Hội nghị Khoa học toàn quốc Cơ học Vật rắn biến dạng lần thứ XII
Đại học Duy Tân, TP Đà Nẵng, 6-7/8/2015

Development and study of tensile properties of aligned multi-walled carbon nanotube sheets and their composites

Trần Hữu Nam

PetroVietnam University, Floor 6, PVMTC Tower, Long Toan Precinct,
Ba Ria City, Ba Ria-Vung Tau Province, Viet Nam.

Email: namth@pvu.edu.vn

Abstract

Carbon nanotubes (CNTs) are considered as molecular-scale tubes of graphite carbon. They have attracted extensive research interest because of their extraordinary mechanical, electrical, and thermal properties. The excellent mechanical properties of CNTs make them ideal for reinforcement in high-performance composite materials. For development of high-performance CNT-reinforced composites, vertically aligned multi-walled CNT (MWCNT) arrays were created using chemical vapor deposition method. For this study, horizontally aligned and multi-ply MWCNT sheets were produced from vertically aligned MWCNT arrays using drawing and winding techniques. Composite based on epoxy resin and 100-ply MWCNT sheet has been developed using hot-melt prepreg processing with a vacuum-assisted system. The hot-melt prepreg processing maintained the alignment of MWCNTs during resin impregnation. Tensile properties of the 100-ply MWCNT sheet, its prepreg and composite have been studied. The composite showed higher tensile strength and elastic modulus, and lower fracture strain in comparison with the prepreg and the MWCNT sheet. The resultant composite exhibited higher elastic modulus and tensile strength than those of composites produced using conventional mixing methods.

Keywords: Carbon nanotubes, Nano-structures, Prepregs, Polymer-matrix composites, Tensile properties

1. Introduction

Carbon nanotubes (CNTs) have exceptional mechanical, electrical, and thermal properties (Ruoff et al., 1995; Ebbesen et al., 1996). Their outstanding mechanical properties along with their low density make CNTs as a potential reinforcement for high-performance composite materials (Dresselhaus et al., 2002). Studies of CNT-reinforced composites have progressed rapidly during the last two decades. Methods to produce CNT-reinforced composites have included (1) dispersing the CNTs (Guo et al., 2007), (2) reinforcing CNT arrays (Wardle et al., 2008), fibers and yarns (Tibbetts et al., 2007, Ghemes et al., 2012), buckypapers (Lopes et al., 2010), and sheets (Cheng et al., 2009) with polymer matrix. Recently, great efforts have been undertaken to synthesize vertically spinnable and aligned CNT arrays for the production of large-scale CNT structures (Inoue et al., 2008). Based on a solid-state drawing technique, Inoue et al. (2011) created highly oriented and continuous multi-walled CNT (MWCNT) sheets by stacking and shrinking long-lasting MWCNT webs without binder materials from vertically aligned MWCNT arrays. Highly aligned and multi-ply MWCNT sheets have been particularly promising as the reinforcement for advanced composite materials.

The aligned MWCNT sheets allow production of advanced composites with desirable structural characteristics (Ogasawara et al., 2011). The composites based on aligned MWCNT sheets have attracted great interest because they are envisioned as a revolutionary advanced composite material for a host of demanding applications. This paper describes the processing of horizontally long-aligned and multi-ply MWCNT sheets from vertically aligned MWCNT arrays through drawing and winding processes. Composite based on epoxy resin and aligned 100-ply MWCNT sheet was developed using hot-melt prepreg processing. Tensile properties of the 100-ply MWCNT sheet, its prepreg and composite have been studied. The MWCNT volume fraction was ascertained using thermogravimetric analysis (TGA). Field emission scanning electron microscopy (FE-SEM) was used to investigate the respective microstructures of the MWCNT sheet and the MWCNT/epoxy composite.

2. Experimental procedures

2.1. Materials

Vertically aligned MWCNT arrays with about 0.8 mm height were grown on a bare quartz substrate using chloride-mediated chemical vapor deposition (Inoue et al., 2008). Figure 1(a) portrays a vertically aligned MWCNT array used for this study. An FE–SEM image showing horizontally aligned MWCNTs drawn from the MWCNT array was inserted in Figure 1(a). A transmission electron microscopy (TEM) image showing the high quality of MWCNTs is presented in Figure 1(b). As-grown MWCNTs examined in this study have mean diameter of 38.1 nm (see Figure 1(b) inset). The diameter of MWCNTs in the sheet varies from about 20 nm to 55 nm. A B-stage epoxy resin sheet covered with release paper and plastic film was obtained from Sanyu Rec Co. Ltd. (Osaka, Japan) with the recommended cure condition of 130 °C for 2 h. The areal weight of the B-stage epoxy resin sheet with density of 1.2 g/cm^3 was controlled to approximately 12 g/m^2.

