Interfacial Bonding Property Study of Functionalized Cnt Nanocomposites Based on a Modified Cox's Model

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INTERFACIAL BONDING PROPERTY STUDY OF FUNCTIONALIZED
CNT NANOCOMPOSITES BASED ON A MODIFIED COX’S MODEL

By

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To my parents who sacrifice so much for me and to my husband for his constant support and encouragement
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ABSTRACT

Many researchers have studied the interfacial shear stress (ISS) in nanocomposites through theoretical calculation, computational simulation or sophisticated nanomanipulation experiment measurement. In this research, we attempt to directly calculate ISS values in actual nanocomposites based on a modified Cox’s model using tensile test results of various macroscopic carbon nanotube (CNT) nanocomposites. Young’s modulus, tensile strength and strain of CNT ropes rather than individual CNT properties were applied into the model. The effects of functionalization, CNT rope length, volume fraction and CNT type (SWNT, DWNT, MWNT) on interfacial shear stress were studied. It was found that the functionalization increased the mechanical properties of both interfacial bonding and DWNT and MWNT rope themselves; however, it decreased the mechanical properties of SWNT ropes. The major failure mode of the CNT nanocomposites was identified to be CNT rope rupture. The calculation results revealed that the ISS values in the nanocomposites are comparable with the ones reported in literature.

Keywords: Interfacial shear stress, functionalization, carbon nanotube, nanocomposites, epoxy
CHAPTER 1

INTRODUCTION

1.1 Motivation

Carbon nanotubes (CNTs) possess excellent mechanical properties, such as high Young’s modulus and tensile strength. Due to their high aspect ratios, CNTs have much larger surface area per unit volume than that of the traditional reinforcement fibers. For example, CNTs of 30nm diameter have about 150 times more surface area than fibers of 5μm diameter for the same volume [1]. This makes the CNT composites have a much larger interface area than that of the traditional fiber-reinforced composites with the same reinforcement volume fraction.

Interface in CNT nanocomposites is a very thin layer between the CNT surface and the matrix as shown in Figure 1.1 [2]. The polymer near interface, which called interphase, has different chemical and physical properties from the bulk polymer due to interactions with CNTs. As shown in Figure 1.2, the interphase polymer of CNT composites takes a much greater volume percentage than that of carbon fiber composites at the same fiber volume fraction due to CNT’s exceptional large surface [1]. So the interfacial region should play an important role in the nanocomposites.

Figure 1.1 SEM fracture surface of PC/MWNT
Figure 1.2 Fraction of polymer in the interphase region as a function of volume fraction of fiber and CNT inclusions, where $t$ is the interphase thickness and $r_f$ is the radius of the nanotube/fiber inclusions.

A shear stress will be formed on the interface, which is called interfacial shear (ISS) stress due to mismatch of reinforcement and matrix modulus when the composites are stretched. There are three major mechanisms of interfacial shear stress. The first one is van der Waals force and electrostatic interaction between the reinforcement and matrix. The second one is chemical bonding, which is an effective way to increase interfacial shear stress. The third one is micromechanical inter-locking. This may be difficult in CNT composites due to CNT’s smooth surface.

Exceptional mechanical properties of CNTs do not necessarily lead to high-performance of CNT nanocomposites. Whether or not the high modulus and high strength of CNTs can be fully utilized depends up on load transfer efficiency from matrix to CNTs. Interface is the media of load transfer and thus critically influences both the mechanical properties and failure mode of the nanocomposites.

How does the load transfer work? Let’s make a comparison, in Figure 1.3 (a) there are no CNTs in the matrix, which means it is a neat resin case. The external force will completely impose on the matrix. When the force reaches the matrix tensile strength ($\sigma_m$), the material will be broken. However, in Figure 1.3 (b) if CNTs are introduced as reinforcement, most of the external force will be transferred to CNTs from the matrix and the matrix just takes a little portion of the force. Then the material can sustain a much higher load than the matrix alone, hence the strength of the composite is enhanced.
Interfacial shear stress has a great effect on load transfer ability and hence on composite properties. As shown in Figure 1.4 [2], in CNT composites as well as in SiC fiber composite, carbon fiber composite and glass fiber composite, if interfacial shear stress is very weak, the composite elastic modulus is almost the same with the matrix elastic modulus. However, with stronger interfacial shear stress, the composite elastic modulus will be higher. Compared with the other three kinds of fiber-reinforced composites, if the interfacial shear stress is 50MPa or less, there is no obvious difference for the improvement of composite elastic modulus between fiber composites and CNT composites due to limited load transfer capability in CNT nanocomposites. The CNT composites just present the outstanding modulus with much higher or perfect interfacial shear stress.
There are three possible failure modes in CNT composites, including matrix failure, CNT rupture and interface failure. If the interfacial shear stress is not strong enough, it will cause interface failure. In this case, neither the matrix strength nor CNT’s excellent strength get fully utilized.

In summary, interface property is important for developing high-performance CNT nanocomposites. It is important to quantitatively analyze and to improve load transfer ability and avoid interface failure in CNT nanocomposites.

### 1.2 Technical Challenges

There are several unique challenging issues and problems involved studying the interfacial shear stress in CNT composites. This research will discuss five of them.

