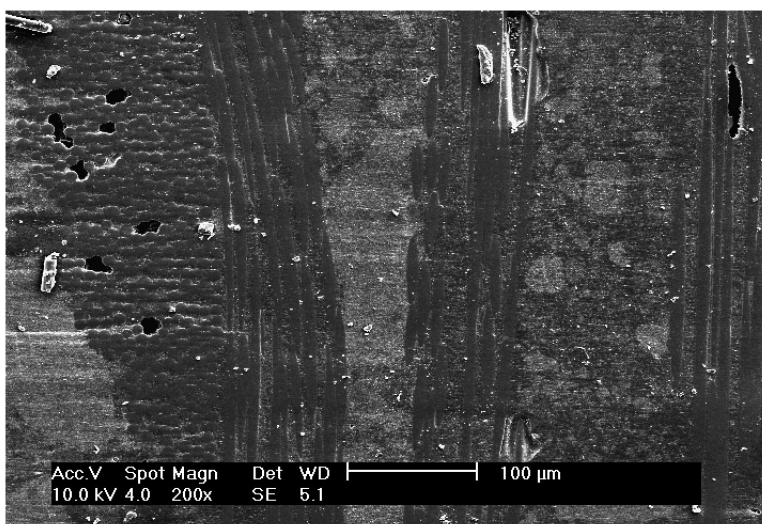
(b)

Figure 3. SEM photograph of MWNT 3.0 and MWNT 5.0. (a) MWNT 3.0; (b) MWNT 5.0.

nitric acid. While the epoxy was dissolved, the temperature was kept at 75°C for 5 h. After washing off not only the nitric acid but also the mixture of MWNT and the epoxy by acetone and distilled water, the remainder of the composites was dried in an oven at 75°C for 1 h. Finally, the glass fibers were weighed. The glass fiber volume fraction was calculated by (1):

$$V_f(\%) = [(W_f/\rho_f)/(W_c/\rho_c)] \times 100, \tag{1}$$

where W_f is the weight of glass fiber; W_c is the weight of composite; ρ_f is fiber density; and ρ_c is the composite density.
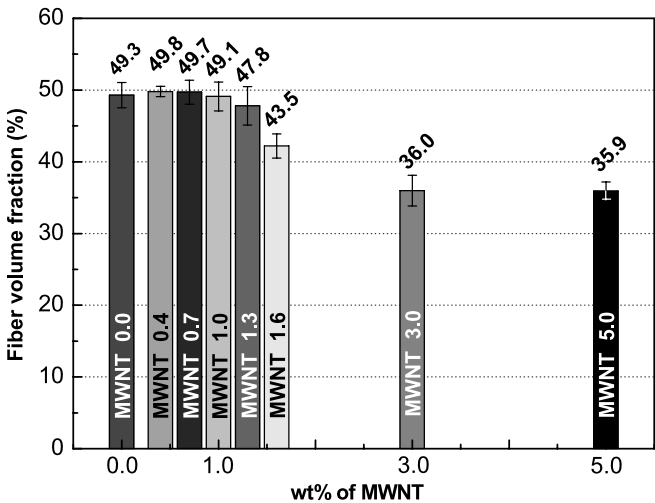
Figure 4. Fiber volume fraction with weight fraction of MWNT.

Figure 4 shows the measured results of the glass fiber volume fraction. The error bars in all graphs correspond to the standard deviation. MWNT 0.0 not containing any MWNT had a volume fraction of 49.3%. Considering standard deviations, the glass/epoxy composites had nearly the same fiber volume fractions up to 1.0 wt% MWNT content, although MWNT 0.4 and MWNT 0.7 showed a little higher value. The fiber volume fraction for specimens with more than 1.0 wt% MWNT contents decreased drastically up to 36.0 vol% due to increased matrix viscosity and poor impregnation as shown in Fig. 3.

4. Mechanical Properties of MWNT-Filled Glass/Epoxy Composites

4.1. Tensile Test

Tensile tests were performed in accordance with ASTM D3039-76. Five specimens were used in each case, and the dimension of the samples is $250 \times 24 \times 4$ mm^3. Emery cloth was attached at the grip section. The crosshead speed was set to 0.2 mm/min. Figures 5 and 6 show the measured results of tensile stiffness and strength.

