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INTERFACIAL SHEAR PROPERTIES OF CARBON NANOTUBES GRAFTED CARBON FIBER POLYIMIDE COMPOSITES

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Summary: *The interfacial shear strength and fracture behavior of CNT-grafted high tensile strength polyacrylonitrile (PAN) -based and high modulus pitch-based carbon fiber polyimide composites were investigated. Interfacial shear tests of CNT-grafted and as-received PAN- and pitch-based carbon fiber polyimide composites were performed using an interfacial micro-bond (microdroplet) evaluation instrument. The results clearly demonstrated that the grafting of CNT are effective in improving the interfacial shear strength of PAN- and pitch-based carbon fiber polyimide composites.*

1 INTRODUCTION

The trend toward the development of carbon fibers has been driven in two directions: high strength fibers with a very high tensile strength and a fairly high strain to failure (~2 %), and high modulus fiber with a very high stiffness and moderate strength. Today, a number of high strength polyacrylonitrile (PAN)-based (more than 6 GPa) and high modulus pitch-based (more than 900 GPa) carbon fibers are commercially available. The mechanical behavior of several high strength and high modulus PAN- and pitch-based carbon fibers had been recently characterized by Naito et al [1-3].

The carbon fiber surface is of great importance in carbon fiber reinforced composites during fabrication and service [4]. Recent interesting technique to modify the carbon fiber surfaces is carbon nanotubes (CNT) grafting. The grafting of CNT on carbon fibers has been reported in the literature [5, 6]. The CNT can be grown on the carbon fibers by chemical vapor deposition (CVD) [5], electrodeposition [6], etc. The CNT-grafted carbon fibers offer the opportunity to add the potential benefits of nanoscale reinforcement to well-established fibrous composites to create multiscale hybrid micro-nano composites [6, 7]. Naito et al. [8-11] reported that the grafting of CNT improves the tensile strength, Weibull modulus and thermal conductivity of high strength PAN-based and high modulus pitch-based carbon fibers.

In the present work, the effects of grafting of CNT on the interfacial shear strength and fracture behavior of T1000GB PAN-based and K13D pitch-based carbon fiber polyimide composites were investigated.

2 EXPERIMENTAL PROCEDURE

2.1 Material

Carbon fibers used in this study are a high tensile strength PAN-based (T1000GB) and a high modulus pitch-based (K13D) carbon fiber. The T1000GB PAN-based carbon fiber was supplied from Toray Industries, Inc. and the K13D pitch-based carbon fiber was supplied from Mitsubishi Plastics, Inc. Note that as-received, both fibers had been subjected to commercial surface treatments and sizing. The physical properties of both types of carbon fibers are summarized in Table 1.

	PAN-based		pitch-based	
	As-received	CNT-grafted	As-received	CNT-grafted
Filaments (Counts)	12000	-	2000	-
Yield *Tex* (g/1000m)	485	-	365	-
Density ρ_f (g/cm^3)	1.80	-	2.20	-
Tensile strength $\sigma_{f.ave}$ (GPa)	5.69 (1.02)	6.73 (1.01)	3.21 (0.81)	4.09 (0.85)
Tensile modulus $E_{f.ave}$ (GPa)	291 (11)	300 (12)	940 (48)	989 (96)
Number of samples (Counts)	23	24	12	15
Interfacial shear strength $\tau_{IFSS.ave}$ (MPa)	64.60 (6.12)	74.76 (5.48)	13.92 (1.64)	17.00 (1.09)

Table 1: Mechanical and physical properties of carbon fibers and microdroplet composites.

The surface features of as-received T1000GB PAN-based and K13D pitch-based carbon fibers were examined using a high resolution scanning electron microscope (SEM) (JSM-6500F, JEOL) at an operating voltage of 5 kV.

The polyamic acid (PAA) solution of aromatic polyimide (SKYBOND 703, solid content = 50 wt.%, Industrial Summit Technology Corp.) consisting of 3,4,3',4'-benzophenone tetracarboxylic dianhydride (BTDA) and 4,4'-methylendianiline (MDA) was used as the polyimide matrix. An initial PAA solution, dissolved in a mixture of solvents of n-methyl pyrrolidone (NMP), ethanol, methanol, and methyl isobutyl ketone, produced 3-7 Pa s viscosity [12].

2.2 Preparation of CNT-grafted carbon fiber

To grow CNT on the carbon fibers, an $Fe(C_5H_5)_2$ (ferrocene) catalyst was applied to the T1000GB and K13D fiber bundles using thermal CVD in vacuum. Experimental details on the CNT synthesis technique can be found elsewhere [5]. Prior to the application of the catalyst, the carbon fiber bundles were heat treated at 750 °C for an hour in vacuum to remove the sizing. The growth temperature and time for CNT deposition were selected as 750 °C (T1000GB) and 700 °C (K13D) for 900 sec. The CNT grown on PAN- and pitch-based carbon fibers were examined using a SEM (JSM-6500F, JEOL) at an operating voltage of 5 kV.