First, due to the very small dimension of CNTs and the difficulty in getting an individual nanotube, it is difficult to directly measure interfacial shear stress by conventional experimental methods.
Second, in traditional fiber-reinforced composites, the calculations of interfacial shear stress are already fairly developed; however, those calculations may not be valid for CNT composite due to the hollow structure of CNTs and large aspect ratio.

Third, it is known that CNT functionalization could increase the composite modulus and strength. However, the functionalization effect on interfacial shear stress is still not fully understood. Therefore the adequate functionalization degree to achieve a perfect interface and avoid over functionalization, which may damage nanotubes and decrease the intrinsic mechanical properties of nanotubes, is not known.

Fourth, literature reports show much low mechanical performance in CNT nanocomposites, compared with expected reinforcement effect. According to the modified Rule of Mixture (Equation 1.1) [3], $\sigma_c$ should increase significantly with introducing a little amount of CNTs, but the experimental results show that the improvement is very limited. This is largely due to the interface load transfer problem.

$$\sigma_c = 1/5 \sigma_{CNT} * V_{CNT} + \sigma_m * (1-V_{CNT}) \quad (1.1)$$

Where $\sigma_c$ is the interfacial shear stress, $\sigma_{CNT}$ is the tensile strength of CNTs, $V_{CNT}$ is the volume fraction of CNTs and $\sigma_m$ is the tensile strength of matrix in a randomly oriented CNT nanocomposites.

Fifth, there are many controversial ISS results of CNT nanocomposites in the literature reports. Many researchers have concluded that interfacial shear stress of CNT composites even without chemical bonding is strong enough, but some other researchers have suggested the interfacial shear stress is very weak. There is a large variation range of interfacial shear stress values reported in literature as shown in Figure 1.5 [4-20]. The results are summarized in three major technical approaches: experimental approach; molecular mechanics (MM) and molecular dynamics (MD) methods and continuum media modeling methods. We will discuss in details of each approach in the later sections.
From Figure 1.5, we could see that most of the interfacial shear stress reported is greater than 50MPa, which is the shear strength in neat epoxy resin, but the results are scattering in a large range. There is no validation effort to conform these results.

1.3 Research Objective

In this research, the interfacial shear stress of CNT nanocomposites for both pristine CNT (P-CNT) and functionalized CNT (F-CNT) are studied. The results will be used to guide the design of strong interface and development of high-performance CNT composites to efficiently utilize CNT exceptional mechanical properties. The major objectives include:

- Identify and use a model to calculate the interfacial shear stress (ISS) of pristine and functionalized CNT nanocomposites with different types of CNTs (SWNT, MWNT, DWNT);
- Determine whether the interfacial strength of CNT nanocomposites is adequate or not based on the properties of CNT nanocomposites and failure mode observations;
• Reveal the effect of CNT types, CNT length, CNT volume fraction and functionalization on ISS values;

• Reveal the relationship between the ISS value and the mechanical properties of the resultant CNT nanocomposites;

• Explore the failure modes of CNT nanocomposites.

The research will advance the understanding and knowledge of interfacial bonding and load transfer to guide design of adequate interfacial bonding and load transfer in CNT composites.
CHAPTER 2

LITERATURE REVIEW

2.1 Experimental Methods of Evaluating ISS for Fiber-Reinforced Composites

The experimental measurements of ISS for traditional fiber-reinforced composites such as push-out test, pull-out test, microbond test and fragmentation test are already fairly well developed.

In a push-out test [21], as shown in Figure 2.1, an indenter is used to push on the fiber end to push it out from the matrix. During the test, the applied load and the indenter tip displacement are continuously monitored, which provides a force-displacement curve as shown in Figure 2.2. By measuring the maximum applied force $F_{\text{max}}$, the embedded fiber length $L_{\text{emb}}$ and the fiber diameter $D$, the interfacial shear stress $\tau$ can be calculated from:

$$\tau = \frac{F_{\text{max}}}{\pi DL_{\text{emb}}} \quad (2.1)$$

Figure 2.1 (a) Schematic representation of SEM fiber push-out setup
(b) SEM image of push-out test on E-glass/epoxy composites
Figure 2.2 Applied loads as a function of tip displacement for E-glass/epoxy composites in a push-out test

In a pull-out test, as shown in Figure 2.3, the pull-out is performed at a constant speed using a controlled load cell [22]. A computer controlled plotter is used to record the pull-out load against displacement. The calculation is the same as Equation 2.1.

Figure 2.3 Schematic diagram of single fiber pull-out test specimen
In a microbond test, as shown in Figure 2.4, a cylinder matrix is placed directly on the fiber and is held by the knife edges from the top side of the fiber during the test [23]. The calculation is still the same as in push-out test Equation 2.1.

