

Enhancement of the In-Plane Shear Properties of Carbon Fiber Composites Containing Carbon Nanotube Mats

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The in-plane shear property of carbon fiber laminates is one of the most important structural features of aerospace and marine structures. Fiber-matrix debonding caused by in-plane shear loading is the major failure mode of carbon fiber composites because of the stress concentration at the interfaces. In this study, carbon nanotube mats (CNT mat) were incorporated in two different types of carbon fiber composites. For the case of woven fabric composites, mechanical interlocking between the CNTs and the carbon fibers increased resistance to shear failure. However, not much improvement was observed for the prepreg composites as a result of incorporation of the CNT mats. The reinforcement mechanism of the CNT mat layer was investigated by a fractographic study using scanning electron microscopy. In addition, the CNT mat was functionalized by three different methods and the effectiveness of the functionalization methods was determined and the most appropriate functionalization method for the CNT mat was air oxidation.

Keywords: composites, carbon and graphite, nanostructured materials, mechanical properties, strength

1. INTRODUCTION

Carbon nanotubes (CNTs) have been investigated as nano-size reinforcements for carbon fiber reinforced polymer matrix composites to improve their mechanical properties as well as contribute to the development of multifunctional properties such as increased electrical conductivity, particularly in the out-of-plane direction of the composites. Among the in-plane properties, the in-plane shear characteristics of the carbon fiber composites are controlled by the properties of the matrix and the interface between the fibers and matrix [1,2]. Hence, there is also room for further improvement of the in-plane shear properties of the composites. In addition, the in-plane shear properties of carbon fiber composites are one of the main concerns in the design of aircraft structural components.

Epoxy materials are widely used as the matrices for carbon fiber composites. Even though CNT/epoxy nano-composites have been investigated for the last two decades, there has not been any remarkable success in terms of enhancement of the mechanical strength, despite the extraordinary mechanical properties of individual CNTs [3-5].

Several studies used a mat-like form of CNTs (CNT mat) and fabricated the composites by infiltration of resin into the CNT mats [6-9]. In these situations, it was possible to incor-

porate high concentrations of CNTs in the epoxy matrix by-passing the cumbersome CNT dispersion process and thus achieve superior mechanical properties.

Several previous studies investigated the in-plane shear properties of fiber reinforced composites with nano-reinforcements [10-13]. In the case of direct mixing of CNTs in a resin, high concentrations of CNTs (> 0.5 wt%) generally resulted in the undesirable high viscosity of the CNT/resin mixture. It is very difficult to fabricate carbon fiber laminate composites of good quality using a viscous resin, particularly when employing resin transfer molding methods.

In a previous study on the direct mixing of CNTs, the CNT concentration was limited to 0.3 wt%. It was reported that the in-plane shear properties of the composites with CNTs did not improve since the low concentration of the CNTs did not much change the matrix properties [10].

In two cases using graphite nanoplatelets (GNPs), up to 5 wt% of GNPs was incorporated into the composites. Since the density of GNPs are much greater than that of CNTs, 5 wt% of GNPs does not increase the resin viscosity as much as 5 wt% of CNTs. In both cases, the in-plane shear strength of the composites with GNPs was improved by 11% compared to the baseline composites without GNPs [11,12]. Only functionalized GNPs improved the in-plane shear strength while the unmodified GNPs acted as impurities and contributed to the deterioration of the shear strength [12].

Single-walled carbon nanotubes (SWNTs) were sprayed

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onto unidirectional carbon fiber preregs and +/- 45 angle-ply laminates were fabricated and tested for in-plane shear (+/- 45 tensile test). The SWNTs were present mostly at the interfaces between the prepreg plies and did not affect the carbon fiber-matrix interface. Hence, the in-plane shear properties did not improve much either in this case [13].

Carbon nanofiber (CNF) mat interleaves were also inserted between unidirectional carbon fiber preregs. The in-plane shear properties were not reported, but three different methods by which to impregnate the CNF mat with epoxy resin was described. The simple soaking method resulted in poor wettability as compared to the hot compression and vacuum infiltration techniques, and also produced a low modulus in the CNF/epoxy composites [14].

In the present study, we have fabricated the carbon fiber composites by implementing CNT mat interleaves between the carbon fiber layers to enhance one of the matrix-dominated properties, namely the in-plane shear characteristics of carbon fiber composites. The mat-like CNT structure was used to bypass a cumbersome dispersion process and high viscosity issues arising from the direct mixing of CNTs with resin. Also, this method allows the incorporation of high concentrations of CNTs in the composites. The in-plane shear properties of the carbon fiber composites with CNT mats were investigated for different materials and processing methods. Furthermore, the reinforcement mechanism of the CNT mat was also discussed. Graphite structure of CNTs usually results in no chemical bonding between CNTs and polymer matrices. The sidewalls of CNTs have been chemically modified to be decorated with functional groups such as carboxyl groups which promote covalent bonding with polymer matrices. Hence, functionalization of CNTs is essential for the enhancement of the mechanical properties of CNT-reinforced composites

[3-5]. In this study, the CNT mats were functionalized by three different methods and the effectiveness of the functionalization was described in detail.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

The CNT mat was fabricated via a patented process by Nanocomp Technologies, Inc. It consisted of millimeter-range multi-walled carbon nanotubes (MWNTs) which were randomly oriented (Fig. 1). Its nominal thickness was about 15 microns [15,16]. However, the thickness increased when it swelled because of resin infusion [6]. The CNT mat was functionalized by three different methods: air oxidization, reflux treatment in nitric acid, and treatment in a mixture of nitric and sulfuric acids (weight ratio of 25:75). The functionalization methods using acids caused wrinkling of the CNT mat after neutralization and the drying process. Hence, the air oxidized CNT mat was used for fabrication of the composite specimens.

