CARBON FIBER COMPOSITES
REINFORCED WITH CARBON NANOMATERIALS

H. Kim1*, H. T. Hahn2, E. Bekyarova3, E. Oh4, G. Lee4
1 Korea Institute of Science and Technology, Jeonbuk, Korea
2 Mechanical and Aerospace Engineering Department, UCLA, Los Angeles, USA
3 Carbon Solutions, Inc., Riverside, USA
4 Dept. of Chemical Engineeringartment, POSTECH, Pohang, Korea
* Corresponding author(hskim@kist.re.kr)

Keywords: Nanocomposites, Carbon fiber composites, carbon nanotubes, graphite

1 Introduction
Carbon nanotubes (CNTs) have been extensively investigated to increase the mechanical properties and the electrical conductivities of polymer materials. Graphite nanoplatelets (GNPs) are disk-like graphite structures whose thicknesses are less than 100 nm and planar dimensions range from few microns to tens of microns. GNPs have drawn interests of researchers since they can be more economical reinforcements compared to CNTs even prior to recent research craze about graphene. Also, CNTs and GNPs have been used to reinforce matrices of carbon fiber composites. This paper reviews published studies and authors’ work on processing – microstructure – property relationship for carbon fiber composites reinforced with carbon nanomaterials (CNMs) such as CNTs, carbon nanofibers (CNFs), and GNPs. The mechanical properties and electrical conductivities depending on different processing techniques are discussed for each case.

2 Processing
CNTs can be incorporated into carbon fiber composites by following methods:
· Mixed with resin followed by resin infiltration methods
· Directly grown onto carbon fibers by chemical vapor deposition (CVD) methods
· Deposited onto carbon fibers by electrophoresis
· Sprayed onto carbon fibers by electrostatic or air spray methods
· Transported (for aligned CNT forests) or sprayed onto prepregs

Fig. 1. shows multi-walled carbon nanotubes (MWCNTs) grown onto and perpendicularly aligned with a carbon fiber by a CVD method at POSTECH, Korea.

Fig. 1. MWCNTs perpendicularly grown onto carbon fibers by a chemical vapor deposition (CVD) method.

GNPs can be also integrated with carbon fiber composites by the similar methods. It should be noted that GNPs with rather large planar dimensions (> 5 microns) can be filtered by carbon fiber layers in case of resin infiltration methods due to their rather large planar dimensions (> 5 microns) and they should be deposited onto carbon fibers prior to a resin infusion process.[1]

In case of spraying CNMs onto prepreg surfaces, CNMs may not be distributed in the thickness direction due to insufficient resin flow during cure process.[2]

The mechanical properties of carbon fiber composites have not been always improved by using CNMs as expected considering superb mechanical
properties of individual CNMs.[3] The main reasons for this less-than-expected mechanical enhancement by using CNMs are as follows:

- Achieving good processing quality of carbon fiber composites by overcoming problems caused by adding CNMs.
- Achieving good dispersion and interfacial adhesion between CNMs and polymers.

A challenge is that the above two problems are closely related. For instance, the better a dispersion of CNMs in a resin system is, the higher the viscosity of the solution gets even at a very low concentration of the CNMs. This increased viscosity can cause voids inside of the composite after a resin infusion process such as a vacuum assisted resin transfer molding (VARTM) method.[4] On the other hand, reasonably low viscosity due to poor dispersion of CNMs in resin can lead to good quality of composite samples in terms of voids inside the composites but the mechanical properties of the composites should be poor due to CNM agglomerates in the composites.

Cumbersome dispersion process of CNMs can be avoided by direct deposition of CNMs onto carbon fibers prior to resin infusion. In this way, the high viscosity problem of the resin for resin infusion processes can be avoided as well. In case of CNTs directly grown onto carbon fibers, adhesion between CNTs and carbon fibers is also important for the mechanical properties such as the mode-I fracture toughness; otherwise, the presence of CNTs reduces the contact area between the fibers and the matrix and decreases the mechanical properties controlled by the interface between the fibers and the matrix.

3 Properties
3.1 Mechanical properties

As expected, it is not effective to improve fiber-dominant properties of carbon fiber composites such as the tensile properties by using CNMs since the mechanical properties of carbon fibers are usually two orders of magnitude higher than those of polymer matrices even after reinforced with CNMs.[3] However, the matrix-dominant properties such as the mode-I fracture toughness (resistance to delamination), the interlaminar shear strength (ILSS), and in-plane shear properties can be enhanced by using CNMs.

For an example, the mode I fracture toughness of carbon fiber composites was 2.5 times increased by inserting vertically aligned multi-walled carbon nanotube (MWCNT) forests between carbon fiber prepreg layers.[5] However, due to the long and stiff MWCNT layers, the thickness resin-rich region of the CNT samples was much larger than that of the control samples. This is a reason why processing – microstructure – property relationship is critical to verify the real reinforcement mechanism of carbon nanotubes in the fiber composites. In another study, a very large increase in the mode-I fracture toughness by growing CNTs perpendicularly onto SiC fibers was shown. However, only the initiating part of the crack propagation was used for the fracture toughness calculation.[6]

In an authors’ work, MWCNTs were grown onto carbon fibers as shown in Fig. 1, and the composites were processed using a VARTM method. From the results of this study, as long as the adhesion between CNTs and carbon fibers is not good, the presence of CNTs did not increase the mode-I fracture toughness of the carbon fiber composites even though CNTs were aligned perpendicularly to the carbon fibers (crack propagation direction). Despite of several studies that showed increased interfacial shear strength (IFSS) for CNT-grafted carbon fibers by pull-out test of single fiber/epoxy samples, we have not seen any reinforcement effect by using aligned CNTs on carbon fibers at least for the mode-I fracture toughness.[7][8] Only after the adhesion was enhanced, the mode-I fracture toughness showed consistent improvement, Fig. 3.

