1 Introduction

Nanoparticles are now commonly used to blend with polymers/resins to form nanocomposites and thus improve their performance and properties which the neat polymers/resins do not possess. Mechanical, physical, thermomechanical properties have been shown to improve significantly by adding small wt fraction of nanoparticles [1-4]. Vaia and Maguire [1] explained the polymer nanocomposite morphologies exhibiting random dispersion of three dimensions such as spherical (0 dimension), rod-like (1-D) and plate-like (2-D) and comprehended the morphologies to control their properties. Kaush et al. [2] studied the effect of nanoparticle size on the mechanical behavior of nanocomposites. Their study showed the importance of nanoparticle shape and relation to the mechanical properties. However, it does not completely explain the effect in terms of differences in properties.

Carbon fiber reinforced plastics (composites) are used in applications where high specific performance is needed. It is understood that the mechanical properties of composites not only depend on the properties of the fibers and resin but also on the fiber/resin interfacial property. Interfacial property between resin containing nanoparticles and carbon fiber is not well understood.

In the present work, we have characterized the effect of halloysite nanotubes (HNT) on the mechanical properties of nanocomposites and fiber/resin interfacial property using the single fiber composite (SFC) method. These properties were compared to SiO2 and clay modified epoxy nanocomposites which have been reported earlier.

2 Experimental

2.1 Materials

Carbon fibers (T300, obtained from TORAY, Decatur, AL, USA) were used in this study. Fiber diameter was approximately 5.94 μm. Two types of epoxy resins, DER 331 and DER 732 and hardener DEH 26 were also used. Both resins and hardener were provided by Dow Chemical Company (Midland, MI, USA). In addition, HNT, obtained from Nanoclays Technology Inc., Utah, were used.

2.2 Plasma treatment

A Harrick Plasma system (Ithaca, NY, USA, PDC-3XG) was used for the fiber surface modification. Ammonia/ethylene (NH3/C2H4) gas mixture was used to obtain a uniform polymer coating on the carbon fiber surface [5, 6]. The fixture with the fibers was placed inside a plasma chamber. The chamber was then pumped down to 20 Pa. Ammonia and ethylene gases were introduced into the chamber at 3:1 ratio so as to obtain a thin polyethylene-like layer with NH2 functional groups on fiber surface. The total gas flow rate was maintained at 40 cm3/min. Once the gas flow was stabilized, the RF power was turned on, thus starting the plasma deposition. The polymer coating deposition was performed at 66 Pa with 66 W power for 30 min, with a deposition rate of approximately 4 nm/min [5]. After the deposition was complete, RF power was turned off and the chamber was purged with pure NH3 gas for 5 min to ensure functionalization of any remaining unsaturated bonds on the fiber surface.

2.3 Fabrication methods

Dried HNT were added into the hardener. These were stirred for 1 hr at 1500 rpm using a mechanical stirrer and then ultrasonicated for 2 hrs to obtain homogeneous dispersion. Blended epoxy resin (DER331:DER732::70:30) was stirred with hardener with and without HNT (Epoxy resin: DEH26::100:12.7). The nanocomposite mixture was then degassed and then pipetted into the SFC mold. The SFC specimens were cured in an air circulating oven for 3 hrs at 80°C, followed by additional 2 hrs at 100°C for postcure. After curing process, specimens were slowly cooled down to room temperature.

2.4 Test methods

To investigate the effect of HNT loading on the mechanical properties of epoxy resin, tensile tests
were performed at a strain rate of 0.1 min$^{-1}$. Specimen gauge length was 15 mm.

SFC tests were performed using a manual strain frame specially designed for the test [3]. Specimen gauge length was 19 mm. During the test, the SFC specimen was mounted on an optical microscope equipped with polarizer/analyzer combination kept at 90\(^\circ\) to each other and a digital camera to monitor the fiber fragmentation process and birefringence patterns at the carbon fiber/epoxy resin interface. The SFC test was considered complete when no further fiber breaks were observed for about 1.5% additional strain.