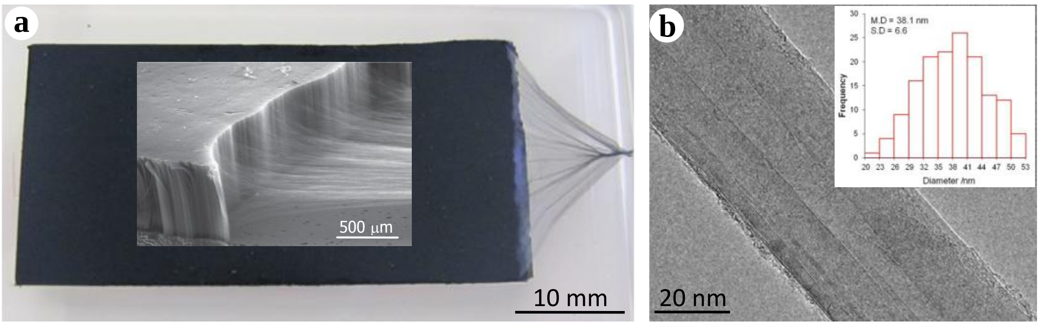

Figure 1. (a) Vertically aligned MWCNT array and an inserted FE–SEM image showing horizontally aligned MWCNTs. (b) A TEM image and diameter distribution of MWCNTs.

2.2. Horizontally aligned MWCNT sheet processing

Vertically aligned MWCNT arrays used in this study are self-oriented and highly drawable. A solid-state drawing and winding techniques were applied to transform a vertically aligned MWCNT array into horizontally aligned MWCNT sheets. The MWCNT webs were easily drawn and stacked together to form horizontally aligned and multi-ply MWCNT sheets. Figure 2 describes the processing of a horizontally aligned MWCNT sheet by drawing and winding the MWCNT webs on a rotating spool. In this study, aligned 100-ply MWCNT sheets were used for composite fabrication.

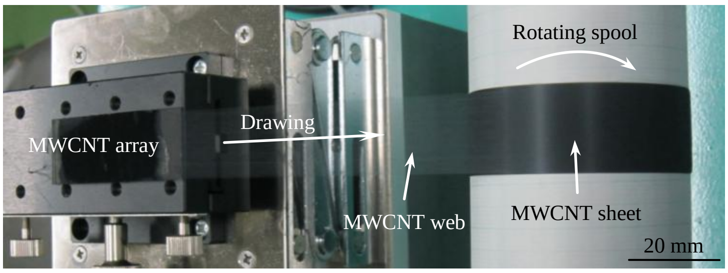

Figure 2. The processing of an aligned MWCNT sheet using drawing and winding techniques.

2.3. Fabrication of aligned MWCNT/epoxy prepreg and composite

The aligned MWCNT-reinforced epoxy composite was developed using hot-melt prepreg processing. This method can maintain the alignment of MWCNTs during epoxy resin impregnation. First, a stacked aligned 100-ply MWCNT sheet with 20 mm width and 50 mm length was covered with an epoxy resin sheet and was set in two release films (WL5200; Airtech International Inc., CA, USA) to produce an aligned MWCNT/epoxy prepreg. The prepreg was fabricated 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 prepreg was peeled off from the release paper and was placed on the VAS. Finally, the prepreg was cured at 130 °C for 2 h under 2 MPa to produce the aligned MWCNT/epoxy composite. A schematic showing the processing of the aligned MWCNT/epoxy prepreg and composite was presented in Figure 3.