AS4 plain weave carbon fabric (Hexcel co., USA) and WSN3K plain weave prepreg (SK chemical co., Korea) were used as the micro-sized reinforcements. For AS4 carbon fabric, EPON862 epoxy resin and Epikure W curing agent (100:26.4 mixing weight ratio) from Hexion chemicals were used for the matrix. The mechanical properties of the WSN3K woven prepreg were measured in a previous study and are shown in Table 1 [17].

2.2. Processing

The CNT mat (10 cm × 10 cm) was functionalized by air oxidation in a muffle furnace at 350 °C for 1 h. As for CF fabric composites, the air-oxidized CNT mat was immersed in degassed EPON862/Epikure W solution (degassing at 60 °C

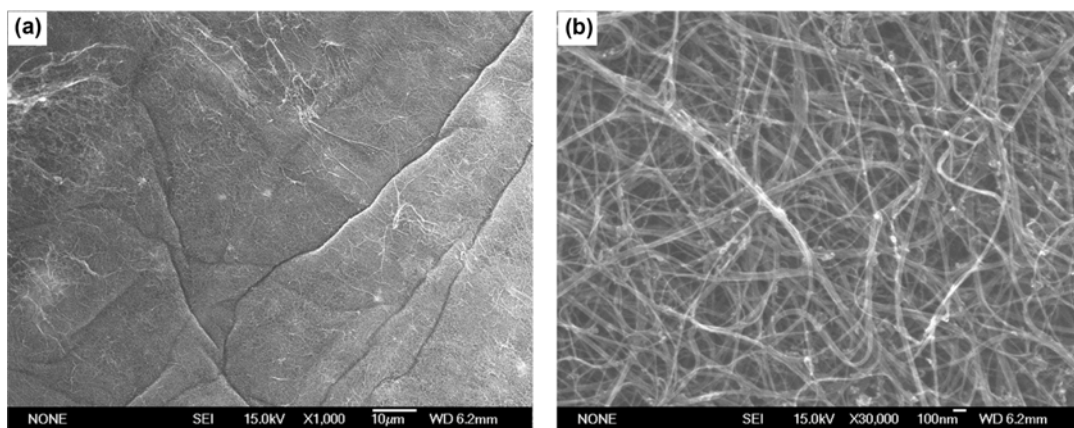


Fig. 1. SEM images of CNT mat: 1000× magnification (a) and 30000× magnification (b).

Table 1. Properties of WSN3K prepreg composite

Elastic modulus (GPa)	Shear modulus (GPa)	Tensile strength (MPa)	Shear strength* (MPa)	Resin Content (vol%)
70	3.59	959.1	118.6	41

*In-plane shear strength measured by Iosipescu shear test method.

for 1 hours in a vacuum oven) for 4 hours at 60 °C to ensure low viscosity of the resin. Then, AS4 plain weave fabric soaked in EPON862/Epikure W solution was placed on a stainless steel mold coated with a release agent. Afterwards, the CNT mat was placed on top of the AS4 layer followed by the placement of another AS4 layer.

One set of CNT mat specimens was fabricated by applying the hand-roller compaction after the lay-up method. The other set of CNT mat specimens was fabricated without hand-roller compaction. This hand-roller compaction process caused the CNTs to mix with the carbon fibers, thus strengthening the CF-matrix interface. Without this compaction, the MWNTs did not exhibit mechanical interlocking with CFs, which resulted in little increase in the in-plane shear strength.

The layup was then vacuum-bagged and excessive resin was removed from the layup by pulling a vacuum for 10 min. In case of the layup with roller compaction, a smaller amount of resin was drawn from the layup, probably because of the excessive resin being squeezed out during the roller compaction process. Afterwards, the vacuum tube was closed and the sample was cured at 130 °C for 6 hours in a convection oven.

The average thickness of the fabric specimens was 0.51 mm. There was no notable difference between the thicknesses of the specimens.

As for the CF prepreg composites, an air-oxidized CNT mat (10 cm × 10 cm) was placed between adjacent CF prepreg plies. Hence, a total of three layers of CNT mats were inserted in a 4-ply prepreg composite laminate. The layup was cured in an autoclave under 0.7 MPa pressure at 175 °C for 6 hours.

The average thickness of the woven prepreg specimen without a CNT mat was 0.9 mm and that with a CNT mat was 1.0 mm. Three layers of CNT mats may have caused this difference between the thicknesses of the specimens.

2.3. Mechanical test

Tests were performed in accordance with ASTM D3518 (Standard test method for in-plane shear response of polymer matrix composite materials by tensile test of a ±45° laminate), although the sample dimensions were smaller than those recommended by the standard. Each specimen was of 120 mm × 11 mm dimensions [18]. The in-plane shear strength of five specimens of each situation were tested. The shear stresses at 3% tensile strain, which closely corresponded to the 5% shear strain, were confirmed as the in-plane shear strengths of the specimens. The shear moduli were obtained by using strain gauges. The in-plane shear test was conducted using a table top universal testing machine (Instron 4411, USA) with cross-head speed of 1 mm/min.