![Figure 2.4 Schematic view of the microbond test](image)

In a fragmentation test [24], a composite specimen which just includes a single fiber filament is subjected to axial tensile load. After tension, the fiber will be broken into several fragments; the fragment length is the critical length, which can be measured by optical microscope or TEM as shown in Figure 2.5. Then the interfacial shear stress can be calculated from:

\[
\tau = \frac{\sigma_f d}{2l_c} \quad (2.2)
\]

Where \(\tau\) is the interfacial shear stress, \(\sigma_f\) is the tensile strength of fiber, \(d\) is the diameter of fiber and \(l_c\) is the critical length of fiber.
Figure 2.5 Fiber fragmentation test (a) Typical optical photomicrograph showing the birefringence pattern around fiber fracture (b) The associated photomicrograph under transmitted light showing multiple break points

Table 2.1 shows the interfacial shear stress for different epoxy composite systems [25]. The materials and specific stress determined are noted. It can be seen that all of the interfacial shear stress is less than 75MPa, which is about the tensile strength of epoxy resin. With such ISS performance, fiber-reinforced composites can reach good mechanical properties; hence the interfacial shear stress is adequate.
Table 2.1 Experimental ISS values for fiber-reinforced composites (in MPa)

<table>
<thead>
<tr>
<th>System</th>
<th>$\tau_{\text{head}}$</th>
<th>$\tau_{\text{pull-out}}$</th>
<th>Comments</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass/poly(butylene terephthalate)</td>
<td>31.1</td>
<td></td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>Kevlar 29/DGEBE epoxy</td>
<td>40</td>
<td></td>
<td></td>
<td>41</td>
</tr>
<tr>
<td>Kevlar 49/DGEBE epoxy*</td>
<td>41.1</td>
<td></td>
<td></td>
<td>41</td>
</tr>
<tr>
<td>Celion/DGEBE epoxy*</td>
<td>65.3</td>
<td></td>
<td></td>
<td>41</td>
</tr>
<tr>
<td>Stainless steel/epoxy*</td>
<td>20</td>
<td></td>
<td></td>
<td>33</td>
</tr>
<tr>
<td>Glass/DGEBE*</td>
<td>33.1</td>
<td></td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>Kevlar/DGEBE epoxy*</td>
<td>39.3 ± 7.8</td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Kevlar/DGEBE epoxy*</td>
<td>21.6 ± 0.51</td>
<td></td>
<td>With release agent</td>
<td>57</td>
</tr>
<tr>
<td>Copper/epoxy</td>
<td>1.4</td>
<td></td>
<td></td>
<td>57</td>
</tr>
<tr>
<td>Copper/epoxy*</td>
<td>0.13</td>
<td></td>
<td></td>
<td>57</td>
</tr>
<tr>
<td>Carbon/DGEBE epoxy*</td>
<td>27</td>
<td></td>
<td></td>
<td>61</td>
</tr>
<tr>
<td>Steel/epoxy*</td>
<td>21.8</td>
<td></td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>Nickel/epoxy</td>
<td>3.6 \times 10^9</td>
<td></td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>Glass/epoxy</td>
<td>21 ± 5</td>
<td></td>
<td>No heat</td>
<td>51</td>
</tr>
<tr>
<td>Glass/epoxy*</td>
<td>34 ± 10</td>
<td></td>
<td>24 h at 60°C</td>
<td>51</td>
</tr>
<tr>
<td>Glass/polyester*</td>
<td>7 ± 7</td>
<td></td>
<td>No heat</td>
<td>51</td>
</tr>
<tr>
<td>Glass/polyester*</td>
<td>10 ± 5</td>
<td></td>
<td>6 h at 80°C</td>
<td>51</td>
</tr>
<tr>
<td>Carbon/DGEBE epoxy*</td>
<td>21.2 ± 4.5</td>
<td></td>
<td>$T_{\text{cure}} = \text{r.t.}$</td>
<td>56</td>
</tr>
<tr>
<td>Carbon/DGEBE epoxy*</td>
<td>40.6 ± 7.8</td>
<td></td>
<td>$T_{\text{cure}} = 60^\circ\text{C}$</td>
<td>56</td>
</tr>
<tr>
<td>Carbon/DGEBE epoxy*</td>
<td>30.0 ± 9.0</td>
<td></td>
<td>$T_{\text{cure}} = 120^\circ\text{C}$</td>
<td>56</td>
</tr>
<tr>
<td>Carbon/DGEBE epoxy*</td>
<td>58.4 ± 12.8</td>
<td></td>
<td>$T_{\text{cure}} = 165^\circ\text{C}$</td>
<td>56</td>
</tr>
<tr>
<td>Carbon/DGEBE epoxy*</td>
<td>66.6 ± 10</td>
<td></td>
<td>$T_{\text{cure}} = 180^\circ\text{C}$</td>
<td>56</td>
</tr>
<tr>
<td>Stainless/epoxy*</td>
<td>1.13 \times 10^7 kg mm$^{-2}$</td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>ALU carbon/DGEBE epoxy*</td>
<td>24.1$^*$</td>
<td></td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>AS carbon/DGEBE epoxy*</td>
<td>74$^*$</td>
<td></td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>AS (300) carbon/DGEBE epoxy*</td>
<td>71.7$^*$</td>
<td></td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>AS (600) carbon/DGEBE epoxy*</td>
<td>68$^*$</td>
<td></td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>AS (750) carbon/DGEBE epoxy*</td>
<td>65.58$^*$</td>
<td></td>
<td></td>
<td>18</td>
</tr>
</tbody>
</table>

*Shell Epon 828
$^*$Not specified
$^{**}$Ciba-Geigy 6610 and Aldrich triethylene tetramine
$^+$Ciba-Geigy Araldite 502 with hardener 996
$^*$Shell Epon 815 with Ancamine XT
/ OGBA + BAS-A MY750
$^+$Debond plateau
$^*$Interfacial shear stress measured by critical length tensile test

However, the above methods are difficult to directly apply in CNT composites due to CNT’s nanoscale dimensions, many entanglements and interaction among CNTs.