3 Results and discussion

3.1 Tensile properties of epoxy resins

Figure 1 shows typical stress-strain curves for epoxy resin with different HNT loadings. The initial part of the plot is straight for all specimens but all of them showed significant yielding. It is interesting to note that the yield point decreased with HNT loading. For neat epoxy specimens the yield point is around 7% strain whereas for specimens with HNT the yield point steadily moved lower as the HNT loading increased. For specimens with 2% HNT the yield point was about 5.54%. While HNTs are randomly dispersed in the epoxy they are comparable to molecules in size. When the resin is being strained, the HNTs that are at an angle to the direction of the stress begin to rotate and align with the stress. As they rotate, the crosslinked epoxy resin may not be able to deform resulting in failure at the interface. As mentioned earlier HNT/resin bond may not strong [7]. As they rotate they also create space surrounding individual HNTs as depicted in Fig.2. That space, also in nm size, can be termed as free volume, in polymer terms. This newly generated free volume lowers the glass transition temperature (Tg) of the epoxy resin. During the tensile test, at the yield point the polymer is considered to be at its Tg, and hence it yields. It is intuitive that as we increase the HNT loading the free volume generated will increase in approximately the same proportion as each HNT will create its own free volume around itself. That means the Tg of the specimen will be lowered as the HNT content is increased resulting in lower yield point. This is exactly what is seen in these experiments. Such lowering of the yield point is commonly observed in polymeric fibers when tensile tested at different strain rates. In this case because the Poisson’s ratio of the polymer, which is not rubbery, is lower than 0.5, when strained, the fiber volume increases as its diameter cannot go down in proportion to the increased strain, resulting in higher volume. The higher volume is generated through creating new free volume. At higher strain rate this effect is more pronounced resulting in lower yield point.

Tensile strength decreased with HNT loading. These results indicate that higher HNT content causes failure as a result of clustering. Thus, there is a limit of HNT content. The improvement in Young’s modulus can be attributed to good HNT dispersion. The orientation of HNT can also contribute to the reinforcing effect. The crack bridging indicates poor interfacial interaction between HNT and epoxy resin. As a result, this effect supports lower fracture strain.

![Fig. 1 Stress-strain curves of nanocomposites with different HNT loadings](image)

![Fig.2 Schematic diagrams showing HNT rotation creating free volume during tensile test](image)
results show similar Young’s modulus. Tensile strengths of HNT and clay nanocomposites show lower values than that of SiO₂. Kaush et al. [2] reported that tensile strength decreases with increasing particle size. Bigger particles seem to be easy to become origin of fracture. The fracture strains of HNT nanocomposites in Fig. 5 keep same level as HNT contents change because HNT works perhaps as a better crack bridging agent.

![Image](image1.png)

**Fig.3** Comparison of Young’s modulus in nanocomposites

![Image](image2.png)

**Fig.4** Comparison of tensile strength in nanocomposites

![Image](image3.png)

**Fig.5** Comparison of fracture strain in nanocomposites

### 3.2 Interfacial shear strength of untreated fibers

SFC tests and fiber fragment length measurements were performed on four HNT loading conditions. The average fragment length, fiber diameter, calculated tensile strength values at average critical fragment lengths and IFSS for all the HNT loadings are presented in Table 1. Typical birefringence patterns during SFC test showed approximately 30 fragment lengths. Intensity of birefringence patterns decreased with HNT loading and the sharpness reduced, as a result of clustering or incomplete exfoliation which reduces the transparency. As a result, the carbon fiber and patterns were not clearly visible and measurements were difficult at a loading of 2.0%. The tensile strength at average critical fragment lengths were calculated from the linear fit obtained from tensile test of single carbon fiber. The IFSS values were calculated using Kelly-Tyson equation [8]. As can be seen from the data, IFSS values increase slightly by the addition of HNT. This is because of stiffening of epoxy resin as explained earlier [7]. The increased stiffness of the resin promotes debonding at the interface as the resin cannot take the shock of fiber fracture [17]. The debonding increases the fragment length as the stress cannot build up along the fiber length to break the fragment further. These two actions mitigate each other. As a result, the critical fragment length and hence the IFSS does not change much.

