JOURNAL OF MATERIALS SCIENCE **34** (1999) 229–233

Tensile properties of VGCF reinforced carbon composites

JYH-MING TING
Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan

Carbon composites based on vapor grown carbon fibers prepared by a fixed catalyst method were fabricated using a pitch infiltration technique. The composites have both unidirectional and bi-directional fiber reinforcement, and different fiber volume fractions ranging from 25% to 56%. Specimens were prepared from these composites for tensile testing at room temperature, and tensile modulus and strength were determined. The composite modulus was then used to estimate the fiber modulus.

1. Introduction

Growth of carbon fibers from vapor phase hydrocarbons was observed more than 100 years ago [1]; however, methods for producing research quantities were not developed until the early 1970's [2–4]. More recent work has been directed to methods of producing this type of fibers or vapor grown carbon fiber (VGCF) with different morphologies and in larger quantities [5–7]. For example, discontinuous VGCF can be produced on a floating, gas-phase catalyst [8], while continuous VGCF can be produced on a catalyst-seeded substrate [9]. Unlike other carbon fibers, VGCF produced by the latter technique is in a form of mat. A VGCF mat consists of interwoven, semi-aligned, fibers. Due to the restricted availability of VGCF mats, composites based on this type of fiber have been limited. Recent efforts have been made to investigate the thermal properties of VGCF mat reinforced composites [10, 11]. In this paper, we further describe the tensile properties of VGCF mat reinforced carbon composites.

2. Experimental

VGCF mats were grown on substrates which were previously seeded with iron particles, in a flowing gas mixture of CH_4 and H_2 at a temperature near 1000 °C. The fibers grew in a unidirectional orientation in the direction of gas flow. After removal from the reactor, VGCF were shaved from the substrate, and cut to the dimensions for preform fabrication. Preforms with both unidirectional (1D) and in-plane orthogonal (0/90, 1:1 ratio) fiber orientation (2D) were made using furfuryl alcohol as the binder. The as-made preforms were carbonized at 950 °C for 2 hours. These preforms were then densified by two cycles of pitch (Ashland A240) infiltration. After densification, the composites were heat treated at 2800 °C for 15 min. Specimens were prepared for microstructural analysis using an optical microscope (OM) under polarized light and scanning electron microscope (SEM).

Tensile tests were carried out using an Instron TTC Universal Testing Machine. Straight-side tensile bars with dimensions of 25.4 mm × 25.4 mm × 1 mm were machined from the VGCF/C composites. Tabs for the Instron grips were applied with epoxy; a biaxial strain gage was applied to the center of the sample to record both longitudinal and transverse strain. The load and strain signals were monitored with a Keithley System 570 Data Acquisition System. The signals were analyzed and stored using a personal computer to calculate the ultimate stress, ultimate strain, and elastic modulus. The cross-head speed was 0.127 mm/min. The tangent modulus was calculated using a linear curve fit between strain values of 0.0025% and 0.02%. For unidirectional fiber reinforced composites, the load was parallel to the fiber axis. For the 0/90 composite, the load was parallel to one of the fiber orientations.

3. Results and discussion

A total of 8 different composites were obtained. The densities, fiber volume fractions, mechanical properties, and fiber architectures of these composites are given in Table I. Depending on the fiber volume fraction and architecture, different composite densities were obtained after two cycles of pitch infiltration. It appears that the composite density increases as the fiber volume fraction increases. It is thought that such an increase mainly came from the increasing fiber volume fraction as the highly graphitic fiber has a higher density than the pitch-derived matrix. It was found from OM microstructural analysis that composite densification was homogeneous, the matrix carbon remains in contact with the fiber.

Tensile testing was performed on various composite specimens with different fiber volume fractions, fiber architecture, and densities as shown in Table I. Representative stress-strain curves for unidirectional and 0/90 composite specimens are given in Fig. 1. They both resemble a typical stress-strain curve of brittle

TABLE I Characteristics of VGCF/C composites. V_f = fiber volume fractions, F_a = fiber architecture

ID	Density kg/m^3	V_f (%)	Modulus (GPa) Longitudinal	Strength (MPa)	Strain (%)	F_a
A	1650	25	43.0	76.6	0.19	1D
B	1720	37	51.0	69.6	0.16	1D
C	1790	48	57.2	66.8	0.15	1D
D	1780	56	86.1	57.2	0.07	1D
E	1580	30	26.2	43.5	0.14	2D
F	1710	39	30.0	40.7	0.16	2D
G	1830	48	48.2	37.9	0.10	2D
H	1850	51	56.9	35.1	0.16	2D

composite material [12]. Data obtained from tensile testing are summarized in Table I. Each datum point shown in Table I represents an average value of at least five samples. It is apparent that composite modulus increases with fiber volume fraction (Fig. 2). To describe the relationship, a modified Cox's model was used [13]. The model has been previously applied to predict mechanical behavior of VGCF reinforced epoxy composite [14].

