A STUDY ON IMPROVING PROPERTIES OF ALIGNED MULTI-WALLED CARBON NANOTUBE/EPOXY COMPOSITES

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Abstract - Composites made of an epoxy resin film and differently stacked aligned multi-walled carbon nanotube (MWCNT) sheets have been developed using hot-melt prepreg processing. The horizontally aligned 20-ply MWCNT sheets were created from vertically aligned MWCNT arrays using solid-state drawing and winding techniques. However, wavy and poor-packed MWCNTs in the sheets have restricted their load-transfer efficiency in the composites. Therefore, mechanical stretching was used to straight the wavy MWCNTs and to increase the dense packing of MWCNTs in the sheets. Improving the composite properties through mechanical stretching of the MWCNT sheets was studied. Mechanical stretching of the MWCNT sheets improved considerably the mechanical properties of the composites. The improvement of the composite properties derived from the straightening of wavy MWCNTs and the increase of MWCNT dense packing caused by mechanical stretching. The decrease of the wavy MWCNTs is more efficient than the enhancement of MWCNT dense packing.

Key words: aligned carbon nanotubes; prepregs; nano composites; mechanical stretching; mechanical properties.

1. Introduction

Carbon nanotubes (CNTs) were discovered by Iijima in 1991 [1]. They have attracted extensive research interest because of exceptional mechanical, electrical, and thermal properties [2,3]. The excellent properties make CNTs an ideal reinforcement in high-performance composites. Most studies of CNT-reinforced polymer composites have focused on dispersing CNTs into polymer matrices [4]. However, mechanical properties of such composites fall far short of the corresponding properties of high-performance structural composites. Therefore, great efforts have been recently undertaken to synthesize vertically aligned CNT arrays [5] for production of long-aligned CNT sheets. The easiest way of processing aligned CNT sheets from the aligned CNT arrays is the use of solid-state drawing and winding techniques [6].

The aligned MWCNT sheets can be used to fabricate advanced composites with desirable structural characteristics [7]. Despite those composites contain aligned MWCNTs, their mechanical properties are inadequate partly because of wavy and poor-packed MWCNTs. Therefore, stretching has been applied to the aligned MWCNT sheets to improve composite properties [8,9]. Results in my earlier report [9] show that the stretching of the MWCNT sheets with 50 and 100 plies is less efficient than that of 20-ply MWCNT sheet. Consequently, in this study 20-ply aligned MWCNT sheets were used for development of laminated epoxy composites. Effects of mechanical stretching the 20-ply MWCNT sheets on the composite properties were studied.

2. Materials and Methods

2.1. Materials

Vertically aligned and spinnable MWCNT arrays with approximately 0.8 mm height were grown on a bare quartz substrate using chloride-mediated chemical vapor deposition [5]. As-grown MWCNTs used in this study have mean diameter of 38 nm [10]. The MWCNT diameter in the sheets varies from about 20 nm to 55 nm. B-stage epoxy resin films covered with release paper and plastic film were obtained from Sanyu Rec Co. Ltd. (Osaka, Japan) with the recommended cure condition of 130 °C for 2 h. The areal weight of the epoxy resin sheet with density of 1.2 g/cm^3 was controlled approximately 12 ± 6 g/m^2.

2.2. Methods

2.2.1. Processing of horizontally aligned MWCNT sheets

Solid-state drawing and winding techniques were applied to transform a vertically aligned MWCNT array into horizontally aligned MWCNT sheets. The MWCNT webs are drawn from vertically aligned MWCNT arrays and are wound on a rotating spool to create horizontally 20-ply aligned MWCNT sheets. Detailed procedures for the fabrication of multi-ply MWCNT sheets are depicted in the literature [7–10]. Although most MWCNTs are aligned, many wavy and entangled MWCNTs are visible in pristine sheets [7–9]. In this study, the aligned 20-ply MWCNT sheets were used for laminated composite fabrication.

2.2.2. Mechanical stretching of the MWCNT sheets

To straight wavy MWCNTs, mechanical stretching with a ratio of 2% was applied to pristine MWCNT sheets. Stretch ratio Δ was calculated using the following equation.

$$\Delta = \frac{L_2 - L_1}{L_1} \tag{1}$$

Therein, L_1 and L_2 are segment lengths of the MWCNT sheets between the clamped grips before and after stretching, respectively. More details about the stretching device and processing were presented by Nam et al. [9].