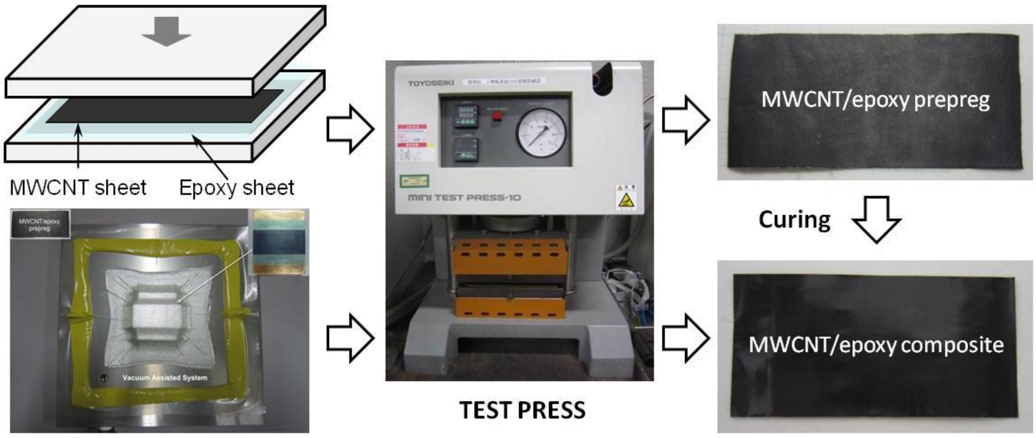

Figure 3. Schematic showing the processing of aligned MWCNT/epoxy prepreg and composite.

2.4. Thermogravimetric analysis

The thermal degradation processes of epoxy resin, the MWCNTs, and the MWCNT/epoxy composite were 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.

2.5. Characterizations and tensile testing

The properties of the aligned 100-ply MWCNT sheet, its prepreg and composite were measured using conventional methods for macroscopic samples. Tensile tests were conducted for the aligned MWCNT sheet, the prepreg and composite in a laboratory environment at room temperature (RT). Tensile specimens with 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. Specimen widths were measured using an optical microscope (SZX12; Olympus Corp., Tokyo, Japan), whereas their thickness was measured using a micrometer with 0.001 mm accuracy (102-119; Mitutoyo Corp., Kanagawa, Japan). The thickness measurements using this micrometer were conducted carefully to minimize the measurement error. The strain of tensile specimens was measured using a non-contacting video extensometer (TRIViewX; Shimadzu Corp., Tokyo, Japan) with two targets. Mean tensile properties were obtained from at least five specimens for the aligned MWCNT sheet, the prepreg and composite. The microstructure morphologies of MWCNTs in the sheet and fracture surfaces of the composite were observed using a field emission scanning electron microscope (FE-SEM, SU8030; Hitachi Ltd., Tokyo, Japan).

3. Results and discussion

3.1. Surface morphologies of aligned MWCNT sheets

Aligned MWCNT sheets were created from spinnable aligned MWCNT arrays using the drawing and winding processes. The widths of aligned MWCNT sheets can be controlled by changing the widths of the spinnable MWCNT arrays. The thickness of MWCNT sheets is controlled by stacking MWCNT plies along the same direction. FE-SEM micrographs showing the surface morphologies of MWCNTs in the sheet are depicted in Figure 4. Figure 4(b) portrays the high magnification FE-SEM image of the MWCNTs. The MWCNTs in the sheet had been highly aligned along the drawing direction. However, wavy MWCNTs were visible in the MWCNT sheet. The wavy MWCNTs can reduce their load transfer efficiency in the composites. The sizes of voids among MWCNTs were mainly varied from several nanometers to hundreds of nanometers. In general, the MWCNT sheets have a high volume fraction without a great amount of entanglement, which are ideal properties for use in reinforcement of the composites.