### 2.2 Experimental Methods for ISS Study of CNT Nanocomposites

Experimental studies both qualitatively and quantitatively have been conducted and provided some insights into the interfacial bonding properties of CNT nanocomposites. Most experimental results suggest that the interfacial shear stress of CNT nanocomposites is strong, while some other research implies the interfacial shear stress is weak. What’s the benchmark of an adequate interfacial shear stress in CNT nanocomposites? Phenomenally, if there is some resin still on the surface of a CNT when it is pull out from matrix or the CNT is ruptured, the interfacial shear stress is strong. On the other hand, if the pull-out CNTs have a clean surface and there are maybe lots of pull-out holes left in the resin matrix,
we consider the interface is weak. From actual ISS value, the interface is strong if the interfacial shear stress is greater than the matrix strength and leads to high stress level in CNTs; if not, the interfacial shear stress is weak.

**2.2.1 Strong Interface Evidences**

Strong interface evidences were observed as the CNTs bonded with matrix resin. W. Ding et al. reported a wonderful image as shown in Figure2.6 [26]. It is shown that a thin functionalized tube was covered with a thick polymer when protruding from the fracture surface. Upon close examination of the fracture surface of a MWNT/epoxy composite, M. Wong et al. observed most pullout ends were covered by epoxy as shown in Figure2.7, indicating failure of the matrix but not the CNT-epoxy interface [14]. This group also observed the CNT diameters were not uniform because of the coverage of epoxy resin as in Figure2.8 [14]. C.Bower et al. showed the polymer wetted the CNTs very well to form an intimate contact as illustrated in Figure2.9 [27]. The CNTs pulled the polymer out when it was pull out. A further evidence for a strong interaction is from microscope pull-out experiment reported by F.H. Gojny et al.[28]. In Figure2.10, they observed the outer shell of MWNT is directly bonded to the matrix, while the inner tubes is pulled out from the outer shell, implying the interfacial shear stress is stronger than the interactions between the shells of a MWNT.

![Figure2.6 SEM of CNT/PS bundle fracture surface](image1)

![Figure2.7 SEM of MWNT/polycarbonate composites](image2)
Strong interfaces are also indicated as the appearance of CNT ruptures. Lourie and Wagner first showed MWNT fragmentation in epoxy matrix as in Figure 2.11, implying that force was transmitted to the CNTs from the surrounding matrix [29]. In another paper, these authors provided evidence of significant polymer-nanotube wetting and interfacial adhesion as shown in Figure 2.12; fracture of SWNT rope occurred in tension within the whole polymer region rather than in shear within the gripping polymer region at the ends of the bundles [30]. This group also observed rupture of a MWNT with the intact walled-polymer interface in Figure 2.13 [4]. Z. Jia et al. demonstrated there is a strong interface between the CNTs and the PMMA matrix, because there are no naked CNTs on the fracture surfaces of the composite samples as shown in Figure 2.14 [31].
2.2.2 Weak Interface Evidences

Weak interface evidences were also reported by several groups. CNTs were pull out from the matrix with very clean nanotube surface; there are lots of voids left in the resin matrix, suggesting the load transfer from matrix to CNTs is very low. This phenomenon was observed by F.H. Gojny et al. [28] and this study as shown in Figures 2.15, 2.16 respectively.
2.2.3 Experimental Measurements of Interfacial shear stress in CNT Nanocomposites

Until now, all experimental methods of the nanotube-polymer interfacial shear stress are indirect measurements due to the nanoscale dimension and dispersion problems. Barber et. al. [5] used AFM to conduct a nanopull-out experiment as shown in Figure 2.17. The plotted $F_{\text{max}}$ is against $A_{\text{emb}}$ as shown in Figure 2.18, so the interfacial shear stress can be directly calculated as

$$F_{\text{max}} = \tau A_{\text{emb}} \quad (2.3)$$

Where $F_{\text{max}}$ is the maximum pullout force, $\tau$ is the interfacial shear stress and $A_{\text{emb}}$ is the CNT embedded surface area.

They calculated an average ISS value from the slope of the liner fitted in Figure 2.17, which is about 47 MPa. This interfacial shear stress is about ten times greater than the tensile strength of the matrix. This is a direct measurement of CNT ISS values.
Using a modified Kelly-Tyson model as shown in Equation 2.4, Wagner et al. estimated the interfacial shear stress is of the order of 500 MPa and up, thus, an order of magnitude higher than the interfacial shear stress of current fiber reinforcement advanced composites [4].

\[
\tau_{NT} = \left( \frac{\sigma_{NT} (l_c)}{2(l_c/D_{NT})} \right) \left( 1 - \frac{d_{NT}^2}{D_{NT}^2} \right)
\]  

(2.4)

Where \( \sigma_{NT} \) is CNT tensile strength, \( l_c \) is the critical length of CNTs, \( d_{NT} \) is the inner diameter of CNTs and \( D_{NT} \) is the outer diameter of CNTs.