3. RESULTS AND DISCUSSION

3.1. In-plane shear properties

From previous studies, it is evident that the major failure

mode of carbon fiber composites under in-plane shear loading is the interface failure between the fibers and the matrix [1,2]. The ultimate failure of the ±45° woven fiber composites under tensile loading occurs due to fiber breakage and pullout followed by fiber scissoring [18]. The in-plane shear tested specimens exhibited this fiber breakage as shown in Fig. 2.

Figure 3 depicts the in-plane shear properties of CF fabric/CNT mat composites fabricated via different processes. For CF fabric composites, the CNT mat increased the in-plane shear strength when the layup had been roller compacted

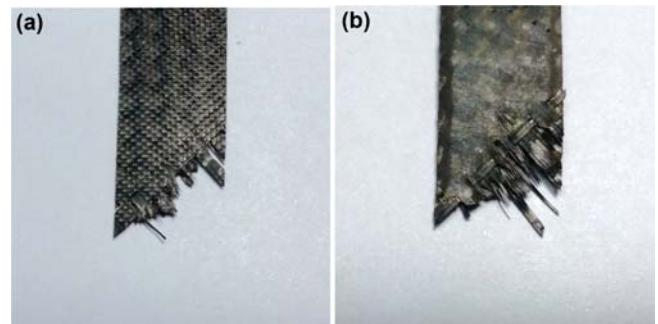


Fig. 2. In-plane shear tested specimens: fabric (a) and prepreg (b) specimens.

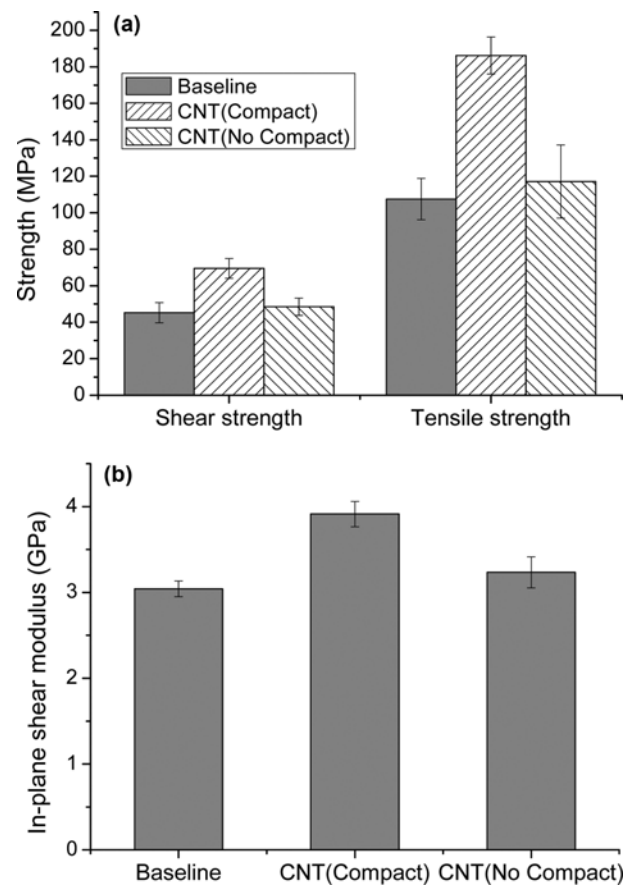


Fig. 3. In-plane shear properties of carbon fabric/CNT mat composites: in-plane shear strength (a), in-plane shear modulus (b).

during processing. This roller compaction process may have opened the carbon fiber bundles, and made possible the penetration of long CNTs into the carbon fiber bundles where they mechanically interlocked with individual carbon fiber filaments. The CNT mat specimens with roller compaction showed increases of 54% and 29% in the in-plane shear strength and modulus, respectively, as compared to the baseline specimens without a CNT mat. CF fabric/CNT mat composites without roller compaction did not show much improvement of the in-plane shear properties as compared to the baseline samples. Even for the CNT mat specimen without roller compaction, the inter-ply resin layer was reinforced by the CNTs and the layer thus may possess superior mechanical properties than the baseline specimens [6,14]. This implies that for the improvement of the in-plane shear properties of the laminate composites, reinforcing the interface between the CF and matrix is more important than reinforcing the inter-ply resin layer.

Figure 4 shows typical shear strain-shear stress charts for three different cases of CF fabric/CNT mat composites. The CNT mat specimen with roller compaction shows higher in-plane shear modulus than the others. The charts show the strain ranging up to 2.5% because of the limitations of the strain gauge used for the shear tests on the CF fabric specimens.

The tensile strain-tensile stress charts exhibit a large strain behavior in the composites (see Fig. 5). All three cases show similar strain and failure values, but superior strength and higher modulus for the CNT mat specimen processed using roller compaction is observed. The CNT mat specimen with roller compaction also displays similar behavior to fiber composites with a ductile matrix as compared with the other cases [19]. As shown in Figures 4 and 5, the CNT mat specimen without roller compaction demonstrates more ductile matrix behavior than the baseline specimen without a CNT mat.