The addition of MWNTs up to 1.6 wt% had little effect on the stiffness and strength, whereas the addition of 3.0 and 5.0 wt% MWNTs caused a drastic degradation of the tensile property. Considering that the variation of the glass fiber volume fraction according to MWNT contents displays a tendency similar to that of the tensile property, it could be concluded that the addition of MWNTs did not provide an improvement in the tensile property. On the other hand, it was found that the composites containing MWNTs up to 1.6 wt% could be potentially used as material for multi-layered RAS because the composite properties were not degraded, compared to MWNT 0.0. MWNT 3.0 and MWNT 5.0 showed lower tensile property
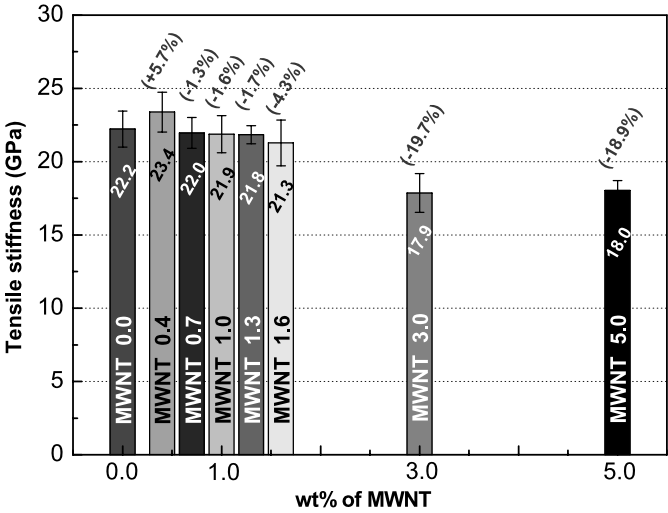
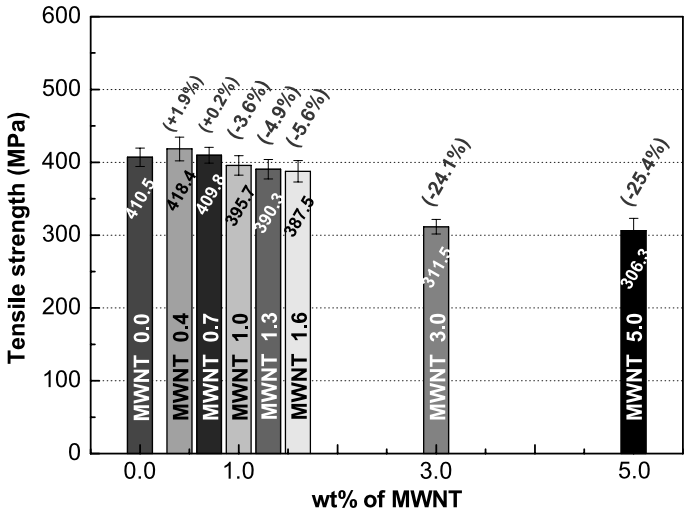**Figure 5.** Tensile stiffness with weight fraction of MWNT.

Figure 6. Tensile strength with weight fraction of MWNT.

than the other composites, because the composites with high MWNT loadings have more pores and lower glass fiber volume fraction. Therefore, the two glass/epoxy composites were determined to be unsuitable as RAS material, and they were not considered in the subsequent experiment.

4.2. Compressive Test

Compressive tests were conducted according to ASTM D3410M-94. Glass/epoxy composite taps were attached to specimens with an adhesive film at 120°C for 2 h.
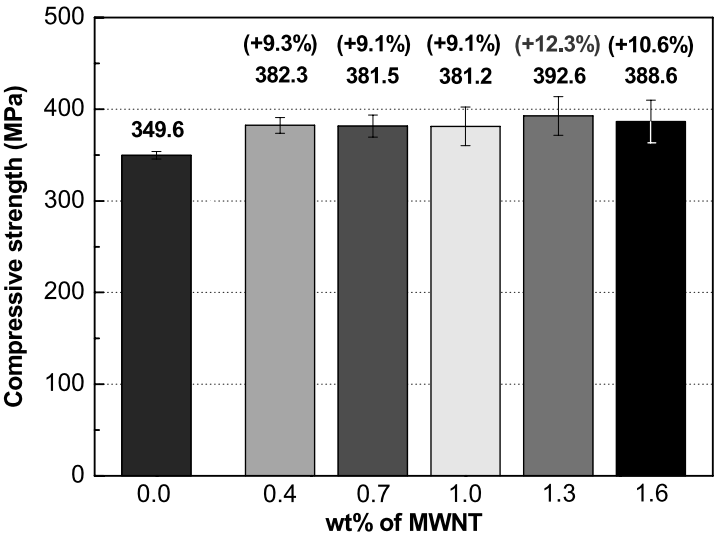
Figure 7. Compressive strength with weight fraction of MWNT.

Five specimens were used in each case, and the dimensions of the composites were $140 \times 6 \times 2.5$ mm^3. The loading rate was 1.5 mm/min.

Figure 7 shows the variation of compressive strength with regard to MWNT loadings. The compressive strength of the composites containing MWNTs increased above 9.0% compared to MWNT 0.0, and MWNT 1.3 showed a maximum increase, around 12.3%, in spite of the slight decrease in the glass fiber volume fraction. The above results show that the addition of MWNT has a positive effect on the compressive strength.