More recently Copper et al. showed that interfacial shear stress between MWNT and epoxy matrix ranged from 35-376 MPa as shown in Table 2.2, from the pullout experiments using scanning probe microscope tips [7]. The same tests were also run on SWNT/epoxy composite and found that only one SWNT rope could be pulled out, which interfacial shear stress is about 366 MPa, however, the rest 6 ropes underwent fracture.
<table>
<thead>
<tr>
<th>Specimen</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (μm)</td>
<td>8.2</td>
<td>11.0</td>
<td>24.0</td>
<td>13.4</td>
<td>13.4</td>
<td>24</td>
<td>11.6</td>
</tr>
<tr>
<td>Embedded length (mm)</td>
<td>484</td>
<td>256</td>
<td>2570</td>
<td>379</td>
<td>708</td>
<td>1870</td>
<td>193</td>
</tr>
<tr>
<td>Interfacial area (μm²)</td>
<td>0.01</td>
<td>0.88</td>
<td>19.4</td>
<td>1.60</td>
<td>2.99</td>
<td>14.07</td>
<td>0.71</td>
</tr>
<tr>
<td>Max. force (μN)</td>
<td>3.8±0.5</td>
<td>2.8±0.6</td>
<td>6.8±1.7</td>
<td>0.6±0.04</td>
<td>2.3±0.6</td>
<td>12.8±2.1</td>
<td>2.6±0.5</td>
</tr>
<tr>
<td>Work (J×10⁻¹²)</td>
<td>2.9</td>
<td>3.3</td>
<td>16</td>
<td>1.3</td>
<td>1.6</td>
<td>7.8</td>
<td>4.1</td>
</tr>
<tr>
<td>Pullout energy (J/m²)</td>
<td>26.4</td>
<td>36.9</td>
<td>8.2</td>
<td>0.9</td>
<td>5.35</td>
<td>5.54</td>
<td>25.6</td>
</tr>
<tr>
<td>Shear strength (MPa)</td>
<td>375±40</td>
<td>318±16</td>
<td>35±9</td>
<td>38±2</td>
<td>77±20</td>
<td>91±15</td>
<td>366±74</td>
</tr>
</tbody>
</table>

### 2.3 Computational Simulation Method of ISS Study for CNT Nanocomposites

Due to difficulties in experiments to study the CNT nanocomposites interface, molecular mechanics (MM) and molecular dynamics (MD) simulations have become increasingly popular in the investigations of reinforcement mechanisms and interfacial bonding in CNT nanocomposites.

These computational simulations are energy-based methods. The mechanism of this method is to simulate the pull out process and calculate the pull out energy, then calculate the interfacial shear stress by Equation 2.5.

\[
E_{\text{pull-out}} = \int_0^L 2\pi a(l-x)\tau_i dx = \pi a\tau_i L^2 \tag{2.5}
\]

Where \( E_{\text{pull-out}} \) is the total pull-out energy, \( a \) is the radius of CNTs, \( \tau_i \) is the interfacial shear stress and \( L \) is the embedded length of CNTs.

A typical pull out configuration is shown in Figure 2.19 and Figure 2.20 shows the typical energy curve which can be offered by commercial MM and MD simulation software [11] [15]. The total pull-out energy \( (E_{\text{pull-out}}) \) is the energy difference between the fully embedded nanotube and the complete pull-out configuration.
Several research has studied the influential factors of interfacial shear stress such as matrix type, matrix density and functionalization degree.
2.3.1 Effect of Different Types of Matrices

Simulation results of interfacial shear stress between non-bonded CNTs and different matrices are summarized in Table 2.3 [9, 10, 14, 15, 17 and 32]. It can be seen that large variations existing due to difference model setup.

Table 2.3 Simulation data of interfacial shear stress

<table>
<thead>
<tr>
<th>Composite System</th>
<th>ISS (MPa)</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/SU-8 epoxy</td>
<td>138</td>
<td>Strong</td>
<td>[9]</td>
</tr>
<tr>
<td>CNT/PS</td>
<td>160</td>
<td>Strong</td>
<td>[10]</td>
</tr>
<tr>
<td>SWNT/PS</td>
<td>186</td>
<td>Strong</td>
<td>[14]</td>
</tr>
<tr>
<td>SWNT/epoxy</td>
<td>138</td>
<td>Strong</td>
<td></td>
</tr>
<tr>
<td>SWNT/PE</td>
<td>133</td>
<td>Strong</td>
<td>[32]</td>
</tr>
<tr>
<td>SWNT/Epon862</td>
<td>44.4</td>
<td>N/A</td>
<td>[17]</td>
</tr>
<tr>
<td>SWNT/PS</td>
<td>43.1</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>SWNT/PE(Crystalline)</td>
<td>48.9</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>SWNT/PE(Amorphous)</td>
<td>42.3</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>SWNT/Epon862</td>
<td>75</td>
<td>N/A</td>
<td>[15]</td>
</tr>
</tbody>
</table>

2.3.2 Effect of Matrix Density

The matrix density effect on interfacial shear stress is reported by Chowdhury and Okabe [13]. ISS will increase with the matrix density increase as shown in Figure 2.21. This is because more molecules of matrix surround the CNT surface, so the interaction between CNTs and matrix will increase.
2.3.3 Effect of CNT Functionalization Degree

Functionalization has a significant effect on the interfacial shear stress. Frankland et al. studied the influence of chemical cross-links on the interfacial shear stress of CNT/PE composites [33]. The bonded system with 6 cross-linking chain is illustrated as in Figure 2.22.

21
From the simulation results as shown in Table 2.4, they concluded that the functionalization with a relatively low density (<1%) could make the interfacial shear stress increase by over an order of magnitude compared with the non-bonded interface.