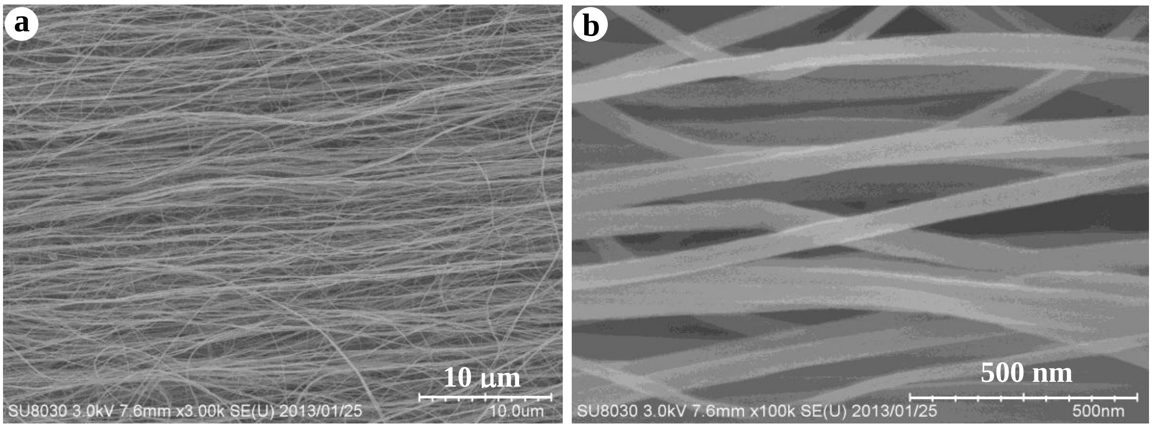

Figure 4. FE-SEM micrographs showing the surface morphologies of MWCNTs in the sheet.

3.2. Estimation of MWCNT volume fraction

The MWCNT volume fraction in the composite was estimated using TGA data as follows: To begin with the respective mass losses of the MWCNTs, epoxy resin, and the composite were measured at 150–750 °C. Subsequently, the MWCNT mass fraction (m_f) in the composite was calculated from the mass loss of the MWCNTs (Δm_f), epoxy resin (Δm_m), and the composite (Δm_c) as follows:

$$m_f = \frac{(\Delta m_m - \Delta m_c)}{(\Delta m_m - \Delta m_f)} \quad (1)$$

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

$$V_f = 1 - \frac{(1 - m_f)\rho_c}{\rho_m} \quad (2)$$

The mass losses, MWCNT mass fraction, and volume fraction in the composite are presented in Table 1. Results show that the MWCNT volume fraction in the composite reinforced by 100-ply MWCNT sheet is rather high. Therefore, the composites with ultrahigh volume fraction of MWCNTs can be fabricated based on the aligned MWCNT sheets using hot-melt prepreg processing method.

Table 1. Mass losses and MWCNT fractions in the composite estimated from TGA results

Materials	Mass loss (%)	Mass fraction (%)	Volume fraction (vol. %)
Epoxy resin	87.9	–	–
MWCNTs	2.59	–	–
Composite	45.2	50.1	37.5

3.3. Properties of aligned MWCNT sheet, its prepreg and composite

The thickness, areal weight and density of aligned MWCNT sheet, aligned MWCNT/epoxy prepreg and composite are presented in Table 2. As Table 2 shows, the thickness of the aligned MWCNT/epoxy composite is lower than that of the prepreg. The thickness reduction is attributed to the hot pressing under 2 MPa pressure during the cured process.

Table 2. Properties of the MWCNT sheet, MWCNT/epoxy prepreg and composite.

Properties	Epoxy resin	MWCNT sheet	MWCNT/epoxy prepreg	MWCNT/epoxy composite
Thickness (μm)	~10	7–9	17–19	9–11
Areal weight (g/m^2)	12.0	7.48	25.7	15.2
Density (g/cm^3)	1.20	0.98	1.41	1.50
Tensile strength (MPa)	64.4 ± 0.83	79.0 ± 3.1	60.2 ± 4.0	217.5 ± 17.2
Elastic modulus (GPa)	2.55 ± 0.09	3.50 ± 0.2	6.56 ± 0.4	56.4 ± 5.17
Strain at max stress (%)	4.84 ± 0.24	3.14 ± 0.2	1.12 ± 0.1	0.39 ± 0.02

Typical stress–strain curves of epoxy resin, the MWCNT sheet, the MWCNT/epoxy prepreg and composite are depicted in Figure 5.

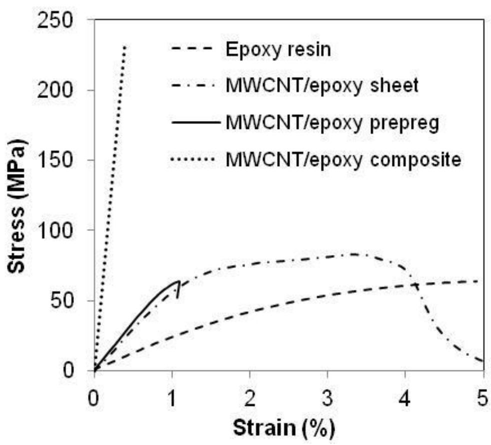

Figure 5. Typical stress–strain curves of epoxy resin, the MWCNT sheet, the prepreg and composite.