According to the model, the composite modulus, E_c, can be expressed as

$$E_c = E_m(1 - V_f) + f(\theta)g(a_f)E_f V_f \qquad (1)$$

where E_m, and E_f, are the matrix modulus and fiber modulus, respectively, and a_f is the fiber aspect ratio (length to diameter). The function $f(\theta)$ is a fiber distribution function and

$f(\theta) = 1$ for perfectly aligned fibers,
$f(\theta) = 1/3$ for 2D randomly oriented fibers, and
$f(\theta) = 1/6$ for 3D randomly oriented fibers.

The function $g(a_f)$ is defined as

$$g(a_f) = 1 - \frac{\tanh B}{B}$$

where

$$B = 2a_f\sqrt{\frac{G_m/E_f}{\ln(\pi/2V_f)}}$$

where G_m is the matrix shear modulus.

The moduli of VGCF have been determined using direct measurements on the fiber by various research groups. The data obtained were scattered. The moduli were determined to be in the range of 360 GPa to 600 GPa [15], 225 to 465 GPa [16], or 130 to 196 GPa. Taking $E_m = 12$ GPa, $G_m = 1$ GPa [17], fiber length = 1 cm, and fiber diameter = 7 μm (length and diameter are based on observation using scanning electron microscopy), experimental data for 1D composites are best described by Equation 1, with $f(\theta) = 1$, when the fiber modulus is within a range of 100 GPa to 150 GPa as shown in Fig. 3. For the 2D composites, the modified Cox's model describes only random 2D composites but not 2D orthogonal composites. From

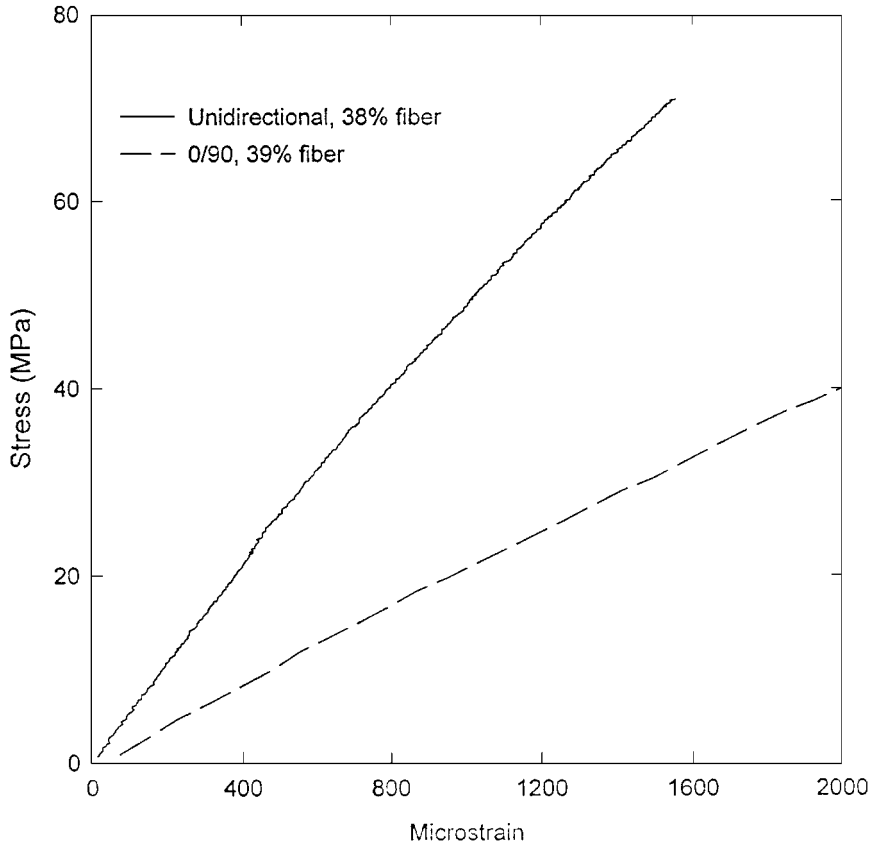

Figure 1 Stress-strain curves of VGCF/C composites.