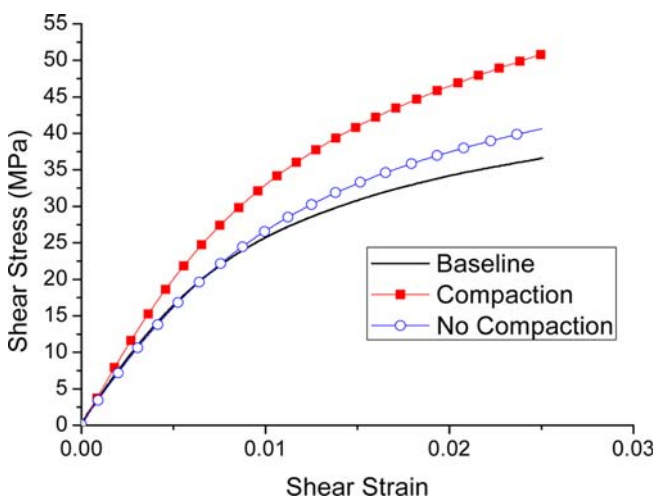


Fig. 4. Typical shear strain vs. shear stress curves of the fabric specimens.

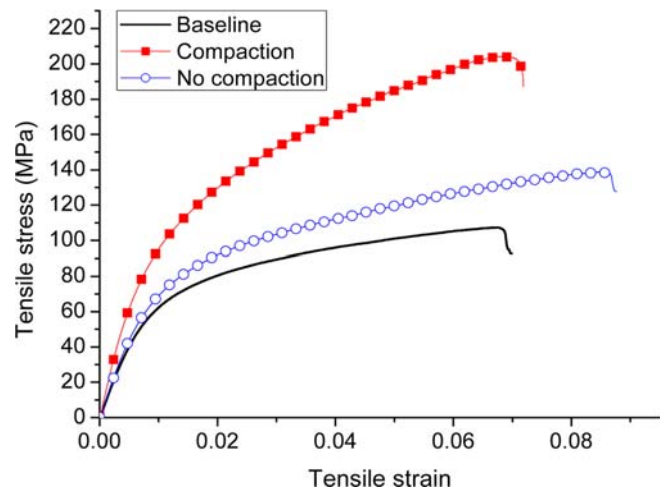


Fig. 5. Typical tensile stress vs. tensile strain of the $\pm 45^\circ$ fabric specimens.

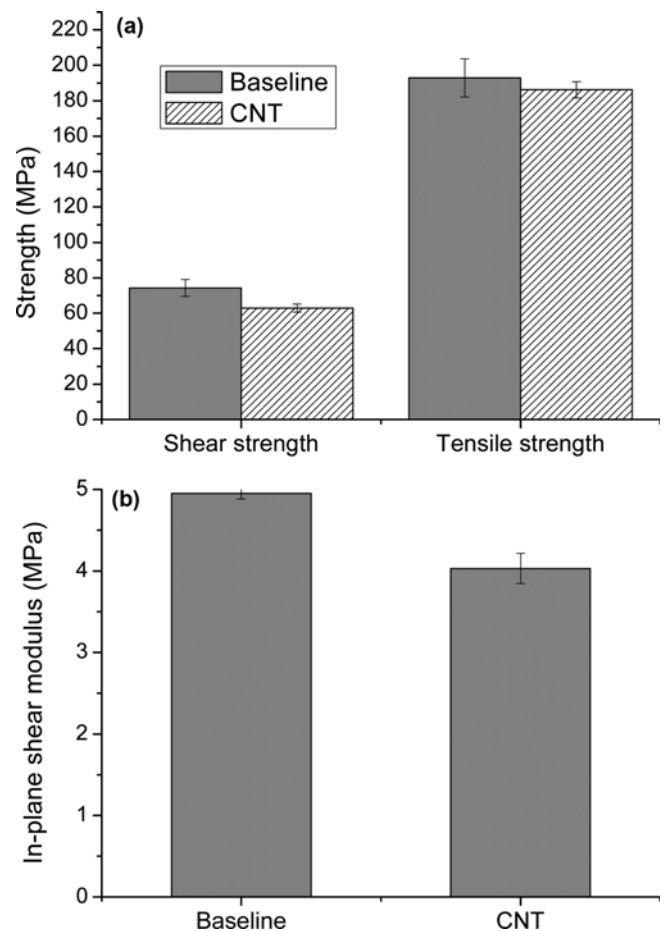


Fig. 6. In-plane shear properties of prepreg specimens with and without CNT mat: in-plane shear strength (a), in-plane shear modulus (b).

Figure 6 shows the in-plane shear properties of the prepreg specimens with and without CNT mat. The in-plane shear properties of the CNT mat specimen did not show any improve-

ment compared to the baseline specimen. In case of the prepreg specimens, the in-plane shear modulus was measured up to 10% for all specimens. Therefore, the in-plane shear strength values of the prepreg specimens were equivalent to the values of the in-plane shear stresses for 3% in-plane shear strains, as suggested by the ASTM standard. Figure 6 also displays the tensile strengths. The in-plane shear strength of the baseline specimen is observed to be 15% higher than that for the CNT mat specimen. However, the thickness of the CNT mat specimen was 11% greater than that of the baseline specimen. Hence, the increased thickness of the CNT mat specimen due to the presence of the CNT mat layers resulted in a decrease in the in-plane shear strength. The loading value corresponding to the in-plane shear strength of the CNT mat specimen was only 5.9% lower than that for the baseline specimen. Also, the ultimate tensile strengths of the 45° specimens were similar, which may imply that the CNT mat layer tough-

ens the inter-ply resin areas.

