Tensile Mechanical Properties of Carbon Nanotube/Epoxy Composite Fabricated by Pultrusion of Carbon Nanotube Spun Yarn Preform

Yoshinobu Shimamura^{1,*}, Kahori Oshima², Keiichiro Tohgo¹, Tomoyuki Fujii¹, Keiichi Shirasu³, Go Yamamoto³, Toshiyuki Hashida³, Ken Goto⁴, Toshio Ogasawara⁵, Kimiyoshi Naito⁶, Takayuki Nakano⁷ and Yoku Inoue⁷

1 Department of Mechanical Engineering, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8561, Japan

2 Graduate Student, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8561, Japan

3 Fracture and Reliability Research Institute, Tohoku University, 6-6-11-707 Aza-Aoba, Aramaki, Aobaku, Sendai 980-8579, Japan

4 Department of Space Flight System, Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, 3-1-1 Yoshinodai, Chuo, Sagamihara, Kanagawa 252-5210, Japan.

5 Advanced Composites Technology Center, Japan Aerospace Exploration Agency, 6-13-1 Osawa, Mitaka-shi, Tokyo 181-0015, Japan

6 National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

7 Department of Electronics and Materials Science, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8561, Japan

* Corresponding author: 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8561, Japan, Tel/Fax +81-53-478-1045, E-mail tysimam@ipc.shizuoka.ac.jp

ABSTRACT

In order to achieve a sufficiently high volume fraction and the preferred alignment of long carbon nanotubes (CNTs), CNT spun yarns were used as preforms for fabricating epoxy-based composite materials with excellent mechanical properties using the pultrusion technique. Epoxy resin was well impregnated into the preforms, resulting in better load transfer from the resin to the CNTs. By using CNT spun yarn as the preform, the Young's modulus and tensile strength were improved by up to 15 times and 7 times over those of the epoxy resin, respectively. SEM observation suggested that the dominant fracture mode of the composite was fiber breakage of the CNTs.

KEYWORDS: A. Polymer-matrix composites (PMCs); A. Yarn; B. Mechanical properties; Carbon nanotube

1. Introduction

Carbon nanotubes (CNTs) possess excellent mechanical properties, including a high modulus of about 1 TPa, a high tensile strength of more than 10 GPa, and a low density of 2.1 g/cm³. Thus, CNTs may have great potential for use with reinforcing polymer resin. A large amount of research has been performed on CNT-reinforced polymers [1-4]. However, the challenge lies in simultaneously achieving a sufficiently high volume fraction and the preferred alignment of long carbon nanotubes in order to take advantage of the excellent mechanical properties of each CNT [3]. Recently, CNT spinning techniques using long CNTs for producing CNT spun yarns have been developed [5-11]. CNT spun yarns have higher nanotube packing fractions and better fiber alignment in spite of using long CNTs. These characteristics are ideal for the preform when fabricating high-performance composite materials. Zhang et al [12] demonstrated that impregnating polyvinyl alcohol (PVA) into a single-ply spun yarn of multi-walled carbon nanotubes (MWNTs) enhances the Young's modulus and tensile strength. Several papers have also been published on polymer-impregnated spun yarns using PVA [13, 14], polyurethane elastomer [15], polymerized acrylic acid [16], cross-linked polymers, polyimide, and bismaleimide [17]. These reports indicated that spun yarns were prospective candidates for preforms of composite materials.

To date, few studies have been published on epoxy-based composites using spun yarns, even though epoxy is widely used for the matrix of advance composite materials. Mora et al [18] used

single-ply spun yarns of double-walled carbon nanotubes to reinforce the epoxy resin. The Young's modulus and tensile strength of the composites were lower than those of the as-spun yarns, and the mechanical properties of the composites were estimated by the rule of mixtures using those of the epoxy resin and the spun yarn, not the CNT. The results raised the question of whether the excellent mechanical properties of each CNT would fully contribute to reinforcing the epoxy matrix. Ma et al [14] used single-walled carbon nanotube (SWNT) fibers for reinforcing epoxy resin, and Bogdanovich and Bradford [19] used plied and braided spun yarns of MWNTs for reinforcing epoxy resin. In contrast to Mora's findings, the Young's modulus and tensile strength of the composite were higher than those of neat yarns. The maximum Young's modulus and tensile strength among the composite systems were 50 GPa and 1.6 GPa for SWNT/epoxy[14] and 23.9 GPa and 319.8 MPa for MWNT/epoxy[19], respectively.