2.2.3. Fabrication of aligned MWCNT/epoxy composites

The composites made of an epoxy resin film and stacked MWCNT sheets were fabricated using hot-melt prepreg processing with a vacuum assisted system (VAS) [10]. Figure 1 portrays the schematic views of stacking the MWCNT sheets on an epoxy resin film to form the composite laminates. Firstly, aligned MWCNT/epoxy prepregs were prepared by stacking 1, 5, and 10 non-stretched (pristine) or stretched 20-ply MWCNT sheets with 20 mm width and 40 mm length on an epoxy resin film. The prepregs were set in two release films (WL5200; Airtech International Inc., CA, USA) and were pressed under 0.5 MPa pressure for 5 min at 100 °C using a test press (MP-WNL; Toyo Seiki Seisaku-Sho Ltd., Tokyo, Japan). Subsequently, the prepregs were peeled off from the release films. Finally, the prepregs were cured at 130 °C for 2 h under 2 MPa in the VAS to produce the composites. The non-stretched and stretched composites are assigned respectively as NCom-X and SCom-X, in which X corresponds to the MWCNT sheets in number (1, 5 and 10).

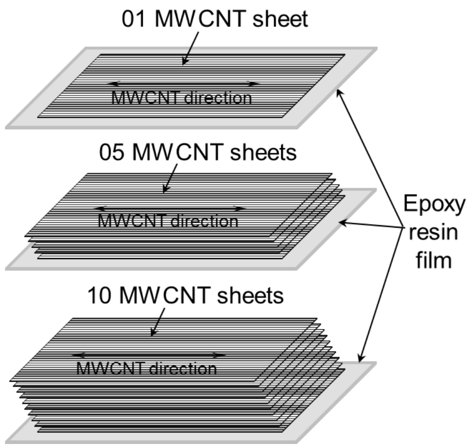

Figure 1. *Schematic views of stacking the MWCNT sheets on an epoxy resin film to form the composites.*

2.2.4. Thermogravimetric analysis (TGA)

The thermal degradation of epoxy resin, MWCNTs, and their composites was analyzed up to 800 °C in argon ambient at a flow rate of 300 ml/min using a thermogravimetric analyzer (DTG–60A; Shimadzu Corp., Kyoto, Japan). About 5 mg of each specimen was loaded for each measurement at a heating rate of 10 °C/min.

2.2.5. Microstructural characterization and testing

Tensile tests were conducted for the aligned MWCNT sheets and composites in the laboratory environment at room temperature (RT). Tensile specimens with 6–10 mm gauge length and 3–5 mm width were tested on a testing machine (EZ-L; Shimadzu Corp., Kyoto, Japan) with a load cell of 50 N and a crosshead speed of 0.1 mm/min. Specimens width was measured using an optical microscope (SZX12; Olympus Corp., Tokyo, Japan), whereas their thickness was measured using a micrometer with 0.001 mm accuracy (Model 102-119, Mitutoyo Corp., Kanagawa, Japan). The strain of tensile specimens was measured using a non-contacting video extensometer (TRIViewX; Shimadzu Corp., Kyoto, Japan) with two targets. Mean tensile properties were obtained from at least five specimens for each MWCNT sheet and composite. The microstructural morphologies of MWCNTs in the sheets and composite fracture surfaces were observed using field emission scanning electron microscopy (FE-SEM) (SU8030; Hitachi Ltd., Tokyo, Japan). Polarized Raman spectra were measured to determine the degree of MWCNT alignment in the composites using Raman spectroscope with laser excitation of 532 nm (XploRA-ONE; Horiba Ltd., Kyoto, Japan).