Figure 7 shows typical shear strain-shear stress charts of the prepreg specimens. The baseline sample shows higher in-plane shear modulus than the CNT mat specimen since the smaller thickness of the baseline specimens results in higher volume fractions of the fiber. The in-plane shear modulus of the fiber composites increases as the fiber volume fraction increases [1,2].

The CNT mat specimen also exhibited behavior similar to ductile matrix composites while the baseline specimen presented behavior similar to that of composites with a low-ductility matrix (Fig. 7). The baseline specimen displayed higher stress values particularly for less than 5% shear strain, but the stress values for both specimens became similar as the strain increased.

As for the prepreg specimens, a CNT mat layer was observed by optical microscopy to not directly touch the CF layer (Fig. 8). Hence, the CNT mat did not affect the carbon fiber/matrix interface. In this case, the CNT mat layer just increased the thickness of the laminate and this resulted in the unimproved in-plane shear properties. On the other hand, a CNT mat layer in the fabric composites completely fills the interply layer in the composites and comes into contact with the carbon fibers (Fig. 8).

Also, as shown in Fig. 8, the CNT mat layer in the prepreg specimen is almost two times thicker than that in the fabric specimen. Compaction process in the case of the fabric specimen may have caused this difference in the thickness of the CNT mat layer. A thinner CNT mat layer implies more in-plane alignment of the CNTs and enhanced in-plane mechanical properties. This can be another reason for the improved in-plane shear properties of the fabric specimen with CNT mat.

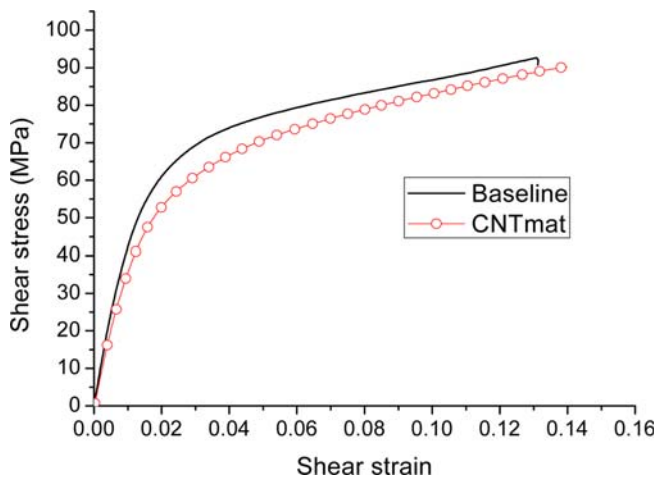


Fig. 7. Typical shear stress vs. shear strain curves of the prepreg specimens.

3.2. Fractography results

Figure 9 shows the fracture surfaces of the fabric composites with and without CNT mat. Figure 9 (a) exhibits fiber-matrix

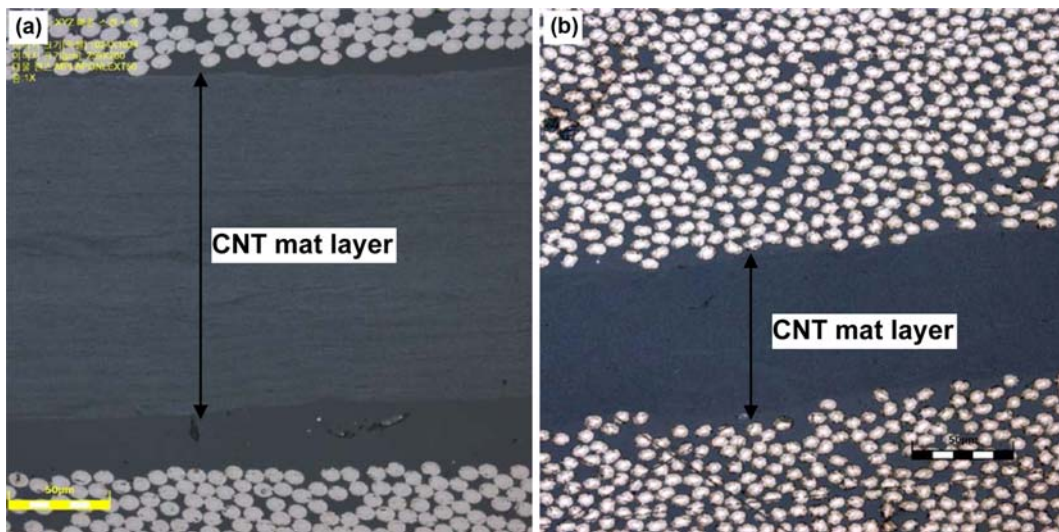


Fig. 8. Cross-sections of prepreg/CNT mat composite (a) and carbon fabric/CNT mat composite (b).