Table 2.4 Calculated Values for \( \tau_c \) in Non-Bonded and Cross-Linked Systems

<table>
<thead>
<tr>
<th></th>
<th>( \tau_c ) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Non-Bonded Composites</strong></td>
<td></td>
</tr>
<tr>
<td>amorphous</td>
<td>2.7 ± 0.2</td>
</tr>
<tr>
<td>crystalline</td>
<td>2.8 ± 0.3</td>
</tr>
<tr>
<td><strong>Cross-Linked Composites</strong></td>
<td></td>
</tr>
<tr>
<td>amorphous</td>
<td></td>
</tr>
<tr>
<td>initial nanotube motion</td>
<td>2.0 ± 0.3</td>
</tr>
<tr>
<td>chain and nanotube motion</td>
<td>30 ± 3</td>
</tr>
<tr>
<td>crystalline</td>
<td></td>
</tr>
<tr>
<td>initial nanotube motion</td>
<td>6.8 ± 0.2</td>
</tr>
<tr>
<td>chain and nanotube motion</td>
<td>110 ± 13</td>
</tr>
</tbody>
</table>

Q. Zheng et al. demonstrated that the non-bonded interfacial shear stress of CNT nanocomposites can be improved by about 1000% with introduction of a relatively low density of chemical crosslink [11]. They also found the critical functionalization degree, which is about 5% for both SWNT-PMMA system and SWNT-PE system, as shown in Figure 2.23 and 2.24 respectively.

![Figure 2.20 Influence of chemical functionalization on the interface for SWNT-PMMA](image)

Figure 2.20 Influence of chemical functionalization on the interface for SWNT-PMMA
2.3.4 Effect of CNT Functionalization Position

The position of functionalization on CNTs could also affect the interfacial shear stress according to Chowdhury et al. [13]. In Figure 2.25, the ISS in the lower region is 2.30GPa and is 1.95GPa in the upper region because the upper region cross-links have a longer traveling distance on the CNTs; so the interface will transfer energy up to a longer pull out displacement. According to the Equation 2.5, the interfacial shear stress of the upper region should be smaller than that of the lower region.

\[ W = \pi r_{CNT} \tau_i L^2 \]  \hspace{1cm} (2.5)

Where \( W \) is the total work done in pulling the CNTs from the matrix; \( r_{CNT} \) is the radius of the CNTs; \( L \) is the length from the cross-links to the embedded end of CNTs and \( \tau_i \) is the interfacial shear stress.
2.3.5 Effect of the CNT Ends

Oliver studied the effect of CNT end functionalization (see results listed in Table 2.5 [17]) and found that the end effects (capped or uncapped) on interfacial shear stress are only moderate. Even with end functionalization the interfacial shear stress just increased slightly; however, tube filling is a more effective way to improve the interfacial shear stress.

Table 2.5 Energy differences and stress values deducted from MD simulation

<table>
<thead>
<tr>
<th></th>
<th>base</th>
<th>capped</th>
<th>filled 100</th>
<th>filled 40</th>
<th>attached</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diff. E. (kcal/mol.)</td>
<td>1526.1</td>
<td>1553.2</td>
<td>1791.9</td>
<td>1585.6</td>
<td>1577.9</td>
</tr>
<tr>
<td>stress (MPa)</td>
<td>49.9</td>
<td>50.8</td>
<td>58.6</td>
<td>51.9</td>
<td>51.6</td>
</tr>
</tbody>
</table>

2.4 Continuum Media Method for ISS Study of CNT Nanocomposites

A number of continuum media models have been developed in the literature during last several years. Compared with the MD simulation method, the continuum media method is computationally efficient and desirable for parametric study of CNT interfacial properties. The following models are developed by modifying the models applied on traditional fiber-reinforced composites or nanoclay composites.
2.4.1 Modified Kelly-Tyson Model

A modified classic Kelly-Tyson model for a hollow structure was employed to study SWNT nanocomposites by Wagner [19]. According to Figure 2.26, a force balance expression can be deduced as Equation 2.6.

\[
\tau_{NT} (\pi D_{NT}) dx = (\sigma_{NT} + d\sigma_{NT}) \left( \frac{\pi D_{NT}^2 - \pi d_{NT}^2}{4} \right)
\]

Where \( \tau_{NT} \) is the interfacial shear stress; \( D_{NT} \) is the outer diameter of CNTs; \( \sigma_{NT} \) is the tensile stress of CNTs and \( d_{NT} \) is the inner diameter of CNTs.

Integration of this equation provides a calculation of interfacial shear stress as follows:

\[
\tau_{NT} = \sigma_{NT} (l_c) \left[ 0.5 \left( \frac{l_c}{D_{NT}} \right)^{-1} \left( 1 - \frac{d_{NT}^2}{D_{NT}^2} \right) \right]
\]

Where \( \sigma_{NT} (l_c) \) is the tensile stress on CNTs at the middle of critical length, \( l_c \) is the critical length of a CNT.

After tension, a single SWNT will break into several fragmentations. Shorter fragmentations (critical length) suggest greater interfacial shear stress. The diameter effect on interfacial shear stress is not so significant especially when the diameter is larger than 3 nm. This conclusion was elucidated by Figure 2.27.
This model predicts that the interface is stronger than the matrix to sustain shear, which means the interface is strong in SWNT nanocomposites.