3. Results and Discussion

3.1. MWCNT volume fraction of the composites

MWCNT volume fraction of the composites was determined through TGA results. The respective mass loss of MWCNTs, epoxy resin and the composites were measured between 150 ^{o}C and 750 ^{o}C. The MWCNT mass fraction (m_f) of the composite was calculated from the mass loss of MWCNTs (Δm_f), epoxy resin (Δm_m), and the composite (Δm_c) as follows.

$$m_f = \frac{\left(\Delta m_m - \Delta m_c\right)}{\left(\Delta m_m - \Delta m_f\right)} \tag{2}$$

The MWCNT volume fraction (V_f) was ascertained from the MWCNT mass fraction, epoxy resin density (ρ_m), and the density of the composite (ρ_c) as follows.

$$V_f = 1 - \frac{\left(1 - m_f\right)\rho_c}{\rho_m} \tag{3}$$

The MWCNT volume fractions of the composites are presented in Table 1. The MWCNT volume fraction of the composites increases with increasing of the aligned MWCNT sheets.

Table 1. *The MWCNT fractions estimated from TGA results*

Materials	Epoxy resin	MW CNT	Non-stretched composites			Stretched composites		
			MWCNT sheet			MWCNT sheet		
			1	5	10	1	5	10
Mass loss (%)	87.9	2.59	74.4	45.4	35.7	71.6	42.7	33.4
MWCNT m_f (%)	–	–	15.8	49.9	61.2	19.1	53.0	63.9
MWCNT V_f (vol. %)	–	–	10.1	37.4	48.7	12.1	40.4	51.5

3.2. Properties of MWCNT sheets and their composites

Thickness of the pristine 20-ply MWCNT sheets was measured as 1–2 μm. The mechanical properties of epoxy resin, pristine 20-ply MWCNT sheets, and composites were measured using tensile test. The epoxy resin film and pristine MWCNT sheets respectively showed mean tensile strength of 64.4 and 96.8 MPa, elastic modulus of 2.55 and 7.34 GPa, and strain at maximal stress of 4.84 and 2.11%. Typical stress–strain curves of epoxy resin, pristine 20-ply MWCNT sheets, and the composites are depicted in Figure 2. As observed in Figure 2, the composites indicated a linear stress-strain relation until the specimen fractures with no bending of the curves at high loads. Typical stress-strain curve of pristine MWCNT sheets showed that the stress is increased up to the maximum with increasing strain to approximately 2%. In this stage, the wavy CNTs are straightened under the tension. Above 2% strain, the stress decreases concomitantly with enhancing strain up to the specimen fractures. The reduction of the stress is attributed to the MWCNT sliding during the tensile testing, as presented by Inoue et al. [6]. Consequently, mechanical stretching of the MWCNT sheets was conducted with a 2% ratio in the laboratory environment at RT.

The properties of the non-stretched and stretched MWCNT/epoxy composites are given in Table 2. The mechanical properties of the non-stretched and stretched composites increase with increasing of the MWCNT sheets (volume fraction). Tensile strength and elastic modulus of the non-stretched composites enhanced strongly whereas fracture strain increased only slightly. The NCom10 and SCom10 respectively exhibited an increase in tensile strength by 241.6% and 204.2%, in elastic modulus by 204.3% and 181.8%, and in fracture strain by 10.7% and 7.3% compared with the NCom1 and SCom1. The enhancement in the mechanical properties of the composites is attributed to increased MWCNT volume fraction (Table 1).

Table 2. *Properties of non-stretched and stretched MWCNT/epoxy composites*

Property	Non-stretched composites			Stretched composites		
	1 sheet	5 sheets	10 sheets	1 sheet	5 sheets	10 sheets
Thickness (μm)	6 – 7	11 – 13	16 – 18	5 – 6	10 – 12	15 – 17
Density (g/cm^3)	1.28	1.50	1.59	1.30	1.52	1.61
Tensile strength (MPa)	105.6 ± 10.1	258.1 ± 29.4	360.6 ± 31.1	180.3 ± 16.1	430.3 ± 49.4	548.5 ± 52.5
Elastic modulus (GPa)	23.1 ± 2.9	54.5 ± 6.0	70.3 ± 8.0	35.6 ± 3.6	79.3 ± 7.4	100.4 ± 11.3
Fracture strain (%)	0.46 ± 0.08	0.48 ± 0.05	0.51 ± 0.04	0.51 ± 0.07	0.54 ± 0.04	0.55 ± 0.03