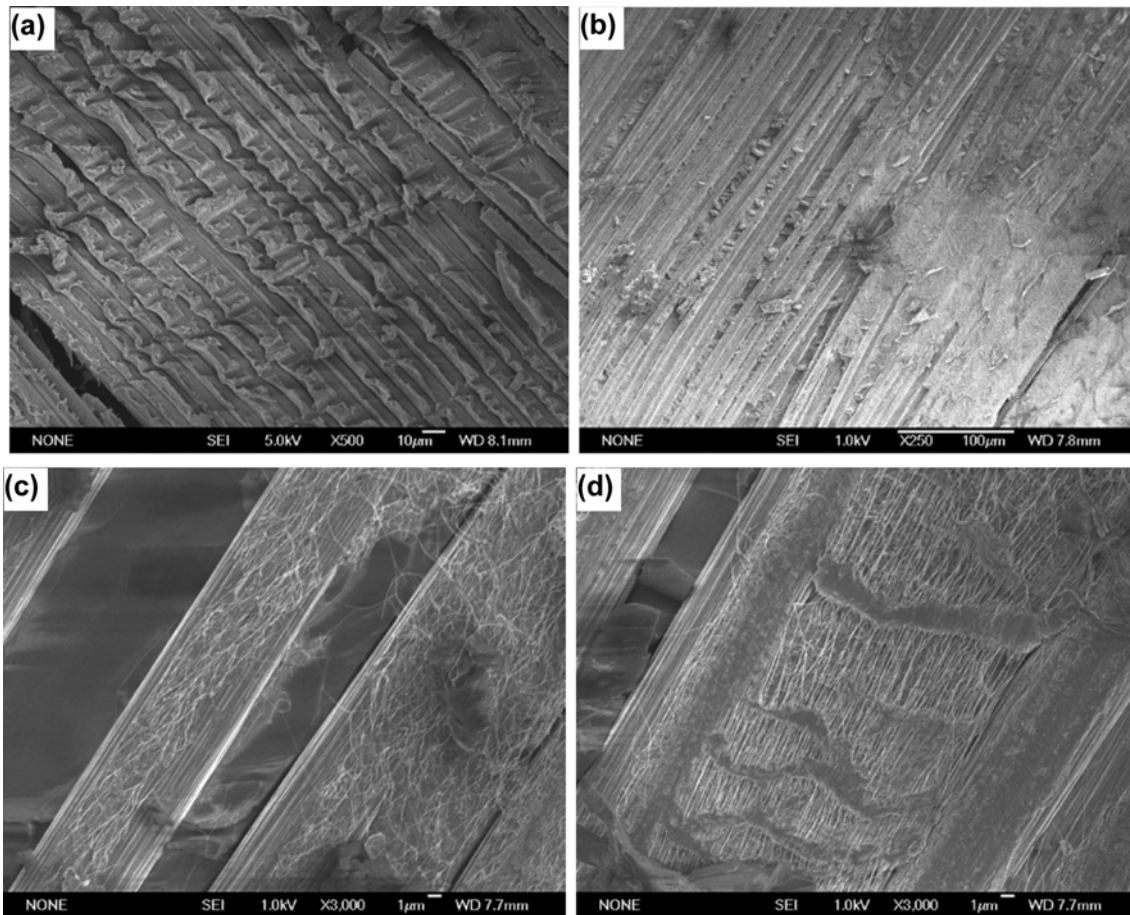


Fig. 9. (a) Fracture surface of a baseline sample. (b) Fracture surface of a CNT mat sample with roller compaction. (c) CNTs attached onto carbon fibers after the in-plane shear test. (d) CNTs stretched in the loading direction.

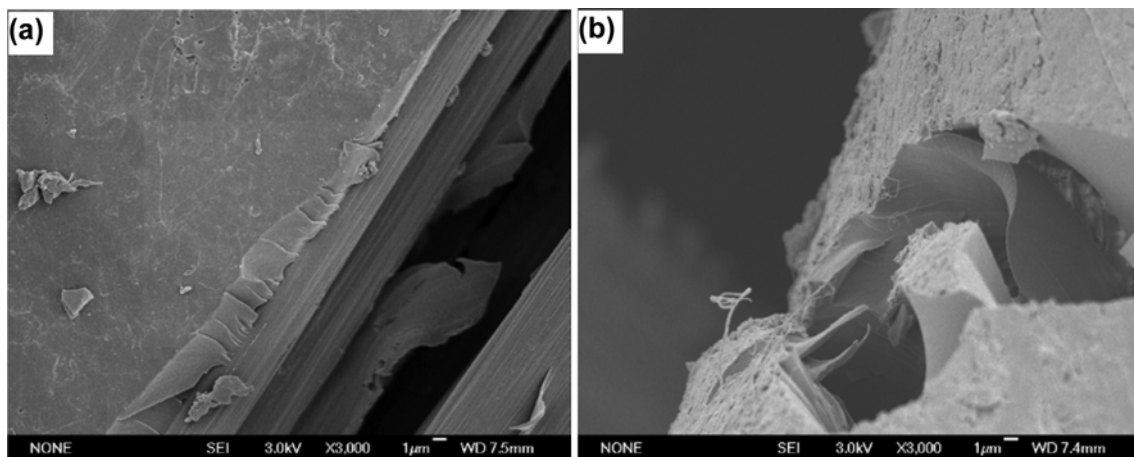


Fig. 10. Fracture surfaces of a CNT mat specimen without roller compaction: (a) fracture through the interface between CNT mat layer and resin area and (b) CNTs on the fracture surface.

debonding for a baseline specimen without CNT mat while Fig. 9(b) displays a region with matrix failure for a CNT mat specimen with roller compaction. Figure 9(c) and (d) are also SEM images of magnified areas of Fig. 9(b).