There are two drawbacks in using this model for the calculation of interfacial shear stress. One is that it doesn’t involve any properties of matrix, which implies the interfacial shear stress should be the same for different type of matrix with a given size of CNTs. This is probably not true. The other drawback is that it is difficult to accurately measure the critical length due to the small size of CNTs, so the results may have large variations.

### 2.4.2 Fiber Pull-out Model

An analytical CNT pull-out model is shown in Figure2.28 [18]. A pull-out force is generated by a crack opening, which propagates perpendicularly to the longitudinal axial of the nanotubes.
After a complex derivation, the final equations of nanotube stress distribution and interfacial shear stress distribution along the tube axis can be given as follows:

\[
\sigma_{NT}(z) = \omega_1 \sinh(\lambda z) + \omega_2 \cosh(\lambda z) - \frac{A_1}{A_2} \sigma_{pullout} \quad (2.8)
\]

\[
\tau(z) = \frac{-R_{NT} \lambda}{2} [\omega_1 \cosh(\lambda z) + \omega_2 \sinh(\lambda z)] \quad (2.9)
\]

Where \( \sigma_{NT}(z) \) is the tensile stress of CNTs along the longitudinal direction of the CNTs; \( \tau(z) \) is the interfacial shear stress along the longitudinal direction of the CNTs; \( \sigma_{pullout} \) is the pullout stress; \( R_{NT} \) is the radius of CNTs and the parameters of \( \omega_1, \omega_2, \lambda, A_1, A_2 \) are calculated by the following equations respectively:
\[ A_1 = \frac{\alpha(1-2k\nu_{NT}) + \gamma(1-2k
u_{m})}{U_2 - 2kU_1} \quad (2.10) \]

\[ A_2 = -\frac{\gamma(1-2k\nu_{m})}{U_2 - 2kU_1} \quad (2.11) \]

\[ U_1 = \frac{\gamma}{8} \left\{ 2\eta_1b^2 \ln \left( \frac{b}{R_{NT}} \right) \left[ 1 + \gamma \left( \frac{b^2}{R_{NT}^2} + 1 \right) \right] \right\} - 2\eta_2 \left( b^2 + R_{NT}^2 \right) + 4b^2 - 2\eta_1(b^2 - R_{NT}^2) \quad (2.12) \]

\[ U_2 = \frac{\nu_m \gamma}{4} \left\{ 2\eta_1b^2 \ln \left( \frac{b}{R_{NT}} \right) (1 + \gamma) \right\} - \eta_2 \left( b^2 + R_{NT}^2 \right) + 2b^2 - \eta_1(b^2 - R_{NT}^2) \quad (2.13) \]

\[ \gamma = \frac{R_{NT}^2}{b^2 - R_{NT}^2} \quad (2.14) \]

\[ k = \frac{\alpha\nu_{NT} + \gamma\nu_{m}}{\alpha(1-\nu_{NT}) + 1 + 2\gamma + \nu_{m}} \quad (2.15) \]

\[ \alpha = \frac{E_{NT}}{E_M} \quad (2.16) \]

\[ \eta_1 = \frac{2(1+\nu_{m})}{\nu_{m}} \quad (2.17) \]

\[ \eta_2 = \frac{1+2\nu_{m}}{\nu_{m}} \quad (2.18) \]

\[ \lambda = \sqrt{A_1} \quad (2.19) \]

\[ \omega_1 = \frac{A_2}{A_1} - \left( 1 + \frac{A_2}{A_1} \right) \cosh (\lambda L) \left( \frac{\sigma_{pullout}}{\sinh (\lambda L)} \right) \quad (2.20) \]
\[ \omega_2 = \left(1 + \frac{A_0}{A_1}\right) \sigma_{\text{pullout}} \quad (2.21) \]

Where \( b \) is the radius of composite; \( \nu_m \) is the Poisson’s ratio of matrix; \( \nu_{NT} \) is the Poisson’s ratio of the CNTs; \( E_m \) is the Young’s modulus of the matrix; \( E_{NT} \) is the Young’s modulus of the CNTs and \( L \) is the length of the CNTs.

The distribution of interfacial shear stress was plotted in Figure 2.29. The interfacial shear stress can reach as high as 200 MPa for SWNT composites, which indicates a strong interface. However, for MWNT composites, the interfacial shear stress decreases dramatically due to the lower modulus of MWNT compared with the SWNT case.

![Figure 2.26 Plot of the interfacial shear stress against the embedding length of a CNT](image)

Compared with the above model, this model has some advantages as it contains most of the important properties of both matrix and CNTs, such as \( E_m, E_{NT}, \nu_m, \nu_{NT}, b \). However, there are still two disadvantages. First, it regards the CNT as a solid structure like the traditional fiber. Secondly, that condition directly applying force on the CNT while holding the matrix does not satisfy the actual situation which applies force on the matrix.
2.4.3 Modified Shear-lag Model

The modified shear-lag model is shown in Figure 2.30 [34]. The CNT ends are no longer treated as traction-free fiber breaks as in other models because the CNT and the matrix layer are not equally long.

In the virtual region, each of the two pure matrix cylinders at the ends of the RVE may still be viewed as a composite cylinder reinforced by a virtual fiber that has the same diameter as that of the effective fiber and the same properties as the matrix material.