Unfortunately, previous studies have not completely demonstrated the potential of CNT spun yarns as preforms for epoxy-based composites. In this study, epoxy-based composites were fabricated with a bundle of single-ply spun yarns as a preform using the pultrusion technique. Pultrusion is a continuous process for manufacturing composite columns and strips with longitudinal reinforcement. This paper demonstrates that pultrusion using CNT yarns enables us to fabricate quasi-unidirectionally reinforced CNT/epoxy composites with long CNT length and high volume fraction. In the curing period of the epoxy resin, a tensile force was applied in order to investigate its

effect because the spun yarn contracts in the radial direction and stretches in the axial direction due to its twisted geometry [20], which may increase the volume fraction and improve fiber alignment. The tensile properties of the composites were explored by using quasi-static tensile tests, and SEM observation of the fracture surface was conducted. In order to discuss the role of CNTs in reinforcement, a simple mechanical analysis was conducted using the rule of mixtures.

2. Materials

MWNTs were vertically grown on a quartz glass plate with chemical vapor deposition using C_2H_2 and $FeCl_2$ as the base material and the catalyst, respectively [21]. Vertically aligned MWNTs on a substrate are called an MWNT array. Figure 1 shows an MWNT array. The length and diameter of each carbon nanotube was about 1 mm and 50 nm, respectively. Spun yarns of MWNTs can be directly drawn from an MWNT array by using the dry-spinning technique. Figure 2 shows a schematic of the dry-spinning process of an MWNT spun yarn. Note that neither a chemical binder nor a surface treatment for the carbon nanotubes is required for dry spinning. More detail on the dry-spinning technique can be found in Ref. [10]. Figure 3 shows an SEM image of an MWNT spun yarn. Spun yarns were drawn at a rate of 100 mm/s with 30,000 rpm of spindle speed. The yarn diameter was about 45 μm . The twist angle, which was defined as the angle between the yarn axis and the outermost fiber direction, was 27–35°. The density was 0.55g/cm³, and the porosity of the

spun yarn was about 70%. No surface treatments were performed on the spun yarns.

Bisphenol-A type epoxy (Z2/H07, Nisshin Resin) was used in this study. The viscosity of the epoxy resin/hardener mixture was 300–500 mPa·s. The curing time of the epoxy was 72 h at room temperature.

3. Specimen

Tensile test specimens were prepared by using the pultrusion technique. A bundle of seven as-spun single-ply yarns was soaked in epoxy resin, and then the bundle was pultruded through a circular die with a diameter of about 120 μm . Finally, the pultruded bundle was cured under a constant tensile force at room temperature in air. In order to investigate the effect of the tensile force on the mechanical properties, the tensile force was changed from 0.1–0.3 N. A typical cross section and a magnified view of the cross section of a composite specimen are shown in Figure 4. The cross section was polished by using an argon ion beam polisher (IB-09010CP, JEOL). Note that gaps between yarns as well as a splitting of one yarn in Figure 4(a) were cracks caused by preliminary polishing for sample preparation. Though small voids in the order of a few μm were observed between and inside yarns, almost full impregnation of epoxy resin into yarns were achieved. Most specimens had resin rich region around the bundle of yarns. In this study, the cross-sectional area was defined as the area including the resin rich region. The densities of the cured specimens were

1.30–1.35 g/cm³.

The fiber volume fractions of composite specimens can be estimated using the density of MWNT ρ_{cnt} , the cross-sectional area of the as-spun yarn A_{yarn} , the density of the as-spun yarn ρ_{yarn} , and the cross-sectional area of the composite A_{compo} with the following equation.

$$V_f = \frac{V_{\text{cnt}}}{V_{\text{compo}}} = \frac{A_{\text{cnt}}}{A_{\text{compo}}} = \frac{\left(\frac{\rho_{\text{yarn}}}{\rho_{\text{cnt}}}\right) A_{\text{yarn}}}{A_{\text{compo}}} \quad (1)$$

where V_{cnt} is the volume of the MWNT, V_{compo} is the volume of the composite, and A_{cnt} is the cross-sectional area of the MWNT. In this study, the density of the MWNT ρ_{cnt} was assumed to be 2.1 g/cm³.

Figure 5 shows the relationship between the fiber volume fraction and the tensile force. Increasing the tensile force in the curing period resulted in an increase in the fiber volume fraction. The highest volume fraction was 25.5%. As mentioned before, applying tensile force to the spun yarn produces radial contraction, which squeezes resin out of the yarns, resulting in higher volume fractions.