In unidirectional fiber-reinforced composites, there are several basic longitudinal compression failure modes: fiber microbuckling in either shear or extensional mode, transverse tensile rupture, fiber shear failure, and fiber kinking [11]. The inherent undulation of the reinforcements in woven fabric composites introduces additional failure modes: failure of longitudinal fibers due to axial compression and bending stresses, failure of longitudinal fibers due to transverse tension/shear stresses, failure of transverse fibers, bond separation between longitudinal and transverse yarns, and pure matrix rich region failure [12]. These various factors make it difficult to clearly identify the compressive failure mechanism. The microstructure observations reveal that the addition of MWNTs could strengthen the matrix material in the matrix rich area and the interface between yarns due to mechanical interlocking of the MWNTs and improved mechanical properties of the matrix. Interlocking and improvement of mechanical properties have been reported in other studies [13, 14]. Moreover, out-of-plane reinforcement due to MWNTs improves the resistance to shear force due to bending and buckling. These factors result in an increase in the compressive strength of the composites.
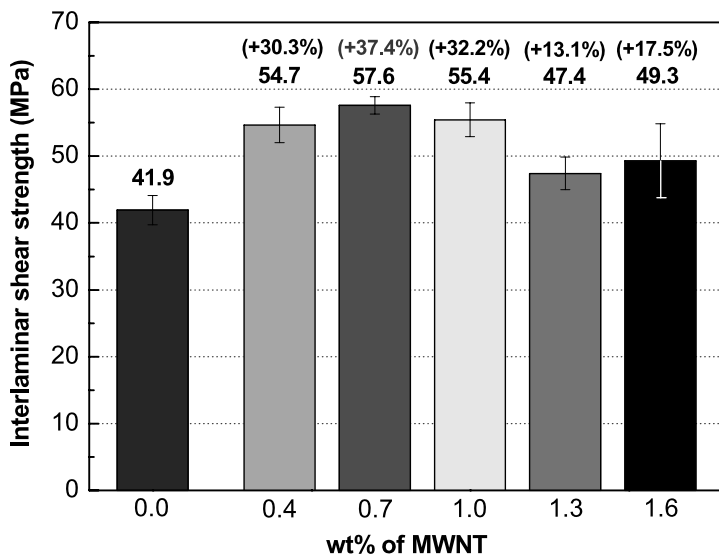
Figure 8. Interlaminar shear strength (ILSS) with weight fraction of MWNT.

4.3. Interlaminar Shear Strength Test

The interlaminar shear strength (ILSS) was measured *via* a three-point bending test using the short-beam method in accordance with ASTM D-2344-84. Six specimens were used in each case, and the dimensions of the specimens were $45 \times 7.2 \times 7.2$ mm^3. The crosshead speed was set to 1.3 mm/min. The specimen was aligned and centered such that its longitudinal axis was perpendicular to the loading nose and side supports, and the loading nose was located equidistant between the side supports. The span length between the two side supports was adjusted properly according to the ASTM.

Figure 8 showed the test results of ILSS. Like the compressive property, all the composites containing MWNTs displayed a strength improvement compared with MWNT 0.0. The maximum increase of ILSS, about 37.4%, was observed in MWNT 0.7. As discussed in the compressive test, most of the MWNTs are distributed in the matrix region and the interface between glass yarns. The strengthened matrix and interface contributes positively to the ILSS, one of the matrix-dominant properties. The use of particles to improve the interlaminar fracture toughness of fiber-reinforced composites has been reported in some studies [15, 16]. The increase in ILSS is attributed primarily to crack propagation hindrance by the interlocking and bridging of MWNTs and additional energy dissipation mechanisms such as MWNT pull-out, fragmentation of matrix material during pull-out of randomly oriented MWNTs. Although these phenomena could not be readily observed in our fractured specimens due to the glass fiber structures, they were easily observed in MWNT/polymer composites [13, 14].

5. Conclusion

MWNT-added plain-weave glass/epoxy composites were developed as a material for a RAS. The mechanical (tensile/compressive/interlaminar) properties of the composites were evaluated with respect to MWNT loadings, microstructure, and glass fiber volume fraction.

The MWNT was added into plain-weave glass/epoxy composites to fabricate the materials used for RASs. MWNTs were detected mainly in the matrix rich region and the interface between glass yarns in the warp and fill directions. Porosity was observed in composites of high MWNT concentrations.

The addition of MWNTs had a considerable effect on the mechanical properties of the plain-weave glass/epoxy composites. Compared to the properties of MWNT 0.0, the compressive strength and ILSS increased up to 1.6 wt% addition of MWNT, whereas the tensile property showed only a slight change. That is, increased amounts of MWNTs led to enhancement of the matrix-dominated properties, while the tensile properties were little affected by the MWNTs and still remained fiber-dominated.

In terms of RAS expected to carry loads and absorb electromagnetic waves, it could be concluded that the MWNT-filled glass fabric composites at least up to 1.6 wt% can be used as RAS material considering the variation of glass fiber volume fractions and mechanical loading conditions.

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