INTERFACIAL SHEAR STRENGTH OF CARBON NANOTUBES GRAFTED CARBON FIBER/EPOXY

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Abstract
The interfacial shear strength and fracture behavior of carbon nanotubes (CNT)-grafted polyacrylonitrile (PAN)-based single carbon fiber/epoxy was investigated. Interfacial shear tests of the CNT-grafted and as-received single carbon fiber/epoxy were performed on a microdroplet test fixture using a universal testing machine. It was found that the grafting of CNT improves the interfacial shear strength of single carbon fiber/epoxy. The fractured surface of the microdroplet composite in the CNT-grafted fiber showed rough surfaces with original surface feature and some adhesion of resins. However, the microdroplet composite in the as-received fiber had smooth surface with original fiber surface feature.

1. Introduction

Carbon fibers are widely used as reinforcements in composite materials because of their high specific strength and modulus. Such composites have become a dominant material in the aerospace, automotive and sporting goods industries [1]. Current trends toward the development of carbon fibers have been driven in two directions; high tensile strength fiber with a fairly high strain to failure (~2%), and high modulus fiber with high thermal conductivity. Today, a number of high tensile strength polyacrylonitrile (PAN)-based (more than 6 GPa), and high modulus pitch-based (more than 900 GPa) carbon fibers have been commercially available. Naito et al. [2-4] characterized the tensile, flexural properties and Weibull modulus of high strength PAN-based, high modulus pitch-based and high ductility pitch-based single carbon fibers.
Carbon nanotubes (CNT) with the extremely high tensile strength (~150 GPa) [5] has attracted attention as reinforcements, but they cannot grow as long, continuous fibers. Although it is possible to obtain twisted CNT yam that are continuous fibers, this strength is exceedingly low compared to the carbon fibers [6,7]. An interesting technique to modify the carbon fiber is CNT-grafted on the carbon fiber surface. The grafting of CNT on carbon fibers has been reported in the literature [8-10]. CNT can be grown on the carbon fibers by chemical vapor deposition (CVD) [8,9], electrodeposition [10], etc. CNT-grafted carbon fibers offer the opportunity to add the potential benefits of nanoscale reinforcement to well-established fibrous composites to create micro-nano multiscale hybrid composites [10-12]. However, the effect of CNT grafting on the mechanical properties of carbon fiber has not been fully evaluated. Naito et al. [13,14] reported that the grafting of CNT improves the tensile strength

and Weibull modulus of high strength PAN-based and high modulus pitch-based carbon fibers. The growth of the dense networks of CNT on carbon fibers may lead to reduction of the strength-limiting defects, which in turn, improves the tensile strength and Weibull modulus.

To evaluate the effect of CNT grafting on the interfacial shear properties is essentially important for understanding the mechanical properties of the carbon fibers that contribute to failure.

In the present work, the interfacial shear tests of CNT-grafted high strength PAN-based carbon fiber/epoxy were performed on the microdroplet test fixture using the universal testing machine. To grow CNT on the carbon fiber, a $Fe(C_5H_5)_2$ (ferrocene) catalyst was applied to the fiber bundle using a chemical vapor deposition (CVD). The CNT was also grown on the carbon fiber surface using the CVD. The CNT could be grafted nearly perpendicular to the carbon fiber surface. The effect of CNT grafting on interfacial shear strength and fracture behavior of PAN-based carbon fiber were evaluated.

2. Experimental procedure

2.1. Materials

The carbon fiber used in this study was a high tensile strength PAN-based (T1000GB) carbon fiber. The T1000GB PAN-based carbon fiber was supplied from Toray Industries, Inc. The physical properties of PAN-based carbon fiber are listed in **Table 1**. Note that as-received fiber had been subjected to commercial surface treatments and sizing (epoxy compatible sizing).

Fiber	**as-received**	**CNT-grafted**
Filaments [a] (Counts)	12,000	-
Yield [a] *Tex* (g/1000m)	485	-
Density [a] ρ_f (g/cm^3)	1.80	-
Average interfacial shear strength obtained from Eq. (1) $\tau_{IFSS.ave}$ (MPa)	63.98 (3.97)	74.99 (5.64)
Average interfacial shear strength obtained from Eq. (2) $\tau_{IFSS.ave}$ (MPa)	75.58	88.43

[a] Producer's data sheet

T1000GB: Catalog for TORAYCA, Toray Industries, Inc., High performance carbon fiber Torayca in Japanese. 2004.