Figure 9(c) shows CNTs attached onto the fiber surfaces

after the test. The CNTs are observed to be stretched in the loading directions as shown in Fig. 9(d).

Figure 10 shows the fracture surfaces of the CNT mat specimen without roller compaction. In this case, the fracture occurred mostly at the interface between the CNT mat layer

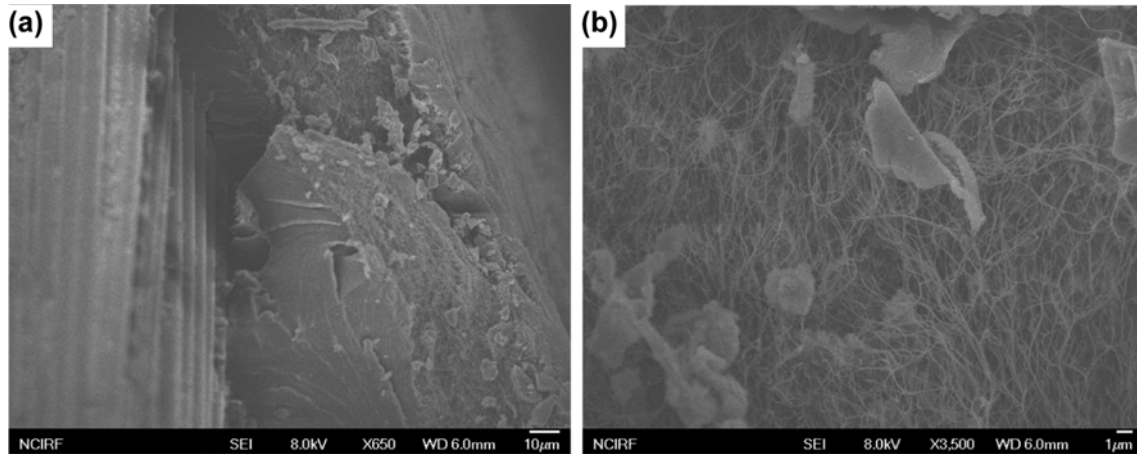


Fig. 11. Fracture surfaces of a prepreg specimen with CNT mat: (a) fracture through the interface between CNT mat layer and resin area and (b) CNTs on the fracture surface.

and resin area.

Figure 11 shows the fracture surfaces of the prepreg specimen. They demonstrate quite similar fracture modes to the fabric/CNT mat specimen without roller compaction: the fracture occurred through the interface between the CNT mat layer and resin area.

Fracture surfaces shown in Figs. 10 and 11 may illustrate the possibility of CNTs affecting the in-plane shear properties of the CF fabric composites when they are mechanically interlocked with the CFs.

3.3. Spectroscopic analysis of CNT mats

Figure 12 shows the mid-IR spectra of pristine CNT mat, air-oxidized CNT mat, nitric-acid treated CNT mat and CNT mat treated with a mixture of nitric and sulfuric acids. The spectra of the CNT mats were collected using attenuated total reflection (ATR) mode. All spectra show peaks which arise from the presence of various types of oxygen-containing groups; however, the spectrum of the pristine CNT mat dis-

plays peak intensity much lower than that observed for the oxidized samples. The peaks in the spectral range between 1000 and 1300 cm^{-1} are assigned to C-O stretching modes in ethers, esters and alcohols or phenols, and the peaks between 1500 and 1800 cm^{-1} are associated with C=O stretches in lactones, carbonyls, carboxylic acids and carboxylic anhydrides.

To understand the evolution of the mid-IR spectra due to the oxidative treatment, the pristine CNT mat spectrum was subtracted from the spectra of the oxidized CNT mat samples (Fig. 12b). Independent of the oxidation techniques, the treatment led to the predominant development of C-O functional groups, which are probably present in many different chemical and carbon environments. Overall, it can be concluded that air oxidation produces the most noticeable change in the surface chemistry of the CNT mats.

While the mid-IR spectroscopy reveals the nature of the chemical groups generated as a result of the oxidative treatment, Raman spectroscopy is used for better understanding of the degree of modification of the graphitic structure of