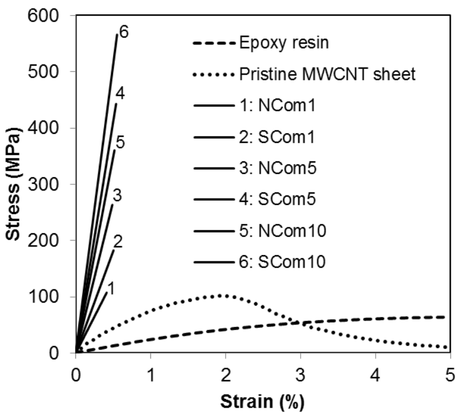

Figure 2. *Typical stress–strain curves of epoxy resin, pristine MWCNT sheet, and the composites.*

3.3. Evaluating of MWCNT alignment and straightening

Microstructural morphologies of the aligned MWCNT sheets before and after mechanical stretching are shown in Figure 3. Although most MWCNTs in the sheets are self-aligned in the drawing direction, the wavy MWCNTs can be clearly seen in the non-stretched samples (Figure 3a). After 2% stretching the wavy MWCNTs were reduced considerably (Figure 3b). The wavy MWCNTs are self-assembled and are straightened along the load direction during stretching. Therefore, the dense packing of MWCNTs in the stretched sheets (Figure 3b) became more compact than that in the non-stretched sheets (Figure 3a).

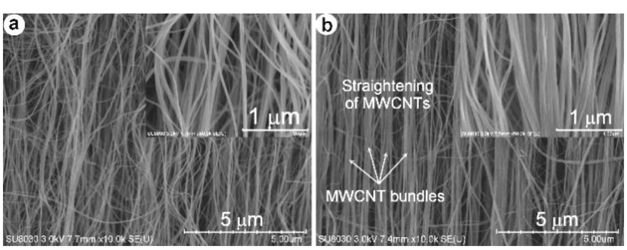

Figure 3. *FE-SEM micrographs showing microstructural morphologies of (a) non-stretched and (b) stretched MWCNT sheets.*

FE-SEM micrographs taken from polished surfaces of the non-pressed and pressed composites reinforced with 10 MWCNT sheets are presented in Figure 4. Those images showed in-plane MWCNT distribution in the non-pressed and pressed composites. As observed in Figure 4, the alignment of MWCNTs in the composites is maintained during resin impregnation using hot-melt prepreg processing. The non-stretched MWCNT/epoxy composites contained many wavy and entangled MWCNTs (Figure 4a). The stretched MWCNT/epoxy composite showed marked straightening of wavy MWCNTs caused by mechanical stretching of the MWCNT sheets (Figure 4b).

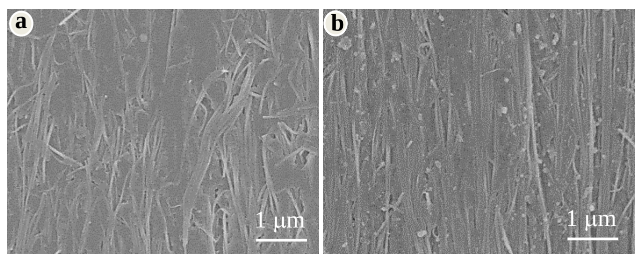

Figure 4. *FE-SEM micrographs showing in-plane MWCNT distribution of (a) non-stretched and (b) stretched composites reinforced by 10 MWCNT sheets.*

The straightening and alignment of MWCNTs after mechanical stretching can be examined using polarized Raman spectroscopy [11,12]. Typical polarized Raman spectra in the range of 1000–2000 cm^{-1} are presented in Figure 5. Raman spectroscopic measurements were conducted with incident light normal to the composite samples, which was polarized parallel and perpendicular to the MWCNT alignment (see Figure 5 inset). Raman spectra for all samples show two main peaks located at approx. 1350 cm^{-1} and approx. 1580 cm^{-1}, which are attributed respectively to the disorder-induced D band and the graphic-like G band. Compared with the non-stretched samples, the stretched ones showed a higher intensity of D and G bands at 0° and lower D and G band peaks at 90°. The G band peaks decreased greatly for the stretched composites at the angle of 90°, which proves that the MWCNT alignment in the composites was improved considerably after stretching the MWCNT sheets.