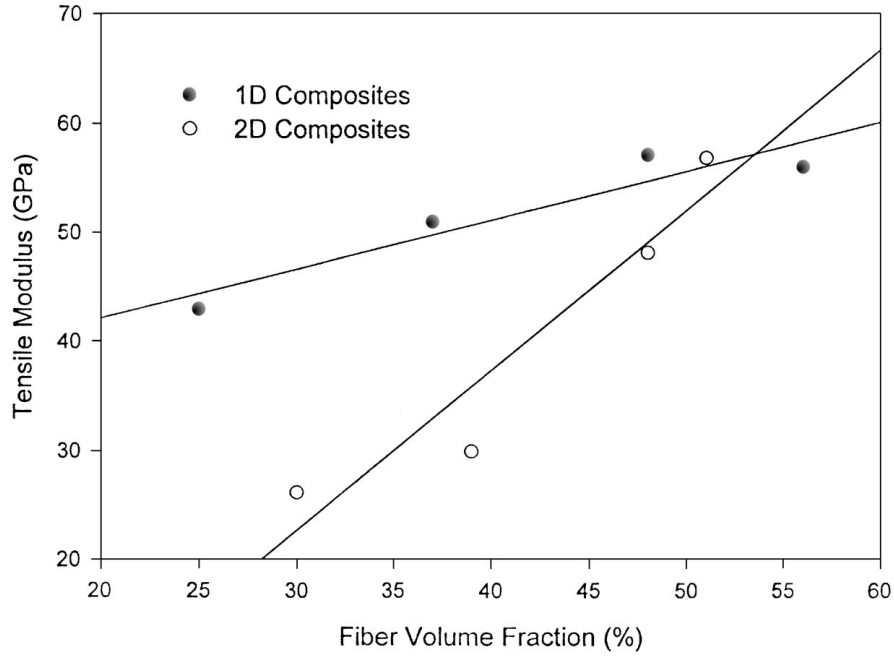

Figure 2 Composite modulus increases as the fiber loading increases.

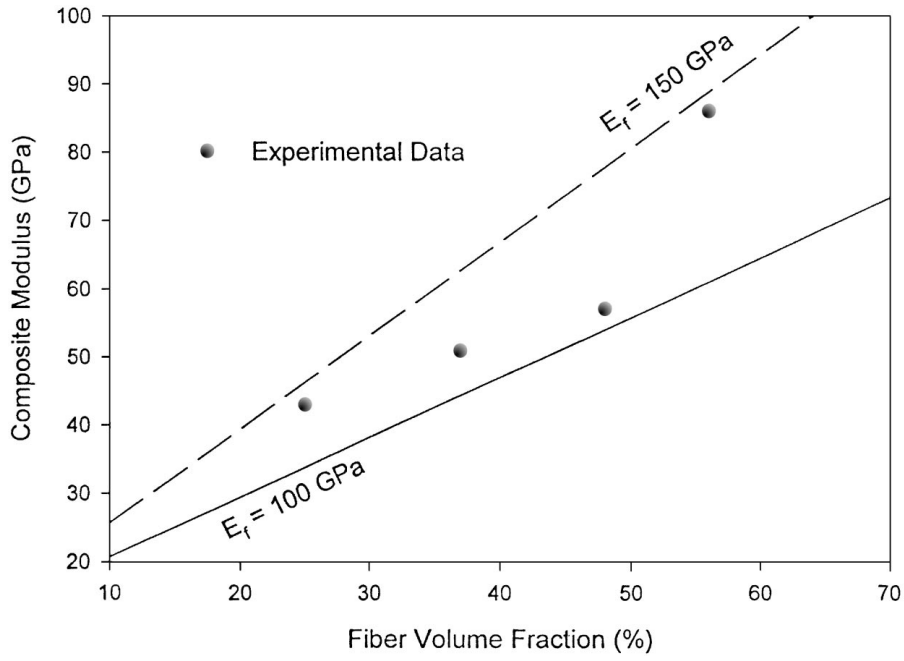

Figure 3 Comparison between experimental data and predited data of 2D composite modulus.

Equation 1, it is seen that $f(\theta)$ is a parameter which reflects that contribution of the fiber according to the fiber architecture. It can be shown that $f(\theta)$ equals 1/2 approximately for 2D orthogonal composites [14, 18]. With $f(\theta) = 1/2$, the experimental data are described by Equation 1 when the fiber modulus is within a range of 110 GPa to 210 GPa as shown in Fig. 4. From the above analysis on 1D and 2D composites, the modulus of VGCF seems to be in the range of 100 GPa and 210 GPa.