![Fracture toughness results of the composites with CNTs grown onto the carbon fibers.](image)

Fig. 3. Fracture toughness results of the composites with CNTs grown onto the carbon fibers.
Fig. 4. shows CNTs with good adhesion to carbon fibers are still attached to the carbon fibers even after the mode-I fracture toughness test.

Fig. 4. Strong adhesion between MWCNTs and carbon fibers (a fracture toughness tested sample).

Despite the fact that single-walled carbon nanotubes (SWCNTs) have higher mechanical properties and larger aspect ratios than MWCNTs, the composites with SWCNTs have always encountered a big challenge, achieving good dispersion of SWCNTs in the composites. Hence, the SWCNT/polymer composites have not seen much enhancement in the mechanical properties as expected. Carbon fiber composites with SWCNTs are not exceptions. From authors’ results, for ILSS, SWCNT-reinforced carbon fiber samples did not always show improvement over the control samples since increased viscosity of SWCNT/resin mixture and SWCNT agglomerates often caused voids inside the composites particularly for resin infusion methods.

Fig. 4 shows ILSS results of carbon fiber composites with or without SWCNTs. Increased viscosity of the resin due to dispersion of SWCNT in the epoxy resin might have caused voids during resin infusion process, Fig. 5. [4] And, ILSS is known to be sensitive to void contents of fiber composites. [9]

Fig. 4. Interlaminar shear strengths (ILSS) of the carbon fiber composites with or without SWCNTs

Fig. 5. (a) No voids in a sample without SWCNTs (x100) (b) Voids in a sample with 0.2 wt% SWCNTs (x100) (c) x500 micrograph of a sample with 0.2 wt% SWCNTs

For both CNTs and GNP, functionalization is critical for good bonding between CNMs and polymer matrices. A study shows that nitric acid treated GNP are observed to increase the in-plane shear strength of the carbon fiber composites while as untreated GNP deteriorated the property. [1]
3.2 Electrical conductivities

The electrical conductivities of carbon fiber composites can be increased by using CNMs particularly for the out-of-plane direction, whereas the electrical conductivities in the in-plane direction are not much affected by CNMs since the in-plane electrical conductivity is mainly controlled by highly conductive carbon fibers.[1,2,11] It should be noted that carbon fiber volume fractions can be more critical factor than CNMs for the out-of-plane electrical conductivity.[1,10] By this token, keeping consistent processing quality for each case of samples is really essential and fiber volume fractions or equivalent information should be reported for each case to discern the effect of CNMs on the out-of-plane electrical conductivities of carbon fiber composites. Reasonably good dispersion of CNMs is generally required to increase the electrical conductivities of the composites. However, poor dispersion of CNTs in the carbon fiber composites still lead to increased the out-of-plane electrical conductivities.[2] Table 1 summarizes the out-of-plane electrical conductivities of fiber composites using CNMs.

Table 1. Out-of-plane electrical conductivities of fiber composites with CNMs

<table>
<thead>
<tr>
<th>CNM type</th>
<th>Concentration (%)</th>
<th>Conductivity (S/m)</th>
<th>Processing, [ref]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GNP</td>
<td>0 wt%</td>
<td>2.1 (47.5 Vf)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0 wt%</td>
<td>3.9 (42.4 Vf)</td>
<td>GNP s sprayed onto fibers, [1]</td>
</tr>
<tr>
<td></td>
<td>2.0 wt%</td>
<td>15.5 (56.7 Vf)</td>
<td></td>
</tr>
<tr>
<td>SWCNT</td>
<td>0 wt%</td>
<td>0.8 (65 Vf)</td>
<td>SWCNTs sprayed onto prepregs, [2]</td>
</tr>
<tr>
<td></td>
<td>1.0 wt%</td>
<td>1.0 (65 Vf)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0 wt%</td>
<td>1.8 (65 Vf)</td>
<td></td>
</tr>
<tr>
<td>SWCNT</td>
<td>0</td>
<td>2.5</td>
<td>SWCNTs deposited onto fibers by electrophoresis [11]</td>
</tr>
<tr>
<td></td>
<td>0.25 wt%</td>
<td>4.9</td>
<td></td>
</tr>
</tbody>
</table>

(Vf: fiber volume fraction (%))

4 Conclusions and Discussions

Carbon fiber composites have already achieved high mechanical and electrical properties in the in-plane direction. However, their out-of-plane properties can still be increased further by using CNMs via effective processing techniques. It is also time to consider scale-up processing more seriously 20 years after the first discovery of CNTs. So far, aligned CNTs on carbon fibers have shown most promising results in mechanical property enhancement for carbon fiber composites, but this may be the most expensive method to incorporate CNTs into carbon fiber composites and has a limitation for scale-up processing. Hence, economical and effective processing methods should be devised further to see more real life applications of CNMs for carbon fiber composites.

References

