THE EFFECT OF CARBON NANOTUBE GRAFTING ON THE TENSILE, SHEAR AND PEEL PROPERTIES OF POLYACRYLONITRILE-BASED CARBON FIBER/EPOXY BUNDLE COMPOSITES

Yuta Inoue1,2,*, Kimiyoshi Naito2, Masashi Koyama1, Hiroshi Fukuda1, Yutaka Kagawa2,3

1Department of Materials Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba, 278-8510, Japan
2Composite Materials Group, Hybrid Materials Unit, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047, Japan
3Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo, 153-8904, Japan

*INOUE.Yuta@nims.go.jp

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Abstract
The effect of CNT grafting on the tensile, shear and peel properties of T1000GB PAN-based carbon fiber/epoxy bundle composites were investigated. The tensile strength of the CNT-grafted bundle composites were almost similar to that in the as-received state. However, the Weibull modulus slightly increased with the CNT grafting. The shear and peel strengths of the composites were about 70~130% higher than those in the as-received state. These results demonstrated that the CNT grafting on the carbon fibers significantly improves the out-of-plane mechanical properties of bundle composites without sacrificing the in-plane mechanical properties.

1 Introduction
Carbon fibers are widely used as reinforcement in composite materials because of their high specific strength and modulus. Currently, the 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 strength polyacrylonitrile (PAN)-based (more than 6GPa) carbon fibers have been commercially available.

Carbon fiber reinforced polymer-matrix composites (CFRP) have become a dominant material in the aerospace, automotive, and sporting goods industries [1]. However, these composites have the disadvantages in the out-of-plane mechanical properties, such as the shear and peel strengths.

CNT-grafted carbon fibers were used to improve the out-of-plane properties. The CNT grafting on carbon fibers has been reported in the literature [2-4], and the CNT-grafted carbon fibers may offer the opportunity to add the potential benefits of nanoscale reinforcement.
In the present works, the effect of CNT grafting on the tensile, shear and peel properties of T1000GB PAN-based carbon fiber/epoxy bundle composites were investigated.

2 Experimental procedure
2.1 Materials
The carbon fiber used in this study was high strength PAN-based (T1000GB) carbon fiber. The T1000GB fiber was supplied from Toray Industries, Inc. The physical properties of the T1000GB fiber are listed in Table 1. This fiber in the as-received state had been subjected to commercial surface treatments and sizing (epoxy compatible sizing).

<table>
<thead>
<tr>
<th>fiber type</th>
<th>Filament tex, t (g/1000m)</th>
<th>density, $\rho$ (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1000GB</td>
<td>12000</td>
<td>485</td>
</tr>
</tbody>
</table>

Table 1. Physical properties of the high strength PAN-based (T1000GB) carbon fiber.

The fiber bundles were impregnated with thermoset epoxy resin (composed from epoxy resin JER813 and curing agent YH306, mix ratio 100:124 by weight). The epoxy resin was supplied from Mitsubishi chemical, Inc.

2.2 Synthesis of CNT
To grow CNT on the carbon fibers, two different catalysts were applied to the bundles.
(1) CNT-grafted(CVD) Fe(C₅H₅)₂ (ferrocene) catalyst was applied to the bundles using a chemical vapor deposition (CVD) method.
(2) CNT-grafted(W.P.+CVD) The bundles were impregnated into a 0.1M ethanol solution of Fe(NO₃)₃ · 9H₂O catalyst using a dipping.

The CNT were grown on the carbon fibers surface using a CVD method. C₂H₅OH (ethanol) was adopted as a carbon resource. The growth temperature and time for CNT deposition were selected as 750°C and 1200s.

2.3 Testing procedure
2.3.1 Tensile test
Tensile tests of bundle composites were carried out using a universal testing machine (Shimadzu, Autograph) with a load cell of 50kN. A gauge length, $L$, of 25mm and crosshead speed of 5mm/min was applied. All tests were conducted under laboratory conditions at room temperature (23 ± 3°C) and 50 ± 5% relative humidity.

2.3.2 Shear test
Shear tests of bundle composites were performed using a universal testing machine (Shimadzu, Autograph) with a load cell of 50kN. A gauge length, $L$, of 25mm, lap length of 1~10mm (for the as-received), 3~5mm (for the CNT-grafted) and crosshead speed of 5mm/min was applied.

2.3.3 Peel test
Peel tests of bundle composites were performed using a universal testing machine (Shimadzu, EZ test) with a load cell of 10N. Initial crack length of 30mm and crosshead speed of 10mm/min was applied.
3 Results and Discussions

3.1 Morphology of CNT
The CNT grown on the carbon fibers were examined using a high resolution scanning electron microscope (SEM). Figure 1 shows the SEM micrographs of the CNT grown on the carbon fibers. The CNT can be grown uniformly and densely on the carbon fibers, forming a three-dimensional network structure. The diameters of the CNT are in the range of 30-50nm for the CNT-grafted(CVD) and of 50-230nm for the CNT-grafted(W.P.+CVD).