As observed in Figure 5, the stress and strain relation of the aligned MWCNT sheet is divided into three main stages. In the first stage, from 0% to about 1.5% strain, the stress of the MWCNT sheet is enhanced gradually with increasing strain. In this stage, the wavy MWCNTs (see Figure 4) are straightened. Subsequently, the stress varies slightly up to maximum with increasing strain to less than 4% in the second stage. In this stage, sliding of several MWCNTs in the sheet occurs along with non-elastic behavior, as presented by Inoue et al. (2011). After achieving maximal peak, the stress in the third stage decreases concomitantly with increasing strain up to the specimen fractures. The stress–strain curve of the aligned MWCNT/epoxy prepreg indicated that sample fracture occurred suddenly at the maximal load. In addition, the aligned MWCNT/epoxy composite showed a linear stress-strain relation until the specimen fractures with no bending of the curves at high loads (see Figure 5).

Tensile properties of the aligned MWCNT sheet and its prepreg presented in Table 2 showed that the prepreg exhibited a higher elastic modulus, and lower tensile strength and the strain at maximal stress in comparison with the aligned MWCNT sheet. In addition, the composite showed higher tensile strength and elastic modulus, and much lower fracture strain compared with the prepreg and the MWCNT sheet (see Table 2). The enhancement in tensile strength and elastic modulus is attributed to the reinforcement of aligned MWCNTs along the tensile direction. When MWCNTs are aligned in the loading direction, excellent mechanical properties of MWCNTs, having a cylindrical structure, might be used effectively (Wang et al., 2013). The aligned MWCNTs carry the load along the length of MWCNTs and provide strength and stiffness in the loading direction. The decrease in fracture strain is attributable mainly to the addition of high MWCNT content, leading to reduction in the amount of epoxy matrix available for the elongation.

Moreover, the composite exhibited much higher elastic modulus and tensile strength than those of dispersed CNT/epoxy composites reported in several papers (Thostenson et al., 2001; Coleman et al., 2006 and Guo et al., 2007). The maximum elastic modulus and tensile strength were respectively achieved as 61 GPa and 235 MPa. Although ultimate strength of the MWCNT/epoxy composite in this study is similarly to that presented in previous reports (Ogasawara et al., 2011; Cheng et al., 2008 and Cheng et al., 2010), maximal elastic modulus of the composite is markedly higher than that reported in those. The high elastic modulus may be due to the high aspect ratio of MWCNTs.

An FE–SEM image taken from polished surface of the composite sample is presented in Figure 6. FE-SEM micrographs showing fracture surfaces of the aligned MWCNT/epoxy composite are presented in Figure 7. The orientation and distribution of MWCNTs in Figure 6 showed that the hot-melt prepreg processing maintained the alignment of MWCNTs during the resin impregnation.

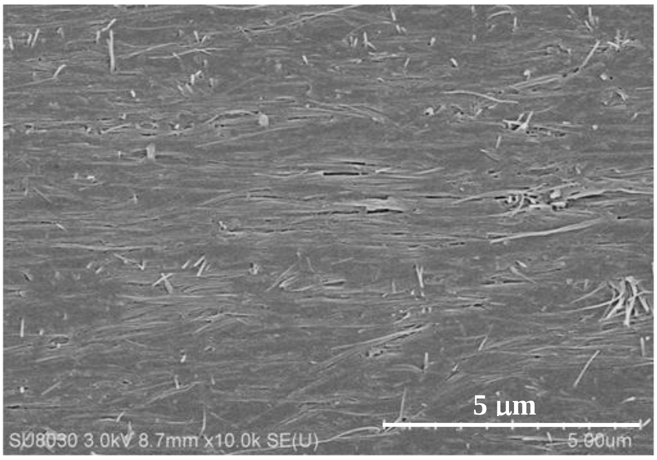

Figure 6. FE–SEM image showing in-plane MWCNT distribution in the composite.

High-resolution micrographs in Figure 7 show that epoxy resin was infiltrated well between the MWCNTs. However, many pulled-out MWCNTs with length varying from several nanometers to a few micrometers are exposed on the fracture surfaces of the MWCNT/epoxy specimens. In addition, several MWCNTs were found to fracture by a sword-in-sheath mechanism. Sword-in-sheath fracturing tends to occur in larger diameter MWCNTs because of higher shear stress at the interfaces between outer walls (Ogasawara et al., 2011). Therefore, the decrease in MWCNT diameter can be effective to improve the strength of the aligned MWCNT/epoxy composites.