( ) indicate standard deviations.

Table 1. Physical and mechanical properties of PAN-based (T1000GB) carbon fiber and microdroplet composite.

The solution of thermoset epoxy consists of a diglycidyl ether of bisphenol A (DGEBA) epoxy (JER813, supplied by Mitsubishi Chemical Corp.) and an acid anhydride grade hardener (HY306, supplied by Mitsubishi Chemical Corp.) at a ratio of epoxy : hardener = 100 : 124 by weight. The solution was prepared by simultaneously rotating and revolving using a rotation/revolution mixer (AR-250, Thinky Co. Ltd.) under the following driving

conditions: mixing mode (rotation: 800 rpm and revolution: 2000 rpm) for 10 min and defoaming mode (rotation: 60 rpm and revolution: 2200 rpm) for 5 min.

2.2. Preparation of CNT-grafted carbon fiber

To grow CNT on the carbon fiber, a $Fe(C_5H_5)_2$ (ferrocene) catalyst was applied to the fiber bundle using a chemical vapor deposition (CVD). The CNT was also grown on the carbon fiber surface using the CVD. Experimental details on the synthesis technique of CNT can be found elsewhere [8,9]. The growth temperature and time for CNT deposition were selected as 750 °C and 1200 sec. The CNT grown on carbon fibers were examined using a high resolution scanning electron microscope (SEM, FEI, Quanta 200FEG) at an operating voltage of 5 kV.

2.3. Preparation of microdroplet composite

Single carbon filament specimens were prepared on the stage with the help of a stereoscope. A single filament was selected from carbon fiber bundles and cut perpendicular to the fiber axis by a razor blade. A single filament of the as-received and the CNT-grafted carbon fiber was fastened to a thin (0.2 mm) stainless steel holder (26 × 65 mm) with an instant high viscosity type cyanoacrylate adhesive. The epoxy microdroplet specimen made by applying liquid-state epoxy resin with hardener was adherend on a single fiber with an embedded length of 20-30 mm using a fine-point applicator. The microdroplet composite specimen was cured at 90 °C for 3 h and at 150 °C for 12 h, with heating rate of 3 °C/min to form a rigid epoxy microdroplet composite. The high curing temperature excursions for long durations were applied to make sure the resin was completely cured. All specimens were stored in a desiccator at 20 ± 3°C and at 10 ± 5% relative humidity prior to testing. The morphology of microdroplet composites was examined using a high resolution scanning electron microscope (SEM, FEI, Quanta 200FEG) at an operating voltage of 5 kV.

2.4. Interfacial shear test

Interfacial shear tests of microdroplet composite were performed on a microdroplet test fixture including the XYZθxθyθz-axes stage units and X-axis stage with razor blade tips (radius of curvature was 600 nm) using a universal testing machine (Shimadzu, Table top type tester EZ-Test, EZ-S) with a load cell of 10 N. A CCD camera mounted on a digital microscope (Keyence, VHX-1000 and VH-Z100) with XY-axes stage allowed to check the fixing condition of specimen, measuring the embedded length of each microdroplet, le, observing/recording of the real time deformation with a maximum magnification of 1000 times.

Firstly, the position of two razor blades was adjusted using the XYZθxθyθz-axes stage units. The razor blades were opened and the microdroplet composite specimen was set up to the testing machine using pin-joint systems. The crosshead was moved in order to select each microdroplet and the embedded length of microdroplet, l_e was measured using the digital microscope. The razor blades were carefully brought close to a specimen and then the fixing condition of the specimen was confirmed using a X-axis stage. Finally, the crosshead speed of 0.05 mm/min was applied. All tests were conducted under the laboratory environment at room temperature (at 23 ± 3°C and 50 ± 5% relative humidity).

After testing, fracture surfaces of microdroplet specimens were coated using an osmium coater (Vacuum Device, HPC-1SW). The fracture surfaces of microdroplet composites were also examined using a SEM (FEI, Quanta 200FEG) at an operating voltage of 5 kV.