It was expected that the composite strength would increase with fiber loading. However, as shown in Table I and Fig. 5, composite strength decreases with increasing fiber volume fraction. It is further seen that no direct correlation between the composite strength and density can be found. The strength and failure strain data shown in Table I and Fig. 5 indicate that the composites failed at strains below that of the reinforcing fiber (typically $\sim 0.5\%$ [9]) and did not receive any strengthening effect from the reinforcing fiber. It has been reported in a number of brittle composite systems that the composite strength can decrease with increasing fiber loading [19–22]. The strength behavior has been attributed to matrix damage associated with the introduction of fiber. This is thought to take place in the present case. Such damage is believed to occur as

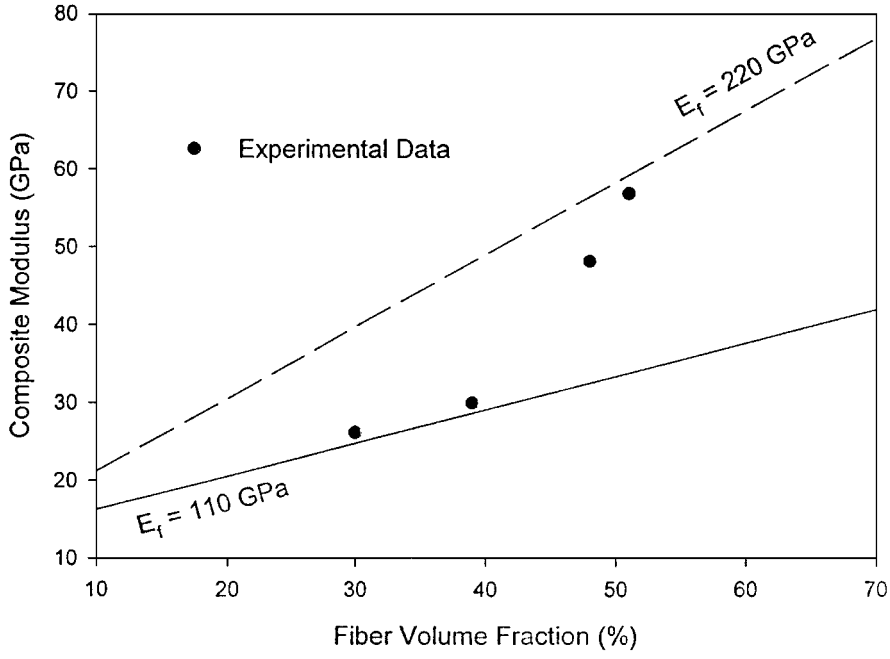

Figure 4 Comparison between experimental data and predited data of 1D composite modulus.

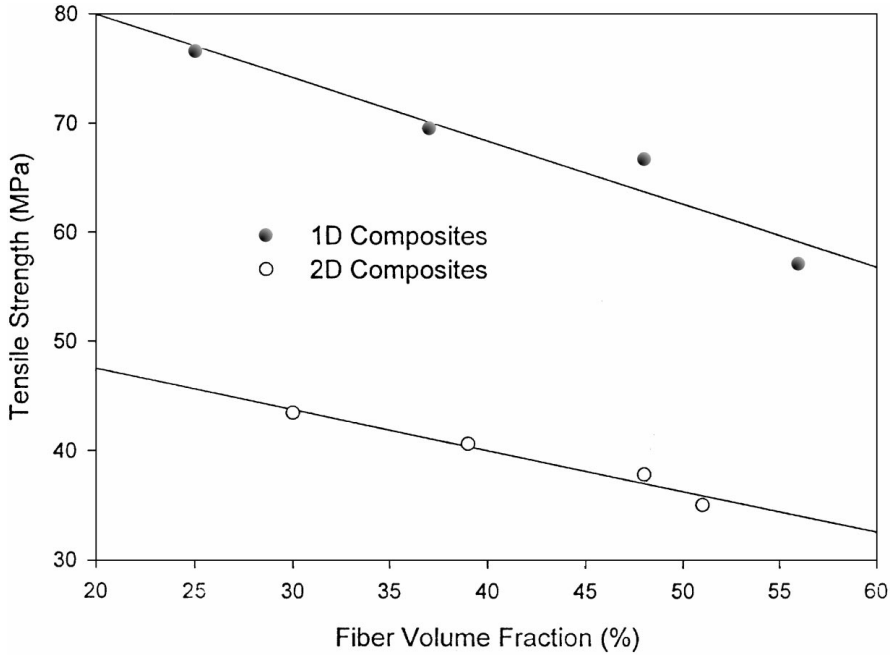

Figure 5 Composite strength decreases as the fiber loading increases.

