INTERLAMINAR REINFORCEMENT BY ALIGNED CARBON NANOTUBES IN CARBON FIBER REINFORCED POLYMER COMPOSITES

F.N. Nguyen1*, S. Than Tun1, A.P. Haro1, N.Hirano2, K. Yoshioka1, R. Ovalle-Robles3
1 Toray Composites (America), Inc, Washington, USA; 2 Toray Industries, Inc., Ehime, Japan; 3 University of Texas at Dallas, Texas, USA; (*Corresponding Author: fnquyen@toraycompam.com)

Keywords: Carbon fiber reinforced polymer composite, aligned carbon nanotube, CNT forest, CNT sheet, interlaminar toughener, mode I, mode II fracture toughness

1 Introduction

Fracture toughness in a carbon fiber reinforced polymer (CFRP) composite is very important for damage resistance and tolerance of an aircraft’s primary structures. Mode I fracture toughness could be improved by a nanosized reinforcement incorporated into the polymer matrix while Mode II utilizes an interlaminar toughener localized in an interlayer region between two fiber beds. The latter leads to formation of insulation layers of interlaminar tougheners in the composite, and hence could reduce its z-direction electrical conductivity.

Multi-wall carbon nanotubes (MWCNTs) offer significant strength and modulus in addition to high thermal conductivity and stability, and electrical properties [1]. MWCNTs can potentially be utilized in many industries including semiconductor, electronic, energy, healthcare, automobile, and aerospace.

Under proper conditions, MWCNT forests (vertically aligned CNT arrays of at least 350 um tall) exhibit special properties of drawability in that forests can be drawn into continuous, high quality sheets. These sheets, in turn, can be twisted into nanotube yarns [2, 3]. It was observed that the drawability of MWCNTs depended strongly on the degree of MWCNT alignment in a forest. In addition, a MWCNT forest with volumetric density of at least 39 mg/cm³ was drawable. Higher volumetric MWCNT densities would yield better aligned and more drawable forests, hence continuous CNT sheets.

CNTs in a drawn sheet are held strongly by Van der Waals forces and aligned in the drawing direction. Better alignment of CNTs could be achieved by applying some tension to the sheet before being wound onto a roller [4].

Recently, some researchers have attempted to use MWCNTs to reinforce structural polymers for their strength and modulus improvements. Cheng et al. [5] showed that a mat of random CNTs and BMI polymer (up to 60% CNTs by volume) increased tensile strength significantly, comparable to IM7 CFRP. Other researchers tempted to use aligned CNTs drawn from a CNT forest [4-6]. Wang et al. [4] showed that when CNT volume exceeded 50% and CNTs were well aligned by stretching the drawn sheet, the composite had tensile strength and modulus exceeding intermediate modulus CFRP.

While promising a potential for light-weighing applications in automobiles and aerospace, producing a large scale of aligned CNTs beyond laboratory is ultimately challenging. Recent attempts include University of Texas at Dallas (UTD) for growing CNT forests on a flexible stainless steel substrate [7] with a length more than 10 in, University of Cincinnati [8] for an electric driven double roller-belt apparatus for automatically drawing CNT sheets from CNT forests and depositing them on a substrate up to 300 mm x 2000 mm. Other efforts include growing CNT forests on silicon wafers wider than 2 in.

Nevertheless, real potentials of CNTs would rather be fully realized for structural applications when combined with carbon fibers. Yet, due to high aspect ratio of CNTs, incorporating a large amount of random CNTs into a structural polymer is very difficult. Aligned CNT sheets, on the other hand, could address this issue by being applied directly.
onto surfaces of a resin film and/or a resin impregnated reinforcing fibers, viz. a prepreg. In addition, due to their thinness they provide better flexibilities than CNT mats to be incorporated in the prepreg at a desired location.

This paper introduces aligned CNT parallel to the fiber’s direction as an interlaminar reinforcement to address both mode I and mode II interlaminar fracture toughness of CFRP. The importance of tube’s alignment and location of the CNT layer with respect to the carbon fiber bed in model prepregs with and without interlayer tougheners are discussed.

2 Materials and Methods

2.1. Materials

Spinnable non-functionalized MWCNT forests of about 400um tall were prepared by University of Texas at Dallas (UTD) on silicon wafers [1-3]. A model intermediate modulus carbon fiber was supplied by Toray Industries, Inc. (Japan). Two model aerospace-grade resin systems with and without interlayer tougheners were formulated by Toray Composites (America) Inc.

2.2 Methods

2.2.1. Prepreg fabrication with aligned CNT sheets.

A continuous dry aligned CNT sheet with a densified density of about 0.02 g/m² and up to 2-in wide was drawn from a CNT forest and transferred onto a roller wrapped around by a model resin film on a support paper (230 mm x 50 mm) as shown in Fig. 1. An infrared tachometer was placed above the rotating motor to count the number of turns. Maximum rotation was 15 rpm. Multiple turns of the CNT sheet was applied onto a certain area of the film to achieve an appropriate loading of CNTs before the next area was fabricated with the same number of turns. One turn represents one CNT sheet on the film.