In addition, the ratio of G-band intensity in the parallel configuration to the perpendicular configuration $\left(R = I_{G\parallel} / I_{G\perp}\right)$ was used to characterize the degree of

MWCNT alignment [6]. The higher MWCNT alignment produces the higher G-band intensity ratio, because Raman scattering is more intense when the polarization of the incident light is parallel to the axis of a MWCNT [12]. The G-band intensity ratio R of the non-stretched composites reinforced by 10 MWCNT sheets was 1.33, as presented in Figure 5. After stretching, the R value of the stretched composites reinforced by 10 MWCNT sheets was markedly enhanced to 1.95. The marked enhancement in the R is ascribable to the better alignment of MWCNTs in the composites caused by mechanical stretching. Therefore, the mechanical stretching improved considerably the MWCNT alignment in the stretched composites.

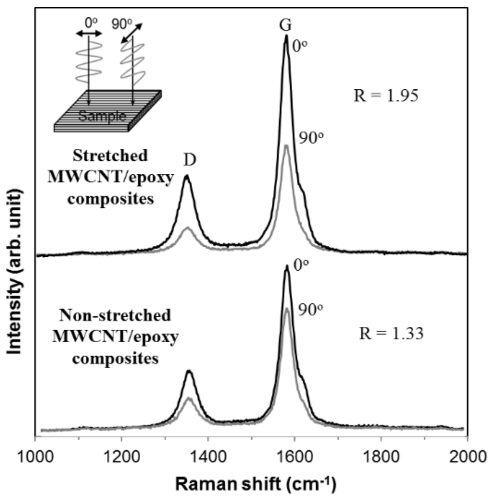

Figure 5. *Polarized Raman spectra of the non-stretched and stretched composites reinforced by 10 MWCNT sheets at 0° and 90° (0° and 90° directions correspond to configurations where the polarization direction of the laser light are, respectively, parallel and perpendicular to the direction of CNT alignment).*

3.4. Effects of stretching on the composite properties

As Table 1 shows, MWCNT volume fractions of the stretched composites are higher than those of corresponding non-stretched ones. The increased MWCNT volume fraction of stretched composites is explainable by the decrease of the composite thickness (Table 2). The reduction of the composite thickness is attributable to straightening of wavy MWCNTs and dense packing of MWCNTs in the sheets caused by stretching (Figure 3). The MWCNTs in the stretched sheets tend to contract in the directions transverse to the stretching direction [9]. Therefore, the thickness of stretched sheets became thinner than that of the non-stretched ones. The mean thickness of the stretched composites reinforced by 1, 5, and 10 MWCNT sheets respectively reduced by 8.1%, 13.6%, and 16.4% compared with that of the non-stretched ones.

Enhancement of the mechanical properties of the composites as a result of stretching the MWCNT sheets is presented in Figure 6. The mechanical properties of the stretched composites are significantly higher than those of the non-stretched ones. The stretched composites reinforced by 1, 5, and 10 MWCNT sheets respectively exhibited an increase in tensile strength by 70.8, 66.7, and 52.1%, in elastic modulus by 54.4, 45.5, and 42.9%, and in fracture strain by 9.7, 14.2, and 6.4% compared with corresponding non-stretched ones. The non-stretched composites evidently showed many wavy MWCNTs along the axial loading direction (Figure 4a). Therefore, just a small fraction of MWCNTs in the non-stretched composites carries load effectively during tensile testing. The wavy MWCNTs are straightened during the stretching of the MWCNT sheets (Figure 3b). The straight MWCNTs have a larger fraction of their length aligned with the loading direction, which resulted in improved mechanical properties of the stretched composites [8].