<table>
<thead>
<tr>
<th>HNT loading (%wt)</th>
<th>Critical length (μm)</th>
<th>Fracture strength (MPa)</th>
<th>Fiber diameter (μm)</th>
<th>IFSS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>464 (22)</td>
<td>5018 (0.26)</td>
<td>6.10 (1.9)</td>
<td>30.3 (5.5)</td>
</tr>
<tr>
<td>0.25</td>
<td>437 (22)</td>
<td>5049 (1.24)</td>
<td>5.93 (2.8)</td>
<td>33.6 (24)</td>
</tr>
<tr>
<td>1.0</td>
<td>479 (10)</td>
<td>5035 (0.57)</td>
<td>6.07 (1.7)</td>
<td>32.2 (9.8)</td>
</tr>
<tr>
<td>1.5</td>
<td>452 (8.9)</td>
<td>5052 (0.52)</td>
<td>5.97 (4.7)</td>
<td>33.7 (11)</td>
</tr>
</tbody>
</table>

( ) Values are coefficients of variation.

### 3.3 Interfacial shear strength of plasma-treated fibers

Ammonia/ethylene plasma polymer-coated fibers were embedded in epoxy resin with and without HNT to fabricate SFC specimens and the tests were performed. It is known that the plasma polymerization does not affect the tensile properties of carbon single fiber as it just provides a thin coating on the fiber [5]. Approximately 80 fragment patterns were observed during the SFC test in the case of plasma treated carbon fibers. These patterns show significantly shorter fragment lengths than those obtained for untreated carbon fiber SFC specimens, suggesting a higher stress transfer and better interaction between the fiber and matrix compared to untreated fibers. This is because of the significantly higher fiber/resin...
interaction between the plasma polymer layer as a result of amine groups reacting with the epoxy resin creating covalent bonds [3, 4]. The resin crack at the fiber fracture location and birefringence patterns were similar to those obtained for untreated carbon fiber SFC specimens. However, very little debonding was observed along the length of the fiber. Thus strong interface was obtained by the ammonia/ethylene plasma treatment.

The average fragment length, fiber diameter, calculated fiber tensile strength values at average critical fragment lengths and IFSS for all the HNT loadings are presented in Table 2. IFSS for 0% HNT loading is 72.5 MPa which is 2.4 times the 30.3 MPa obtained for untreated fiber. Comparing the data in Table 1 and Table 2, it is apparent that the plasma treatment of fibers increases in the IFSS significantly. The IFSS values slightly increased with HNT contents but the increase is not significant. Again, as explained earlier, this is because of the two mitigating factors, namely, stiffening of the epoxy resin by the addition of HNT which increases the IFSS and some debonding which decreases the IFSS. Similar results were also obtained by Piggott [28] who used a different epoxy resin and a different test, single fiber pull out, to obtain IFSS values.

Table 2 Interfacial shear strength from SFC test

<table>
<thead>
<tr>
<th>HNT loading (% wt)</th>
<th>Critical length (µm)</th>
<th>Fracture strength (MPa)</th>
<th>Fiber diameter (µm)</th>
<th>IFSS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>222 (12)</td>
<td>5256 (0.64)</td>
<td>6.06 (1.1)</td>
<td>72.5 (13)</td>
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<tr>
<td>0.25</td>
<td>225 (11)</td>
<td>5252 (0.62)</td>
<td>6.33 (3.0)</td>
<td>74.5 (12)</td>
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<tr>
<td>1.0</td>
<td>208 (3.2)</td>
<td>5274 (0.17)</td>
<td>6.18 (3.1)</td>
<td>78.6 (4.8)</td>
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<tr>
<td>1.5</td>
<td>222 (15)</td>
<td>5257 (0.75)</td>
<td>6.07 (3.1)</td>
<td>72.9 (13)</td>
</tr>
</tbody>
</table>

( ) Values are coefficients of variation.

4. Conclusions

In this paper, effect of HNT loading in epoxy resin on its tensile properties as well as interfacial property with carbon fiber has been investigated. Effect of NH3/C2H4 plasma polymer coating on carbon fiber in the epoxy resin with different HNT loading was also characterized. The major conclusions are as below:

1. HNT loading increased Young’s modulus up to a loading of 0.25%. After that it decreased as a result of clustering. The tensile strength of epoxy nanocomposites decreased steadily with HNT loading.
2. Carbon fiber/epoxy resin IFSS increased slightly by adding HNT.
3. IFSS of NH3/C2H4 plasma polymer treated carbon fibers was significantly higher (about 150%) than that obtained for untreated carbon fibers.
4. The increase in the IFSS of the plasma treated carbon fiber/epoxy resin IFSS was independent of HNT loading.

References