Films with and without CNTs were impregnated onto a carbon fiber bed by a hot-melt process using heat and pressure. For other prepregs, CNT sheets were applied directly onto a prepreg’s surface. Table 1 shows all prepreg configurations in the present study. All prepregs have a fiber area weight (FAW) of 190 g/m² and resin content of 35 wt%. The fiber volume was about 55%.

2.2.2. Prepreg fabrication with random CNT sheets.

Non-functionalized random CNTs with a length between 1 to 10 um were mixed by a mechanical mixer in the same host resin as used for aligned CNTs. The modified resin was made into a film on a release paper by a knife coater. The films, one on each side, were impregnated onto a fiber bed.

2.2.3. Laminate fabrication and test methods.

Double cantilever beam (ASTM D 5528) and end notch flexure (JIS K 7086) were used to determine \( G_{IC} \) and \( G_{IIC} \), respectively. Twenty unidirectional (UD) plies were needed for these tests. A Teflon film was placed in the mid-plane of each stack at one end for crack initiation. The stack was cured in an autoclave at 180 °C for two hours with a ramp rate of 1.7 °C/min and pressure of 0.59 MPa.

For laminates with CNTs, only two plies with CNTs were placed in the center of each laminate where crack is propagating through during testing. Other plies were the corresponding control plies without CNTs.

2.2.2 Failure mode observation.

A Nikon OPTIPHOT-100 optical microscope was used to look at fracture surfaces. For higher magnification, a JEOL 7500F SEM was used to examine in-depth failure modes including alignment of CNTs, adhesion of CNTs to a resin, and distribution of CNTs in a laminate.

3. Results and Discussion

3.1. Aligned CNTs

3.1.1. Prepreg and laminate quality.

Fig. 2 shows an example of aligned CNT sheets deposited on prepreg #2. Good alignment of CNTs in the fiber’s direction was observed.

Fig. 3 shows an example of cross-section of a laminate made from prepreg #6, where the CNT layer comprising 100 CNT sheets was sandwiched between a zone without interlayer tougheners and a zone with interlayer tougheners. From the micrograph void content less than one percent
similar to laminate #4 (control) was observed, indicating a high quality laminate #6. In addition, the laminate had a layer of interlayer tougheners of about 20-25 um thick in the center, followed by two layers of CNTs, one on each side, of about 10-15 um. Note that since resin could impregnate these CNT layers, their thicknesses were increased about twice compared to a dry densified layer. As a result the total interlaminar thickness was about 40-55 um.

3.1.2. Prepreg without interlayer tougheners. Table 2 shows the normalized values of $G_{IC}$ and $G_{IC}$ of the laminates with CNTs to those of the control. Laminate #1 made from prepreg #1 is the control whereas laminates #2 and #3 were made from corresponding prepregs #2 and #3. These prepregs do not contain interlayer tougheners and have CNT sheets located at or away from the center of the laminate, respectively.

Laminate #2 with the CNT layer located at the center resulted in a significant reduction of $G_{IC}$. Optical micrograph in Fig. 4 indicates that crack propagated within the thick interlayer of the laminate of about 20-30 um (200 CNT sheets totally). SEM image in Fig. 5 confirms that no carbon fibers were exposed after fractured. In addition, there might be weak adhesion of CNTs to the resin. It was noticed that when the interlayer thickness was reduced to about 5 um (50 CNT sheets totally), some carbon fibers were exposed and yet crack still somehow propagated in the mid-plane, resulting in some fiber bridging. This increased $G_{IC}$ from the previous case, but still substantially lower than the control.

Laminate #3 with CNT layers located closer to carbon fibers compared to laminate #2 had $G_{IC}$ similar to laminates #2. For both configurations, improving adhesion between CNTs and resin could lead to an improvement in $G_{IC}$.

Compared to the control, laminate #2 provided a similar $G_{IC}$ similar to laminate #2 had $G_{IC}$ similar to laminates #2. For both configurations, improving adhesion between CNTs and resin could lead to an improvement in $G_{IC}$.

Compared to the control, laminate #2 provided a similar $G_{IC}$. For this case the thick interlayer (20-30 um) comprising CNTs alone could resist crack growth just as much as the control with much less of the interlayer thickness. Similar $G_{IC}$ value was rationalized for laminate #3 if the test was carried out. In either case, crack escaped the interlayer and propagating into the intraply. Better adhesion of CNTs to the resin might provide a higher $G_{IC}$.