4. Results and discussion

4.1 Tensile test

Tensile tests of as-spun yarns and composite specimens were conducted in order to measure their tensile properties. The gauge length was 15 mm. The tensile tests were conducted at 1 mm/min

of cross head speed, and the elongation of the gauge length was measured by a non-contact extensometer. There were a total of 25 as-spun yarn specimens, and there were four or five composite specimens for each volume fraction.

Typical stress-strain curves are shown in Figure 6. The stress-strain behavior of the as-spun yarn was nonlinear, and the average tensile strength was 175 MPa. On the other hand, the stress-strain behavior of composite specimens was almost linear, and the average tensile strength was higher than 200 MPa. In contrast to the earlier findings using single-ply yarns [18], the rule of mixtures using the mechanical properties of the as-spun yarn and epoxy resin does not hold; our experimental results strongly imply that the composite specimens were reinforced by each of the carbon nanotubes, not the spun yarns. The results of the tensile tests are summarized in Table 1, where the Young's modulus of the as-spun yarns and the composite specimens was defined as the slope between $\varepsilon = 0.25\%$ and 0.5% , and that of the epoxy resin was defined as the slope between $\varepsilon = 0.05\%$ and 0.25% .

The Young's modulus, tensile strength, and failure strain are plotted as a function of the fiber volume fraction in Figure 7. Both the Young's modulus and tensile strength significantly increased with increasing volume fraction. The Young's modulus and tensile strength at $V_f = 25.5\%$ were 15 times and 7 times as high as those of the epoxy resin, respectively. The failure strain ranged from 0.52% to 1.04% , which are almost the same as the failure strains in Ref. [18, 19]. The failure strain

was supposedly determined by the failure strain of the carbon nanotubes because SEM observation suggested that the dominant fracture mechanism was fiber breakage. The fracture mechanism will be discussed in Sec. 4.2.

Figure 7 has a large degree of scatter, and to determine the reason for this, the tensile strength is plotted as a function of the Young's modulus in Figure 8. A linear relationship with a smaller scatter band was obtained between the tensile strength and the Young's modulus. Figure 8 shows that the scatter of the mechanical properties for each volume fraction is partly caused by the variation of the volume fraction in each lot.

As mentioned before, Young's modulus and tensile strength increased with increasing volume fraction, but they were not linear relationships. The upper deviation in the highest volume fraction was probably due to the change in twist angle caused by the tensile force during the cure period. In order to verify the change in twist angle, the stiffness is plotted as a function of the tensile force in Figure 9, where the stiffness is defined as the spring constant of the specimen. The increase in the tensile force obviously resulted in an increase in stiffness. Keep in mind that the number of as-spun yarns in each specimen was constant. The results indicated that the twist angle was reduced because of the tensile force during the cure process.

4.2 Fracture surface

Entire fracture surfaces for a lower volume fraction (19.7%) and a higher volume fraction

(25.5%) are shown in Figure 10. The individual spun yarns are clearly recognized in each fracture surface. Figure 11 shows details of the fracture surfaces shown in Figure 10. Figure 12 shows detailed side views of the fracture surfaces. The sliding lengths of carbon nanotubes for both fracture surfaces were about 10 μm . Keep in mind that the length of the carbon nanotube was about 1 mm, so the sliding length was considerably smaller than the length of the carbon nanotubes. Figure 13 shows close-up views of the carbon nanotubes at the fracture surface. Sword-in-sheath fractures of carbon nanotubes were observed. This is a typical fracture mode of MWNT when subjected to tensile loading [22, 23]. These observations strongly suggest that the fracture mode of the composites was fiber breakage.

4.3 Discussion

The findings of this study indicate that the spun yarns worked well as preforms. This implies that sufficient load transfer from the surrounding matrix to each carbon nanotube should be achieved.

The apparent longitudinal modulus and strength of the MWNTs used in this study are roughly estimated based on the rule of mixtures from the bulk properties of the composite specimens, assuming that the carbon nanotubes are unidirectionally aligned along the specimen axis as a first-order approximation.

The elastic modulus of a unidirectional discontinuous fiber-reinforced composite can be

estimated as [24]

$$E_{\text{compo}} = \eta V_f E_f + (1 - V_f) E_m \quad (2)$$

$$\eta = \left(1 - \frac{\tanh(ns)}{ns} \right) \quad (3)$$

$$n = \sqrt{\frac{2E_m}{E_f(1 + \nu_m) \ln\left(\frac{1}{V_f}\right)}} \quad (4)$$

where E_f is the apparent longitudinal Young's modulus of the MWNT, E_m is the Young's modulus of the matrix, ν_m is the Poisson's ratio of the matrix, and s is the fiber aspect ratio $l_f/d_f = 20000$. Elastic behavior of the matrix and perfect bonding between the fiber and matrix are assumed in Equation (3)