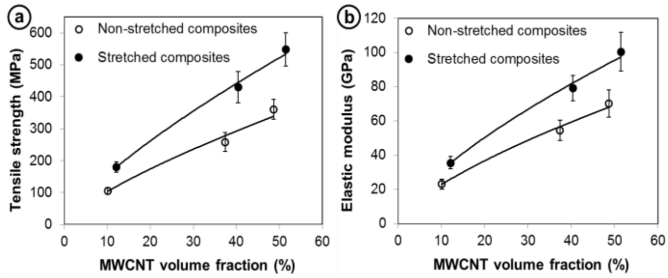

Figure 6. *Mechanical properties of the composites versus MWCNT volume fraction.*

The increased mechanical properties of the stretched composites probably derived from enhancing the MWCNT volume fraction (Table 1) and from reducing the wavy MWCNTs (Figure 3). To assess the effects of these two factors, the respective percentage increases of elastic modulus and MWCNT volume fraction in comparison between stretched and non-stretched composites were analyzed, with results presented in Figure 7. The percentage increases of the MWCNT volume fraction are markedly much lower than those of elastic modulus. Therefore, the percentage increase of elastic modulus by the enhanced MWCNT volume fraction is lower than that coming from reducing of the wavy MWCNTs. The increased MWCNT volume fraction of the stretched composites is attributed to the decreased composite thickness caused by the dense packing of MWCNTs (Figure 3). Generally, the increase of MWCNT volume fraction is less efficient than the decrease of wavy MWCNTs. Moreover, the percentage increase of elastic modulus showed a reduced trend with increasing of the MWCNT sheets (Figure 7).

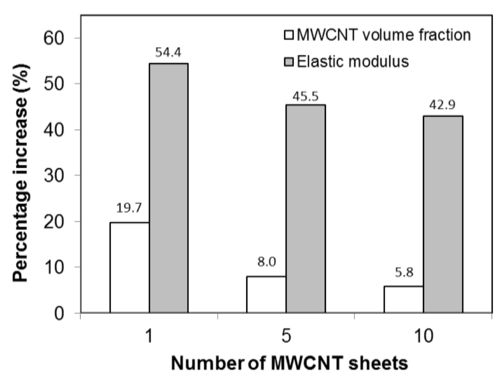

Figure 7. *Percentage increase of MWCNT volume fraction and elastic modulus of stretched composites compared with non-stretched ones.*

The fractured surface morphology of the non-stretched and stretched composites reinforced by 5 MWCNT sheets is depicted in Figure 8. High-resolution micrographs in

Figure 8 show that epoxy resin was infiltrated well between the MWCNTs. However, many pulled-out MWCNTs with length of a few micrometers are apparent on the fractured surface of the composites (Figure 8). For the stretched MWCNT/epoxy composites, the MWCNT bundles can be seen on the fracture surfaces (Figure 8b). The bundled MWCNTs forming by stretching are evidently observed on surface morphologies of the stretched MWCNT sheets (Figure 3b). The MWCNT bundles indicated the dense packing of MWCNTs in the stretched sheets. In general, mechanical stretching of the MWCNT sheets enhanced their composite properties considerably.

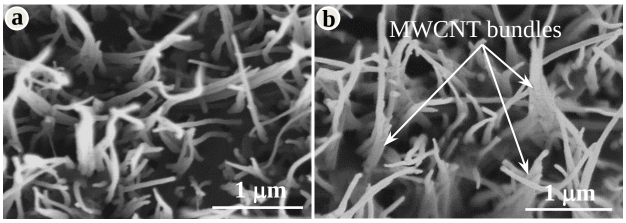

Figure 8. *FE-SEM micrographs showing the fracture surfaces of (a) the non-stretched and (b) stretched composites reinforced by 5 MWCNT sheets.*

4. Conclusions

The composites based on epoxy resin and stacked aligned 20-ply MWCNT sheets were developed using hot-melt prepreg processing with the VAS. The mechanical properties of the composites enhanced gradually with increasing of the MWCNT volume fraction. Mechanical stretching of the MWCNT sheets decreased the composite thickness and increased MWCNT volume fraction. Mechanical stretching the MWCNT sheets with a 2% ratio considerably improved the composite properties. The improved mechanical properties of stretched composites proceeded from decreased wavy MWCNTs and from increased dense packing of MWCNTs caused by stretching. The reduction of the wavy MWCNTs is more efficient than the enhancement of MWCNT dense packing.

Acknowledgements. This research is funded by PetroVietnam University under grant code GV1514.

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(The Board of Editors received the paper on 12/04/2015, its review was completed on 12/25/2015)