3. Results and discussion

Figure 1 shows the SEM micrographs of surface views for the CNT-grafted and as-received T1000GB PAN-based carbon fiber filaments.

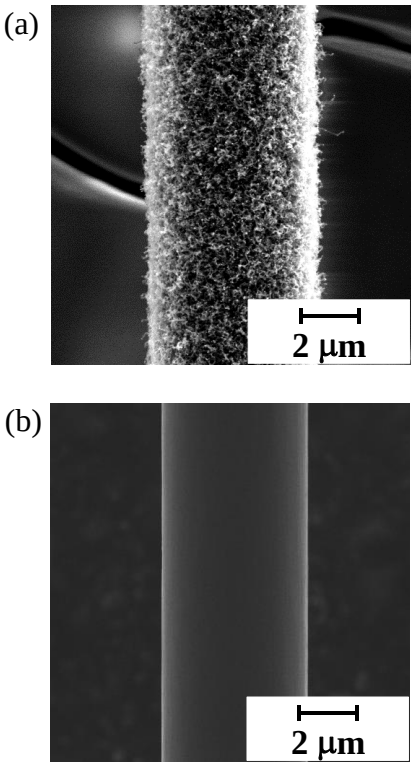

Figure 1. SEM micrographs of the surface views for the CNT-grafted and as-received T1000GB PAN-based carbon fibers. (a) CNT-grafted fiber, and (b) as-received fiber.

The as-received T1000GB PAN-based carbon fiber has a comparatively smooth surface, as shown in **Fig. 1** (b). The CNT can be grafted nearly perpendicular to the T1000GB fiber surfaces, and grown uniformly and densely on the T1000GB fibers. The individual CNT can be interconnected with each other in the several positions, forming a three-dimensional network structure on the fiber surface, as shown in **Fig. 1** (a).

For all microderoplet composites, the load was almost linearly proportional to the displacement until the load reached its maximum and the interfacial fracture between the fiber and the matrix occurred. Afterwards, the load decreased abruptly to the low value of the frictional load. The friction load was maintained during the move of the deboned microdroplet along the fiber.

There are some methods to calculate the average interfacial shear strength, $\tau_{IFSS.ave}$ from the experimental data (these methods do not represent the shear stress distribution along the interface near the edge).

One is the method of calculating the mean of interfacial shear strength on the basis of the maximum fracture load, P_{max} for the embedded length, l_e of the individual microdroplet. The interfacial shear strength, τ_{IFSS} between the fiber and the matrix was calculated from the following Eq. (1):

$$\tau_{IFSS} = \frac{P_{max}}{\pi d_f l_e} \quad (1)$$

This equation assumes a uniform shear lag model of a cylindrical fiber with a surrounding matrix and the interfacial shear stress is uniformly distributed along the fiber-matrix interface. **Figure 2** shows the relation between the interfacial shear strength, τ_{IFSS} and the embedded length, l_e of the microdroplet composites for the CNT-grafted and the as-received T1000GB PAN-based carbon fibers.

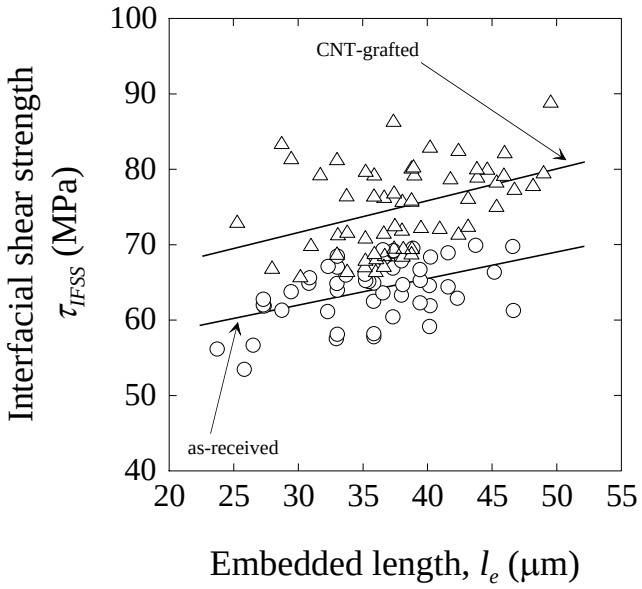

Figure 2. Relation between the interfacial shear strength and the embedded length of the microdroplet composites for the CNT-grafted and the as-received T1000GB PAN-based carbon fibers. ○－as-received fiber and △－CNT-grafted fiber.