Curve fitting of the experimental results in Figure 7(a) gives $E_{\text{cnt}} = 150$ GPa. The tensile strength σ_B of an MWNT can be roughly estimated using Equation (5), which is the rule of mixtures for unidirectional, continuous-fiber-reinforced composites.

$$\sigma_B^{\text{compo}} = V_f \sigma_B + (1 - V_f) \frac{E_m}{E_f} \sigma_B \cong V_f \sigma_B \quad (5)$$

Curve fitting of the experimental results in Figure 7(b) gives $\sigma_B = 1.4$ GPa. For reference, tensile loading tests of MWNTs were performed using a manipulator inside the vacuum chamber of an SEM. There were five specimens. More details about the experimental technique can be found in Ref. [23].

The measured tensile strength was $5.8 \text{ GPa} \pm 1.8 \text{ GPa}$, which is of the same order of magnitude as the estimated strength. The inconsistency between the measured and estimated values seemed to be a result of the misalignment of the MWNTs due to the twisting geometry of the spun yarns as well as

the uncertainty in the direct measurement experiments.

5. Conclusions

In this study, MWNT-reinforced epoxy with a higher volume fraction and better alignment was pultruded by using as-spun single-ply yarn preforms whose MWNT length was 1 mm long. Epoxy resin was well impregnated into the preforms, resulting in sufficient load transfer from the resin to the carbon nanotubes. The composites had excellent mechanical properties, exceeding high-strength aluminum alloys in their specific modulus and specific strength. SEM observation suggested that the dominant fracture mode of the composite was fiber breakage of the CNTs.

6. Acknowledgements

This research was performed with the support of the Japan Science and Technology Agency through the Advanced Low Carbon Technology Research and Development Program (ALCA) and with the support of the ISAS steering committee for space engineering.

7. References

[1] Thostenson E, Ren Z, Chou T. Advances in the science and technology of carbon nanotubes and their composites: a review. *Composites Science and Technology*. 2001;61(13):1899-912.

- [2] Lau K, Hui D. The revolutionary creation of new advanced materials - carbon nanotube composites. *Composites Part B-Engineering*. 2002;33(4):263-77.
- [3] Xie X, Mai Y, Zhou X. Dispersion and alignment of carbon nanotubes in polymer matrix: A review. *Materials Science & Engineering R-Reports*. 2005;49(4):89-112.
- [4] Tibbetts G, Lake M, Strong K, Rice B. A review of the fabrication and properties of vapor-grown carbon nanofiber/polymer composites. *Composites Science and Technology*. 2007;67(7-8):1709-18.
- [5] Jiang K, Li Q, Fan S. Nanotechnology: Spinning continuous carbon nanotube yarns - Carbon nanotubes weave their way into a range of imaginative macroscopic applications. *Nature*. 2002;419(6909):801-.
- [6] Nakayama Y. Synthesis, Nanoprocessing, and Yarn Application of Carbon Nanotubes. *Japanese Journal of Applied Physics*. 2008;47(10):8149-56.
- [7] Behabtu N, Green M, Pasquali M. Carbon nanotube-based neat fibers. *Nano Today*. 2008;3(5-6):24-34.
- [8] Chou T, Gao L, Thostenson E, Zhang Z, Byun J. An assessment of the science and technology of carbon nanotube-based fibers and composites. *Composites Science and Technology*. 2010;70(1):1-19.
- [9] Lu W, Zu M, Byun J, Kim B, Chou T. State of the Art of Carbon Nanotube Fibers: Opportunities and Challenges. *Advanced Materials*. 2012;24(14):1805-33.