2.3 Preparation of microdroplet composite specimen

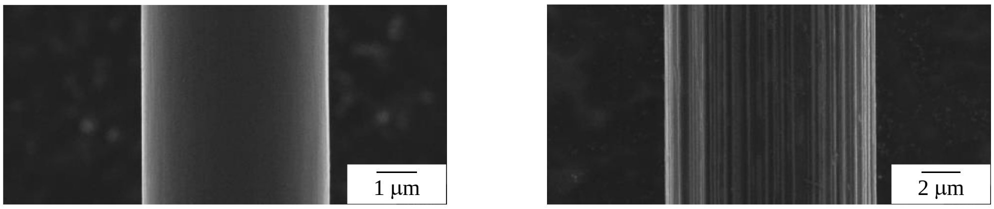
Single carbon filament specimens were prepared on the stage with the help of a stereoscope. A single filament was selected from carbon fiber bundles and cut perpendicular to the fiber axis by a razor blade. A single filament of the as-received and the CNT-grafted carbon fiber was fastened to a thin (0.2 mm) stainless steel holder (26 × 65 mm) with the polyimide matrix (Skybond 703) and the polyimide was cured at 300 °C for 1 h, with heating rate of 3 °C/min. The polyimide microdroplet specimen made by applying liquid-state polyimide resin (Skybond 703) 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 300 °C for 1 h, with heating rate of 3 °C/min to form a rigid polyimide microdroplet composite. All specimens were stored in a desiccator at 20 ± 3°C and at 10 ± 5% relative humidity prior to testing.

2.4 Interfacial shear test

Interfacial shear tests of microdroplet specimens were performed using an interfacial micro-bond evaluation instrument (MODEL HM410, Tohei sangyo) with a load cell of 5 N. The crosshead speed of 0.12 mm/min was applied. All tests were conducted under the laboratory environment at room temperature (at 23 ± 3 °C and 50 ± 5% relative humidity).

3 RESULTS AND DISCUSSION

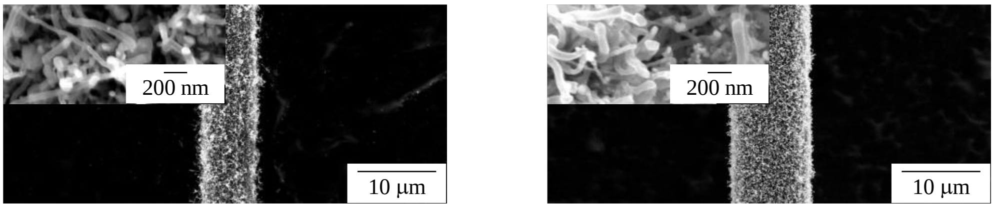
Figure 1 shows the SEM micrographs of surface views for the as-received T1000GB PAN-based and K13D pitch-based carbon fiber filaments. The as-received T1000GB PAN-based carbon fiber has a comparatively smooth surface. However, the as-received K13D fiber derived from anisotropic pitch has a groove-like feature parallel to the fiber axis.



(a) PAN-based (b) pitch-based

Figure 1: SEM micrographs of the surface views for the PAN-based and pitch-based carbon fibers.

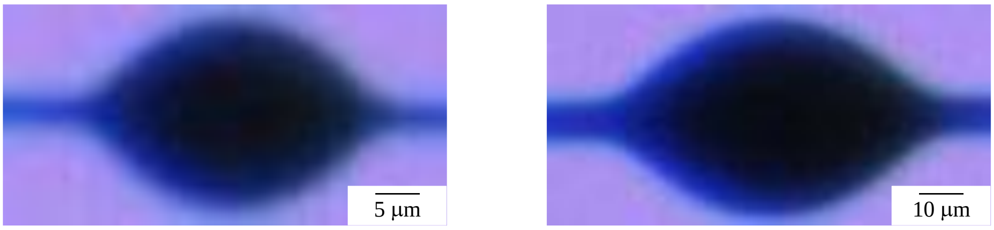
Figure 2 shows the SEM micrographs of the CNT-grafted T1000GB PAN-based and K13D pitch-based carbon fiber filaments. The CNT can be grafted nearly perpendicular to the T1000GB and K13D fiber surfaces, and grown uniformly and densely on the T1000GB and K13D fibers. The outer diameters of the CNT ranged from 30-50 nm for T1000GB and from 60-80 nm for the K13D fibers. The individual CNT can be interconnected with each other in the several positions, forming a three-dimensional network structure on the fiber surface.