3.1.3. Prepreg with interlayer tougheners. Table 2 shows the normalized values of $G_{IC}$ and $G_{IC}$ of the laminates with CNTs to those of the control. Laminate #4 made from the prepreg #4 having interlayer tougheners localized outside of the fiber bed is the control. Additionally, CNT layers were added to the prepreg #4 to make prepregs #5-7 and laminates #5-7, respectively. These laminates have CNT layers located in the center of the laminate (#5), in between two resin layers (#6), and in between the carbon fiber layer and the zone without interlayer tougheners (#7).

Similar to laminate #2 where CNT layers are located in the center, laminate #5 provided a significant $G_{IC}$ reduction. SEM images showed that crack propagated in the CNT layer and therefore, no carbon fibers were exposed after fractured. No $G_{IC}$ were obtained for laminates #6, 7, but it was rationalized that similar $G_{IC}$ could be obtained.

Interestingly, $G_{IC}$ was found to be significantly improved, especially when CNT layers were placed away from the mid-plane, behind the interlayer toughener layer (laminates #6, #7). The higher the amount of CNT sheets led to higher values of $G_{IC}$ more than 50% for these laminates, compared to the control. The substantial improvement in $G_{IC}$ could be due to a more compact interlayer toughener layer induced by CNT layers placed behind it as seen in Fig. 3. Since crack could not find resin rich areas to escape from and penetrate the intraply, it was contained in the mid-plane.

Fracture surfaces of laminates #6 and #7 with high loading of CNT sheets (about 3.7 wt% of total resin) were further examined to understand the failure mechanisms. Three cases responsible to a large coefficient of variation were found and summarized in Figs. 6-8. Fig. 6 shows an example of constant $G_{IC}$ values after the first crack. Note that value from first crack is typically excluded in the calculation of averaged $G_{IC}$. SEM images indicate that no carbon
fibers were exposed, i.e., crack was effectively contained in the interlayer. Fig. 7 shows an example of increasing $G_{IC}$ values after the first crack up to 100% compared to the control. SEM images indicate that some carbon fibers were exposed, leading to intraply delamination. However, crack growth was contained and therefore, no progressive intraply delamination occurred. Fig. 8 shows an example of substantially decreasing $G_{IIC}$ values from 70% higher than the control for the 2nd crack to 30% after the 4th crack. SEM images indicate that a significant amount of carbon fibers were exposed after 2nd crack (white area), i.e., crack was not effectively contained in the interlayer leading to progressive intraply delamination.

From observation of cured ply thickness from cross sections, it was rationalized that prepreg fabrication process could play a big role for the observed three cases. Better control of how aligned CNT sheets were applied onto resin films and subsequently better control of the hot-melt process to impregnate the CNT modified resin films onto fibers could have tightened coefficient of variation in $G_{IIC}$.

It was expected that for laminate #5 when CNT layers were in the center regardless of CNT loading, $G_{IC}$ would not be improved much from the control. It is because the CNT layer might not be effective enough to keep crack growth within this layer as seen in laminate #2. Crack, therefore, could escape this layer easily and propagate in the interlayer toughener layer located right behind, which results in a similar failure mechanism as the control. However, it was anticipated that the thickness of the CNT layer would be narrower compared to that of laminate #2 because the interlayer toughener layer could minimize resin flow into the CNT layer during cure. By having a denser CNT layer, crack might be contained better than laminate #2, which could give some improvement. Future work will look into this.

3.2. Random CNTs
3.2.1. Prepreg without interlayer tougheners. Table 3 shows the normalized values of $G_{IC}$ and $G_{IIC}$ of the laminates with CNTs to those of the control. Laminate #1 made from the prepreg #1 is the control whereas laminate #8 was made from corresponding prepreg #8. For laminate #8 where CNT are located in the center of the laminate, with an amount of CNT in the resin up to 1.9wt%, $G_{IC}$ did not improve versus the control. Yet, certainly it was better compared to similar laminate configurations with aligned CNTs (laminates #2, #3). $G_{IIC}$ on the other hand improved about 20% compared to the control and similar to laminate #2 with aligned CNTs. Effects of CNT alignment on $G_{IC}$ is, therefore, more significant than on $G_{IIC}$ for these prepregs without interlayer tougheners.

3.2.2. Prepreg with interlayer tougheners. Table 3 also shows the normalized values of $G_{IC}$ and $G_{IIC}$ of the laminates with CNTs to those of the control. Laminate #4 made from the prepreg #4 is the control whereas laminate #9 was made from corresponding prepreg #9. Construction of laminate #9 was similar to laminate #6 with aligned CNTs. However, laminate #9 contained about 3.0 wt% of random CNTs in the total resin compared to an estimate 3.7 wt% in laminate #6. Both $G_{IC}$ and $G_{IIC}$ for laminate #9 improved significantly compared to the control. Though $G_{IC}$ was not tested for laminate #6, it was expected to have a lower value than laminate #9. $G_{IIC}$ on the contrary, was much higher for laminate #6 than laminate #9 with a similar CNT loading. As a result, effects of CNT alignment seems to be more profound in $G_{IIC}$ than $G_{IC}$ for these prepregs with interlayer tougheners.