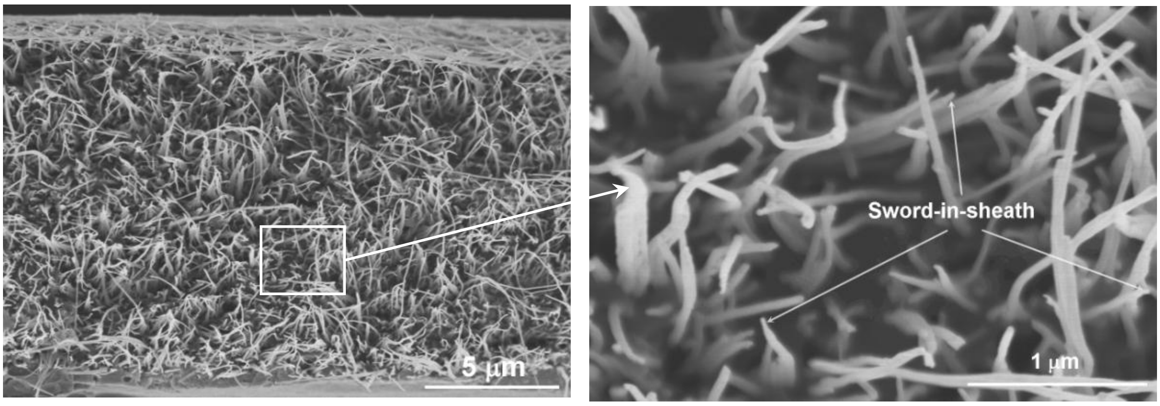

Figure 7. FE-SEM micrographs showing fracture surface of aligned MWCNT/epoxy composite.

Tensile strength and elastic modulus of the aligned MWCNT/epoxy composite can be studied as a function of the MWCNT volume fraction. The length of the MWCNTs used for this study is about 0.8 mm. The aspect ratio (length to diameter ratio) of the MWCNTs is extremely high. Therefore, the elastic modulus of the aligned MWCNT/epoxy composites can be estimated using the rule of mixtures (Ogasawara et al., 2011). The best fit effective elastic modulus of a MWCNT in the composite was found to be approximately 150 GPa. This value is much smaller than either the theoretical or experimental values of CNTs (Ruoff and Lorents, 1995; Dresselhaus et al., 2002). The low elastic modulus is attributable to the imperfect penetration of epoxy resulting in nanoscopic voids. Consequently, further investigation such as TEM and FE-SEM observations is required. In addition, another possibility can be due to sword-in-sheath fracture of MWCNTs (Qian et al., 2001). Moreover, the low effective elastic modulus of a MWCNT in the composite can be attributed to the waviness and entanglement of MWCNTs in the composite. Therefore, the reduction of the MWCNT waviness and entanglement may improve the mechanical properties of the composite.

4. Conclusions

The drawing and winding techniques have produced aligned and multi-ply MWCNT sheets with high alignment from spinnable aligned MWCNT arrays. The aligned MWCNTs reinforced epoxy composite with MWCNT volume fraction of 37.5% was developed using hot-melt prepreg processing with the VAS. The epoxy resin was infiltrated well between the MWCNTs in the composite. The hot-melt prepreg processing maintained the MWCNT alignment during epoxy resin penetration. The prepreg showed higher elastic modulus, and lower tensile strength and fracture strain in comparison with the MWCNT sheet. The composite indicated higher tensile strength and elastic modulus, and lower fracture strain compared with the prepreg and the MWCNT sheet. The resultant composite exhibited higher elastic modulus and tensile strength than those of composites produced using conventional mixing methods. The mean elastic modulus and tensile strength of the aligned MWCNT/epoxy composite achieved as 56.4 GPa and 217.5 MPa, respectively. These values are, respectively, 21 and 2.4 times higher than those of the epoxy resin.

Acknowledgements

This research was supported by Petrovietnam University. The author thanks Dr. K. Goto, Dr. Y. Inoue, Dr. Y. Shimamura for supplying materials and for helpful discussions.

References

Cheng, Q. F., J. P. Wang, K. L. Jiang, Q. Q. Li, and S. S. Fan (2008). Fabrication and properties of aligned multiwalled carbon nanotube-reinforced epoxy composites. *Journal of Materials Research*, 23(11), pp. 2975–2983.