a result of the mis-match in thermal expansion. Carbon fibers have a negative coefficient of thermal expansion (CTE) in the axial direction over a wide range of temperature. As the degree of structural order of the fiber increases, the wider is the temperature range [23]. It has been shown that VGCF has the highest degree of structural order among all carbon fibers; therefore VFCF exhibits the widest range of temperature over which the CTE is negative. As a result, significant thermal stresses could occur after the pitch infiltration which is then further raised when cooling from the high temperature heat treatment. As a result damage in the lower strain-to-fail matrix carbon occurs. The magnitude of such damage is thought to be higher as the fiber volume fraction is higher. Therefore, with increasing fiber volume fraction, the composite strength decreases.

4. Conclusion

Tensile properties of carbon composites reinforced with vapor grown carbon fiber were determined. Although composite modulus increased with increasing fiber loading, composite strength decreased with increasing fiber loading. The latter is thought to be due to matrix damage as a result of thermal stresses. The moduli of composites were also used to estimate the fiber modulus based on a modified Cox's theory. The tensile modulus of VGCF was estimated to be in a range of 100 GPa to 210 GPa.

Acknowledgement

This work was supported by the National Science Council in Taiwan under Contract #NSC87-2218-E006-071 and Applied Sciences, Inc., Cedarville, Ohio, USA.

References

1. T. V. HUGHES and C. R. CHAMBER, U.S. Patent no. 405480, June (1889).
2. T. KOYAMA, *Carbon* **10** (1972) 757.
3. T. KOYAMA, M. ENDO and Y. ONUMA, *Jpn. J. of App. Phys.* **11**(4) (1972).
4. T. KOYAMA and M. ENDO, *Ohyo Butsuri* **42** (1973) 690.
5. G. G. TIBBETTS, *Carbon* **30** (3) (1992) 399.
6. M. ENDO and M. SHIKATA, *Ohyo Butsuri* **54** (1985) 507.
7. G. G. TIBBETTS and D. W. GORKIEWICZ, *Carbon* **31**(7) (1993) 1039.
8. G. G. TIBBETTS, D. W. GORKIEWICZ and R. L. ALIG, *ibid*. **31**(5) (1993) 809–814.
9. G. G. TIBBETTS, "Carbon Fibers, Filaments, and Composites" (Kluwer Academic Publishers, The Netherlands, 1990) pp. 73–94.
10. J.-M. TING and M. L. LAKE, *J. Mater. Res*. **10**(2) (1995) 247.
11. J.-M. TING and M. L. LAKE, *Carbon* **33**(5) (1995) 663.
12. T. VASILOS, Structural ceramic composites, "Composite" (ASM International, Metal Park, Ohio, 1987).
13. H. L. COX, *Brit. J. Appl. Phys*. **3** (1952) 72–79.
14. W. J. BAXTER, Report No. PH-1717, GM Research Lab, Warren, MI, January 1992.
15. G. G. TIBBETTS, M. ENDO and C. P. BEETZ, *SAMPE J.* (1986) 30–35.
16. D. H. ROSE, D. P. ANDERSON and K. E. G. THORP, Extended Abs., 21st Biennial Conf. on Carbon, Buffalo, NY, 1993 p. 22.
17. *Introduction to Carbon Technology*, edited by H. Marsh, E. A. Heintz and F. Rodriguez-Reinoso (University of Alicante, Spain).
18. P. DADRAS, Rep. No. EMTEC-96-05-1, EMTEC, Dayton, OH, July 1996.
19. E. FITZER, K. H. GEIGI and W. HUTTNER, in Proc. 14th Biennial Conf. Carbon, State College Pennsylvania, (1979) p. 236.
20. C. R. THOMAS and E. J. WALKER, *High Temp-High Press.* **10** (1978) 79.
21. J. J. McHUGH and G. G. TIBBETTS, to be published.
22. C. A. A. BERNARDO, J. A. COVAS, O. M. S. CARNEISO, J.-M. TING and R. L. ALIG, to be published.
23. Y. TANABE, E. YASUDA, H. MACHINO and S. KIMURA, *Ext. Abs. Ann. Meeting of Japan. Ceramic Soc*. (1987) 77.

Received 3 September
and accepted 28 September 1998