4 Conclusions
Aligned CNT sheets showed some promise to improve mode II fracture toughness when used with interlayer tougheners and placed between the interlayer toughener layer and the fiber layer. Good alignment of CNTs in the fiber’s direction was found to be important to maximize $G_{IIC}$ given a CNT loading. In addition, CNT sheet fabrication and prepreg process could play an important role. On the other hand, potential of CNT sheets to enhance $G_{IC}$ fracture toughness has not been realized, which might be due to their poor adhesion to the resin. Yet, random orientations of CNTs in prepregs without interlayer tougheners or thin CNT layer in prepregs with interlayer tougheners were shown to be in favor. Additional work is needed to confirm synergistic effects of CNT alignment and good adhesion of CNTs to the resin for both prepregs with and without interlayer tougheners.
Table 1 – All prepreg configurations (through thickness view) for the present study

<table>
<thead>
<tr>
<th></th>
<th>CNT location</th>
<th>Aligned CNT ½ prepreg configurations</th>
<th>Random CNT ½ prepreg Configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>No interlayer tougheners</td>
<td>Control</td>
<td>🟢</td>
<td>🟢</td>
</tr>
<tr>
<td></td>
<td>Mid-plane (outer most layer)</td>
<td>🟢</td>
<td>🟢</td>
</tr>
<tr>
<td></td>
<td>Contact fiber</td>
<td>🟢</td>
<td>🟢</td>
</tr>
<tr>
<td>With interlayer tougheners</td>
<td>Control</td>
<td>🟢</td>
<td>🟢</td>
</tr>
<tr>
<td></td>
<td>Mid-plane (outer most layer)</td>
<td>🟢</td>
<td>🟢</td>
</tr>
<tr>
<td></td>
<td>In-between</td>
<td>🟢</td>
<td>🟢</td>
</tr>
<tr>
<td></td>
<td>Contact fiber</td>
<td>🟢</td>
<td>🟢</td>
</tr>
</tbody>
</table>

Table 2 – Fracture toughness data of laminates with and without aligned CNT sheets. Average values of at least three coupons (three measurements per coupon) are shown.

<table>
<thead>
<tr>
<th></th>
<th>DCB</th>
<th>ENF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A (100 sheets) [3.7% in resin]</td>
<td>B (25 sheets) [0.96% in resin]</td>
</tr>
<tr>
<td>🟢</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>🟢</td>
<td>35</td>
<td>48</td>
</tr>
<tr>
<td>🟢</td>
<td>22</td>
<td>61</td>
</tr>
<tr>
<td>🟢</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>🟢</td>
<td>25</td>
<td>N/A</td>
</tr>
<tr>
<td>N/A</td>
<td>N/A</td>
<td>154</td>
</tr>
<tr>
<td>N/A</td>
<td>N/A</td>
<td>148</td>
</tr>
</tbody>
</table>
Table 3 – Fracture toughness data of laminate with and without random CNTs. Average values of at least three coupons (three measurements per coupon) are shown.

<table>
<thead>
<tr>
<th>Random CNT ½ prepreg configurations</th>
<th>DCB</th>
<th>ENF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>8 (CNT 1.9wt%)</td>
<td>100</td>
<td>119</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>9 (CNT 3.0wt%)</td>
<td>144</td>
<td>125</td>
</tr>
</tbody>
</table>

Fig. 1 – Fabrication of CNT sheets onto the surface of a roller

Fig. 2 – 100 CNT sheets of 0.02g/m² on the prepreg #2 shows substantial alignment of CNT in the fiber’s direction

Fig. 3 – Cross-sections of laminate #4 (control, top) and laminate #6 (bottom) from prepregs #4 and #6, respectively. Laminate #6 with 100 sheets of aligned CNTs (about 3.7 wt% in total resin) shows an interlayer toughener layer at the mid-plane of about 20-25 um thick and two CNT layers, one on each side, of about 10-15 um thick. Scale bar is 20 um.

Fig. 4 – Fracture surface of laminate #2 shows crack propagates in the CNT layer.
Fig. 5 – SEM image of fracture surface of laminate # 2 shows substantial alignment of CNTs in the fiber direction.

Fig. 6 – Fracture analysis of constant $G_{IC}$ after initial crack (#1). Scale bar is 1 um.

Fig. 7 – Fracture analysis of increasing $G_{IC}$ after initial crack (#1). Scale bar is 1 um.

Fig. 8 – Fracture analysis of decreasing $G_{IC}$ after initial crack (#1). Scale bar is 1 um.
References