Cheng, Q. F., J. Bao, J. Park, Z. Liang, C. Zhang, and B. Wang (2009). High mechanical performance composite conductor: multi-walled carbon nanotube sheet/bismaleimide nanocomposites. *Advanced Functional Materials*, 19(20), pp. 3219–3225.

Cheng, Q. F., J. P. Wang, J. J. Wen, C. H. Liu, K. L. Jiang, Q. Q. Li, and S. S. Fan (2010). Carbon nanotube/epoxy composites fabricated by resin transfer molding. *Carbon*, 48, pp. 260–266.

Coleman, J. N., U. Khan, W. J. Blau, and Y. K. Gun'ko (2006). Small but strong: a review of the mechanical properties of carbon nanotube-polymer composites. *Carbon*, 44(9), pp. 1624–1652.

Dresselhaus, M., G. Dresselhaus, and P. Avouris (2002). *Carbon Nanotubes: Synthesis, Structure, Properties and Applications*. New York: Springer.

Ebbesen, T. W., H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi and T. Thio (1996). Electrical conductivity of individual carbon nanotubes. *Nature*, 382, pp. 54-56.

Ghemes, A., Y. Minami, J. Muramatsu, M. Okada, H. Mimura, and Y. Inoue (2012). Fabrication and mechanical properties of carbon nanotube yarns spun from ultra-long multi-walled carbon nanotube arrays. *Carbon*, 50(12), pp. 4579–4587.

Guo, P., X. Chen, X. Gao, H. Song, and H. Shen (2007). Fabrication and mechanical properties of well-dispersed multiwalled carbon nanotubes/epoxy composites. *Composites Science and Technology*, 67(15-16), pp. 3331–3337.

Inoue, Y., K. Kakihata, Y. Hirono, T. Horie, A. Ishida, and H. Mimura (2008). One-step grown aligned bulk carbon nanotubes by chloride mediated chemical vapor deposition. *Applied Physics Letters*, 92(21), pp. 213113.

Inoue, Y., Y. Suzuki, Y. Minami, J. Muramatsu, Y. Shimamura, K. Suzuki, A. Ghemes, M. Okada, S. Sakakibara, H. Mimura, and K. Naito (2011). Anisotropic carbon nanotube papers fabricated from multiwalled carbon nanotube webs. *Carbon*, 49(7), pp. 2437–2443.

Lopes, P. E., F. V. Hattum, C. M. C. Pereira, P. J. R. O. Nóvoa, S. Forero, F. Hepp F, and L. Pambaguian (2010). High CNT content composites with CNT buckypaper and epoxy resin matrix: impregnation behavior composite production and characterization. *Composite Structures*, 92(6):1291–1298.

Ogasawara, T., S. Y. Moon, Y. Inoue, and Y. Shimamura (2011). Mechanical properties of aligned multi-walled carbon nanotube/epoxy composites processed using a hot-melt prepreg method. *Composites Science and Technology*, 71(16), pp. 1826–1833.

Qian, D., and E. C. Eickey (2001). In-situ transmission electron microscopy studies of polymer-carbon nanotube composite deformation. *Journal of Microscopy*, 204, pp. 39–45.

Ruoff, R.S. and D.C. Lorents (1995). Mechanical and thermal properties of carbon nanotubes. *Carbon*, 33(7), pp. 925-930.

Thostenson, E. T., Z. Ren, and T. W. Chou (2001). Advances in the science and technology of carbon nanotubes and their composites: a review. *Composites Science and Technology*, 61(13), pp. 1899–1912.

Tibbetts, G. G., M. L. Lake, K. L. Strong, and B. P. Rice (2007). A review of the fabrication and properties of vapor-grown carbon nanofiber/polymer composites. *Composites Science and Technology*, 67, pp. 1709–1718.

Wang, Z., Z. Z. Yong, Q. W. Li, P. D. Bradford, W. Liu, D. S. Tucker, and et al. (2013). Ultrastrong, stiff and multifunctional carbon nanotube composites. *Materials Research Letters*, 1, pp. 19–25.

Wardle, B. L., D. S. Saito, E. J. Garcia, A. J. Hart, R. G. D. Villoria, and E. A. Verploegen (2008). Fabrication and characterization of ultrahigh-volume-fraction aligned carbon nanotube–polymer composites. *Advanced Materials*, 20(14), pp. 2707–2714.