![SEM micrographs of the CNT grown on the carbon fibers.](image)

3.2 Mechanical properties
3.2.1 Tensile properties (in-plane)
The tensile strength, $\sigma_f$, was calculated using the following equation:

$$\sigma_f = \frac{P_{\text{max}} \cdot \rho}{t \times 10^{-3}}$$

(1)

where $P_{\text{max}}$ is the maximum fracture load, $\rho$ and $t$ are the density and tex of the T1000GB fiber, as shown in Table 1, respectively. Table 2 shows the tensile strength of the bundle composites. This result indicated that the average tensile strength of the CNT-grafted(CVD) and CNT-grafted(W.P.+CVD) bundle composites were almost similar to that in the as-received state.

There is an appreciable scattering of the tensile strength for the bundle composites. The statistical distribution of composite strengths is usually described by means of Weibull equation. The two-parameter Weibull distribution is given by

$$P_f = 1 - \exp \left[ -L \left( \frac{\sigma}{\sigma_0} \right)^{m_f} \right]$$

(2)

where $P_f$ is the cumulative probability of failure at applied tensile strength $\sigma_f$, $m_f$ is the Weibull modulus (Weibull shape parameter) and $\sigma_0$ is the Weibull scale parameter (characteristic stress). Figure 2 shows the Weibull plots for the tensile strength of the bundle composites. The Weibull modulus, $m_f$, for the CNT-grafted(CVD) and CNT-grafted(W.P.+CVD) bundle composites were calculated to be 24.8 and 28.0, respectively. The $m_f$ for the as-received bundle composite was found to be 19.2. The CNT grafting on the carbon fibers enhanced reliability of the tensile strength of the bundle composites.
<table>
<thead>
<tr>
<th></th>
<th>Number of samples, n</th>
<th>Average tensile strength (GPa)</th>
<th>Weibull scale parameter, $\sigma_0$ (GPa)</th>
<th>Weibull shape parameter, $m_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-received</td>
<td>30</td>
<td>5.29(0.30)</td>
<td>5.43</td>
<td>19.2</td>
</tr>
<tr>
<td>CNT-grafted (CVD)</td>
<td>30</td>
<td>5.31(0.24)</td>
<td>5.42</td>
<td>24.8</td>
</tr>
<tr>
<td>CNT-grafted (W.P.+CVD)</td>
<td>20</td>
<td>5.10(0.20)</td>
<td>5.19</td>
<td>28.0</td>
</tr>
</tbody>
</table>

( ) indicate standard deviations

Table 2. Average tensile strength and Weibull parameters.

![Weibull plots for the tensile strength of the bundle composites.](image)

Figure 2. Weibull plots for the tensile strength of the bundle composites.

3.2.2 Shear properties (out-of-plane)

The shear strength, $\tau$, was calculated using the following equation:

$$\tau = \frac{P_{\text{max}}}{S}$$

(3)

where $P_{\text{max}}$ is the maximum shear load, and $S$ is the fracture area. Figure 3 shows the relationship between the shear strength and the lap length. It is clearly observed that the shear strength decreased with increasing the lap length in the as-received state, and the shear strength of the CNT-grafted(CVD) and CNT-grafted(W.P.+CVD) bundle composites were higher than that in the as-received state at the same lap length. The shear strength for the CNT-grafted(CVD) and CNT-grafted(W.P.+CVD) bundle composites were about 70% higher than that in the as-received state.
3.2.3 Peel properties (out-of-plane)

The peel strength, $S$, was calculated using the following equation:

$$S = \frac{P_{\text{ave}}}{b}$$  \hspace{1cm} (4)

where $P_{\text{ave}}$ is the average peel load, and $b$ is the width of the specimen. Figure 4 shows the typical peel strength - displacement curves. The peel strength for the CNT-grafted(CVD) and CNT-grafted(W.P.+CVD) bundle composites were about 130% and 80% higher than that in the as-received state.
4 Conclusions
The effect of CNT grafting on the tensile, shear and peel properties of T1000GB PAN-based carbon fiber/epoxy bundle composites were examined. From the experiments, the following conclusions were obtained.

(1) The tensile strength of the CNT-grafted bundle composites were almost similar to that in the as-received state. However, the Weibull modulus slightly increased with the CNT grafting.

(2) The shear strength of the CNT-grafted bundle composites were about 70% higher than that in the as-received state.

(3) The peel strength of the CNT-grafted bundle composites were about 80–130% higher than that in the as-received state.

These results demonstrated that the CNT grafting on the carbon fibers significantly improves the out-of-plane mechanical properties of bundle composites without sacrificing the in-plane mechanical properties.

Acknowledgements
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