(a) PAN-based (b) pitch-based

Figure 2: SEM micrographs for the CNT-grafted PAN-based and pitch-based carbon fibers.

Figure 3 shows the digital micrographs of surface views for the microdroplet composites in the as-received T1000GB PAN-based and K13D pitch-based carbon fibers.



(a) PAN-based (b) pitch-based

Figure 3: Digital micrographs of the surface views for the microdroplet composites.

The size of meniscus region may have brought about some variations in the results measured from the microdroplet test [13]. The meniscus region of outward convex shape was clearly formed at the top and the bottom of the microdroplet.

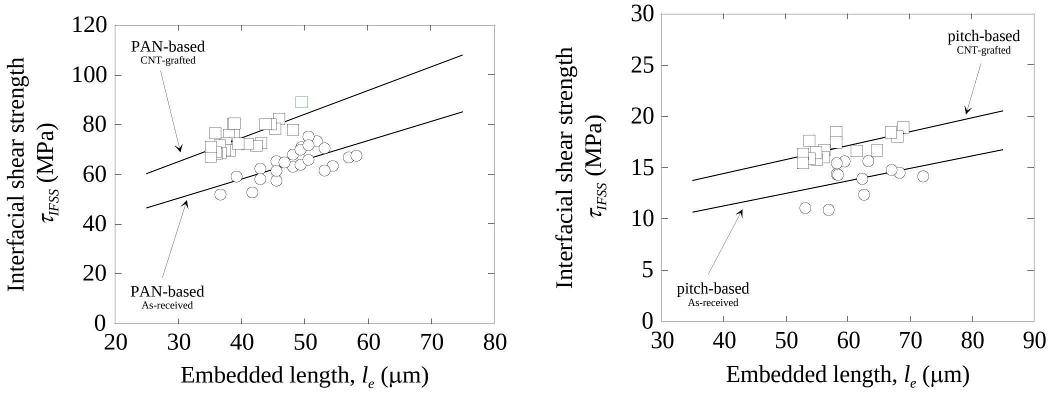
For all microderoplet composite specimens, the load was almost linearly proportional to the displacement until the load reached its maximum and the interfacial fracture between the fiber and the matrix occurred. Afterwards, the load decreased abruptly to the low value of the frictional load. The friction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

The interfacial shear strength, τ_{IFSS} between the fiber and the matrix was calculated from the following Eq. (1):

$$\tau_{IFSS} = \frac{P_{max}}{\pi d_f l_e} \tag{1}$$

where, the maximum fracture load, P_{max} for the embedded length, l_e of the individual microdroplet. 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 4 shows the relation between the interfacial shear strength, τ_{IFSS} and the embedded length, l_e of the microdroplet composite specimens for the CNT-grafted and the as-received T1000GB PAN-based and K13D pitch-based carbon fibers.



(a) PAN-based (b) pitch-based

Figure 4: Relation between the interfacial shear strength and the embedded length of the polyimide microdroplet composites in the as-received and CNT-grafted PAN-based and pitch-based carbon fibers.

The interfacial shear strength slightly increased with increasing in the embedded length for all microdroplet composites. Similar results was observed for the literature [13]. The interfacial shear strength of the microdroplet composite in the CNT-grafted carbon fiber 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 composite in the CNT-grafted T1000GB fiber is 74.76 ± 5.48 MPa, which is 15.7 % higher than that in the as-received state (64.60 ± 6.12 MPa). The average interfacial shear strength of the microdroplet composite in the CNT-grafted K13D fiber is 17.00 ± 1.09 MPa, which is 22.1 % higher than that in the as-received state (13.92 ± 1.64 MPa).

The average tensile strengths ($\sigma_{f.ave}$) obtained from the previous investigation [8] are also summarized in Table 1. The results show that the average tensile strengths of the CNT-grafted T1000GB and K13D fibers are 6.73 ± 1.01 and 4.09 ± 0.85 GPa, which are 18.3 and 27.4 % higher than those in the as-received state (5.69 ± 1.02 and 3.21 ± 081 GPa). Evidently, the grafting of CNT on the carbon fibers significantly improved the interfacial shear properties without sacrificing the tensile properties.

4 CONCLUSIONS

The interfacial shear tests of the polyimide microdroplet composites in the CNT-grafted on T1000GB PAN-based and K13D pitch-based single carbon fibers were performed. The results are briefly summarized.

(1) The average interfacial shear strengths of the microdroplet composites in the CNT-grafted T1000GB and K13D fibers were higher than that in the as-received state.

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