- [10] Ghemes A, Minami Y, Muramatsu J, Okada M, Mimura H, Inoue Y. Fabrication and mechanical properties of carbon nanotube yarns spun from ultra-long multi-walled carbon nanotube arrays. *Carbon*. 2012;50(12):4579-87.
- [11] Miao M. Yarn spun from carbon nanotube forests: Production, structure, properties and applications. *Particuology*. 2013;11(4):378-93.
- [12] Zhang M, Atkinson K, Baughman R. Multifunctional carbon nanotube yarns by downsizing an ancient technology. *Science*. 2004;306(5700):1358-61.
- [13] Liu K, Sun Y, Lin X, Zhou R, Wang J, Fan S, et al. Scratch-Resistant, Highly Conductive, and High-Strength Carbon Nanotube-Based Composite Yarns. *Acs Nano*. 2010;4(10):5827-34.
- [14] Ma WJ, Liu LQ, Zhang Z, Yang R, Liu G, Zhang TH, et al. High-Strength Composite Fibers: Realizing True Potential of Carbon Nanotubes in Polymer Matrix through Continuous Reticulate Architecture and Molecular Level Couplings. *Nano Lett*. 2009;9(8):2855-61.
- [15] Tran C, Lucas S, Phillips D, Randeniya L, Baughman R, Tran-Cong T. Manufacturing polymer/carbon nanotube composite using a novel direct process. *Nanotechnology*. 2011;22(14).
- [16] Guo W, Liu C, Sun X, Yang Z, Kia H, Peng H. Aligned carbon nanotube/polymer composite fibers with improved mechanical strength and electrical conductivity. *Journal of Materials Chemistry*. 2012;22(3):903-8.
- [17] Li S, Zhang X, Zhao J, Meng F, Xu G, Yong Z, et al. Enhancement of carbon nanotube fibres using

different solvents and polymers. *Composites Science and Technology*. 2012;72(12):1402-7.

[18] Mora R, Vilatela J, Windle A. Properties of composites of carbon nanotube fibres. *Composites Science and Technology*. 2009;69(10):1558-63.

[19] Bogdanovich A, Bradford P. Carbon nanotube yarn and 3-D braid composites. Part I: Tensile testing and mechanical properties analysis. *Composites Part a-Applied Science and Manufacturing*. 2010;41(2):230-7.

[20] Hearle J. One-Dimensional Structures: Yarn Geometry. In: Hearle J, Grosberg P, Backer S, editors. *Structural Mechanics of Fibers, Yarns, and Fabrics*. New York: Wiley-Interscience; 1969. p. 61-100.

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

[22] Qian D, Dickey E. In-situ transmission electron microscopy studies of polymer-carbon nanotube composite deformation. *Journal of Microscopy-Oxford*. 2001;204:39-45.

[23] Yamamoto G, Shirasu K, Nozaka U, Sato Y, Takagi T, Hashida T. Structure-Property Relationship in Thermally-Annealed Multi-Walled Carbon Nanotubes. 2013:(in press).

[24] Hull D, Clyne T. *An Introduction of Composite Materials*. 2nd ed. England: Cambridge University Press; 1996.

[25] Curtin W. Theory of mechanical-properties of ceramic-matrix composites. *Journal of the American Ceramic Society*. 1991;74(11):2837-45.

Figure(s)

Figure 1

Figure 2

Figure 3

Figure 4

(a)

(b)

Figure 4

Figure 5

Figure 6

(a) Young's modulus

Figure 7

(b) Tensile strength

(c) Failure strain

Figure 7

Figure 8

Figure 9

(a) $V_f=19.7\%$

(b) $V_f=25.5\%$

Figure 10

(a) $V_f = 19.7\%$

(b) $V_f = 25.5\%$

Figure 11

(a) $V_f=19.7\%$

(b) $V_f=25.5\%$

Figure 12

Figure 13

Table 1

	Young's modulus	Tensile strength	Failure strain	Density
	[GPa]	[MPa]	[%]	[g/cm ³]
Epoxy	3.3	69	2.75	1.10
As-spun yarn	9.4	175	2.69	0.55
Composite (V _f =19.7%)	31	212	0.71	1.30
Composite (V _f =20.0%)	28	262	0.95	1.30
Composite (V _f =23.9%)	33	284	0.85	1.34
Composite (V _f =25.5%)	49	467	0.97	1.35

Figure 1 SEM image of MWNT array

Figure 2 Schematic of CNT dry spinning

Figure 3 SEM image of MWNT spun yarn

Figure 4 Cross section of a composite specimen (a) whole section, and (b) magnified view

Figure 5 Influence of tensile force on fiber volume fraction

Figure 6 Stress-strain curves

Figure 7 Influence of fiber volume fraction on (a) Young's modulus, (b) tensile strength, and (c) failure strain

Figure 8 Relationship between tensile strength and Young's modulus

Figure 9 Influence of tensile force on stiffness

Figure 10 Entire fracture surface of composite at (a) $V_f=19.7\%$ and (b) $V_f=25.5\%$

Figure 11 Magnified view of fracture surface at (a) $V_f=19.7\%$ and (b) $V_f=25.5\%$

Figure 12 Side views of fracture portions at (a) $V_f=19.7\%$ and (b) $V_f=25.5\%$

Figure 13 Sword-in-sheath fracture of MWNT at fracture surface

Table 1 Summary of characteristics and tensile properties of as-spun yarn and composites