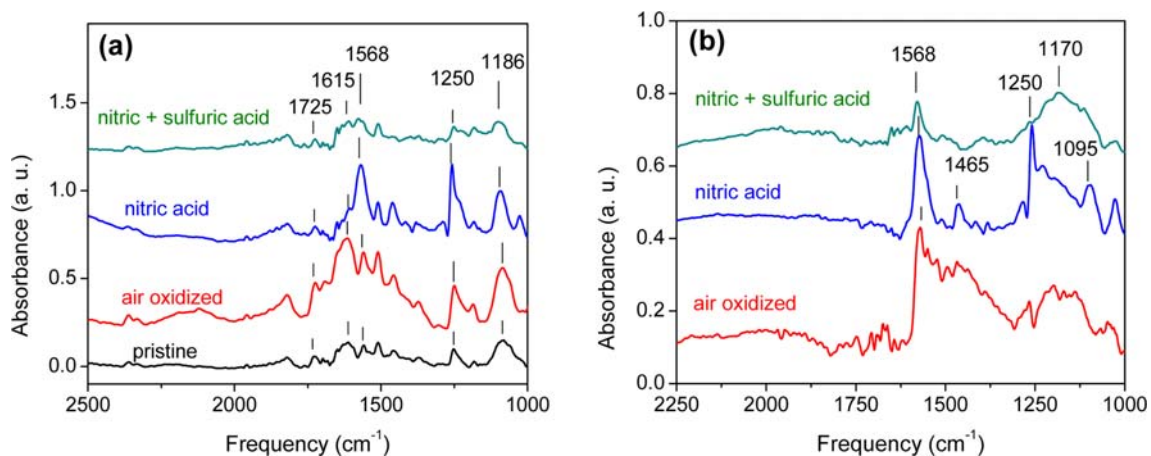


Fig. 12. ATR spectra of CNT mat samples: (a) baseline-corrected spectra of pristine CNT mat and CNT mats oxidized in air, refluxed in nitric acid and treated in a mixture of nitric and sulfuric acids. (b) Spectra of the oxidized CNT mat samples after subtraction of the CNT mat spectrum.

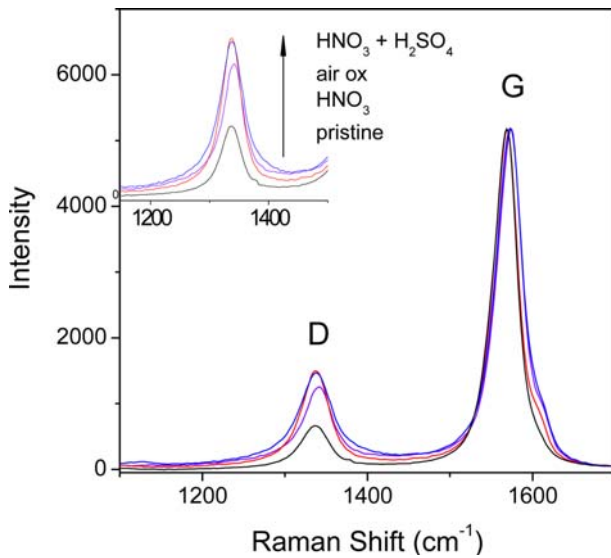


Fig. 13. Raman spectra of pristine CNT mat and CNT mats oxidized in air, refluxed in nitric acid and treated in a mixture of nitric and sulfuric acids. The inset shows the evolution of the D-band.

the multi-wall carbon nanotubes. It is known that disorder in the graphene structure of the tube wall leads to the appearance of a broad disorder band or D-band [20].

The strength of the D-band is related to the periodicity of the carbon structure and any change in the C-atom environment, such as missing C-atoms and/or added functional groups, are reflected in the relative intensity of the D-band to the intensity of the graphitic or G-band. The measured Raman spectra of the CNT mats are presented in Fig. 13 and the intensity of all spectra were normalized to yield the same intensity for the G-band at $\sim 1590 \text{ cm}^{-1}$.

The Raman spectrum of the grown CNT mat shows a small D-band, with an intensity relative to the intensity of the G-band of $I_D/I_G \sim 0.1$. The oxidative treatments increase the intensity of the D-band and the ratio I_D/I_G increases to 0.18 after reflux in nitric acid, while air oxidation and treatment in a mixture of nitric and sulfuric acids more than double I_D/I_G . Structurally, the CNT mats are quite homogeneous and scanning of the surfaces showed relatively small deviations in I_D/I_G (Table 2).

The spectroscopic analysis shows that air oxidation of the CNT mat is the most effective oxidative treatment for composite preparation as it introduces greater amounts of oxygen-containing groups onto the nanotube surface as compared

Table 2. Ratio of D-band to G-band (I_D/I_G) determined from the Raman spectra of CNT mat samples

Sample	I_D/I_G
Pristine CNT mat	0.11 +/-0.02
Air oxidized	0.25 +/-0.03
Nitric acid (HNO ₃)	0.18 +/-0.04
Nitric and sulfuric acids (HNO ₃ + H ₂ SO ₄)	0.25 +/-0.02

to the treatments in mineral acids. The combination of nitric and sulfuric acids led to the same increase in the I_D/I_G ratio as for air oxidation; however, the mid-IR spectra shows that the presence of oxygen-containing groups is relatively small. The large I_D/I_G ratio can be explained by the generation of amorphous carbon due to the strong acid treatment. The nitric acid treatment led to a small increase of the I_D/I_G as compared to the situation for the pristine CNT mat; however, this treatment did not produce a large number of groups containing oxygen.

4. CONCLUSIONS

The in-plane shear properties of the carbon fiber fabric composites with CNT mat were increased compared to the composites without CNT mat when the layup was compacted using a roller. The SEM images demonstrated that mechanical interlocking between long CNTs and carbon fibers led to increased in-plane shear properties. On the other hand, in case of the prepreg composites, the CNT mat layer did not have a great effect on the carbon fiber-matrix interface. Consequently, the prepreg composites with the CNT mat layer did not result in much improvement of the in-plane shear properties. Three different methods were conducted to functionalize the CNT mat and characterize their effectiveness. Air oxidation and treatment using the mixture of nitric acid and sulfuric acid were shown to be effective functionalization procedures. However, wet chemical treatment resulted in wrinkling of the CNT mat. Hence, air oxidation is the most appropriate method at this moment. In the future, research on the minimization of the adverse effect of wet functionalization processes of CNT mat is desired.

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