The interfacial shear strength slightly increased with increasing in the embedded length for all microdroplet composites. The interfacial shear strength of the microdroplet composites in the CNT-grafted carbon fibers was higher than that in the as-received fiber. The average interfacial shear strength ($\tau_{IFSS.ave}$) is summarized in **Table 1**. This average interfacial shear strength did not consider the slope of the experimental τ_{IFSS} vs l_e data ($\tau_{IFSS.ave}$ was simply averaged the experimental τ_{IFSS} data). The results show that the average interfacial shear strength of the microdroplet composites in the CNT-grafted T1000GB fiber is 74.99±5.64, which is 17.2 % higher than that in the as-received state (63.98±3.97 MPa). The standard deviation of interfacial shear strengths for the microdroplet composites in the CNT-grafted fiber was larger than that in the as-received state. The length of meniscus region for the CNT-grafted carbon fibers was larger than that for the as-received fiber and affected the variations in the experimental results.

The other is the method of calculating the average interfacial shear strength, $\tau_{IFSS.ave}$ by using the fitting straight line of P_{max} as a function of embedded length, l_e. The average interfacial shear strength, $\tau_{IFSS.ave}$ was calculated from the following Eq. (2):

$$\tau_{IFSS.ave} = \frac{dP_{max}}{\pi d_{f.ave} dl_e} \quad (2)$$

Figure 3 shows the maximum fracture load, P_{max} vs. the embedded length, l_e obtained from the microdroplet test.

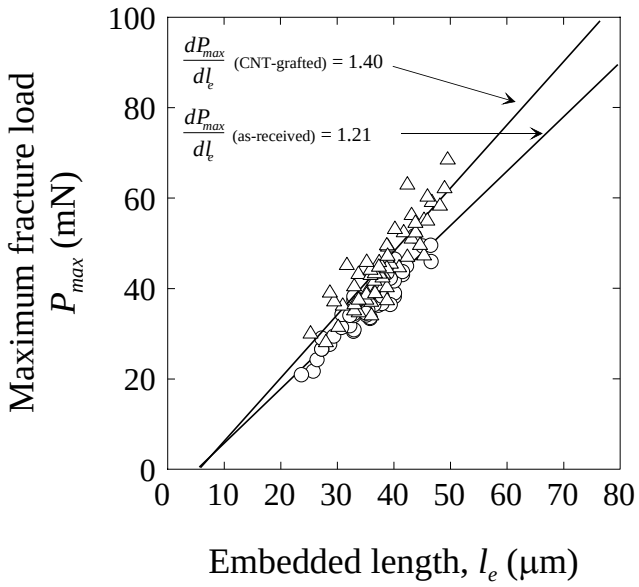

Figure 3. Relation between the maximum fracture load and the embedded length of the microdroplet composites for the CNT-grafted and the as-received T1000GB PAN-based carbon fibers. ○－as-received fiber and △－CNT-grafted fiber.

The maximum fracture load, P_{max} increased with increasing the embedded length, l_e of the microdroplet composite, although the dispersion appeared in the experimental data. The average interfacial shear strengths ($\tau_{IFSS.ave}$) obtained by utilizing Eq. (2) are summarized in **Table 1**. The $\tau_{IFSS.ave}$ of the microdroplet composites in the CNT-grafted T1000GB fiber is calculated to be 88.43 MPa, which is 17.0 % higher than that in the as-received state (75.58 MPa).
The average interfacial shear strengths, $\tau_{FSS.ave}$ obtained from the above two methods of the microdroplet composites in the CNT-grafted T1000GB fibers were higher than that in the as-received state.

4. Concluding remarks

The interfacial shear tests of the microdroplet composites in the CNT grown on T1000GB PAN-based single carbon fibers were performed. The results are briefly summarized.
(1) The length of meniscus region of the microdroplet composites for the CNT-grafted carbon fiber was larger than that for the as-received fiber.
(2) The average interfacial shear strengths of the microdroplet composites in the CNT-grafted T1000GB fiber were higher than that in the as-received state.

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