As a result, the axial distributions of CNTs stress and interfacial shear stress were derived as follows:

$$\overline{\sigma_{zz}} = \left\{ \begin{array}{l}
\frac{R^2}{a^2 + \frac{E_m^e}{E^e}(R^2 - a^2)} + \left[ 1 - \frac{R^2}{a^2 + \frac{E_m^e}{E^e}(R^2 - a^2)} \right] \frac{\cosh(\alpha z)}{\cosh(\alpha L_t)} \right\} \sigma \quad (2.22)
\end{array} \right.$$
\[ \tau_i = \frac{a \alpha \sinh(\alpha z)}{2 \cosh(\alpha L)} \left( R^2 - a^2 \right) \left( 1 - \frac{E_m}{E_f} \right) \frac{a^2 + \frac{E_m}{E_f} (R^2 - a^2)}{\sigma} \]  

(2.23)

Where,

\[ \alpha^2 = \frac{1}{1 + \nu^m} \left( \frac{R^2 - a^2}{a^2} \right) \frac{a^2 + \frac{E_m}{E_f} (R^2 - a^2)}{R^4 \ln \frac{R}{a} - \frac{1}{4} (R^2 - a^2)(3R^2 - a^2)} \]  

(2.24)

Where \( \bar{\sigma}_{zz} \) is the stress on CNTs; \( R \) is the radius of the composite cylinder; \( a \) is the radius of CNTs; \( z \) is the distance from the middle of CNTs; \( E_m \) is the Young’s modulus of matrix; \( E_f \) is the Young’s modulus of CNTs; \( \nu^m \) is the Poisson’s ratio of matrix and \( L \) is the CNT length.

As mentioned above, this model pays attention to the end-traction effect which is important; however, it still considers the CNT as a solid fiber.

### 2.4.4 Modified Nanoclay Stress Transfer Model

The stress transfer model developed for platelet nanoclay reinforced composites was extended to CNT reinforced composites by Haque and Ramasetty [35]. In this model as shown in Figure 2.31, the CNT was assumed to be equally long with the matrix, suggesting without end bonding. The effect of end cap is also neglected due to high aspect ratio of CNTs.
The final equations to calculate the ISS value were given as:

\[
\sigma_n = \frac{(b + R_o - R_i)E_n \sigma_o}{(R_o - R_i)E_n + bE_m} + \frac{e^{\alpha y} + e^{-\alpha y}}{e^{\alpha L} + e^{-\alpha L}} \left[ 1 - \frac{(b + R_o - R_i)E_n}{(R_o - R_i)E_n + bE_m} \right] \sigma_o
\]  
(2.25)

\[
\tau_i = \frac{(R_o - R_i)\alpha}{2} \left[ \frac{b(E_n - E_m)}{(R_o - R_i)E_n + bE_m} \right] \frac{e^{\alpha y} + e^{-\alpha y}}{e^{\alpha L} + e^{-\alpha L}} \sigma_o
\]  
(2.26)

Where,

\[
\alpha = \frac{1}{b} \left\{ \frac{6[(R_o - R_i)E_n + bE_m]G_m}{(R_o - R_i)E_m \cdot E_m} \right\}^{1/2}
\]  
(2.27)

Where \( \sigma_n \) is the CNT tensile stress; \( b \) is the thickness of matrix; \( R_o \) is the outer diameter of CNTs; \( R_i \) is the inner diameter of CNTs; \( E_n \) is the Young’s modulus of CNTs; \( E_m \) is the Young’s modulus of matrix; \( \sigma_o \) is the applied force; \( y \) is the distance from the middle of CNTs; \( L \) is the CNT length; \( \tau_i \) is the interfacial shear stress and \( G_m \) is the shear modulus of matrix.
Figure 2.32 shows a comparison of the modified nanoclay stress transfer model with some other models. This model demonstrates reasonable agreement with the finite element analysis. But there is some discrepancy compared with Cox’s model because the analytical model is a 2D-based model while Cox’s model is a 3D-based model. Such discrepancy was also reported by other research.

![Figure 2.29 Comparison of various models](image)

### 2.4.5 Modified Cox’s Model

Cox’s model is set for a solid fiber, assuming a perfect interfacial bonding, and can be extended to a hollow SWNT shown in Figure 2.33 [20]. This generates the following calculations for the tube’s tensile stress and interfacial shear stress along the axis of the SWNT:

![Figure 2.30 Schematic representation of a single SWNT composite cylinder under an applied strain e](image)
\[
\tau = \frac{E_i e A_i \beta}{2\pi r_2} \times \frac{\sinh \beta (L/2 - x)}{\cosh \beta L/2} \tag{2.28}
\]

\[
\sigma_i = E_i e \left[ 1 - \frac{\cosh \beta (L/2 - x)}{\cosh \beta L/2} \right] \tag{2.29}
\]

\[
\beta = \sqrt{\frac{G_m}{E_i}} \left( \frac{2\pi}{A_i \ln(R/r_i)} \right) \tag{2.30}
\]

\[
A_i = \pi \left( r_2^2 - r_1^2 \right) \tag{2.31}
\]

Where \( \tau \) is interfacial shear stress; \( E_i \) is the Young’s modulus of CNTs; \( e \) is the applied strain; \( A_i \) is the cross section area of CNTs; \( x \) is the distance from the end of CNTs; \( L \) is the length of CNTs; \( r_2 \) is the outer radius of CNT; \( r_1 \) is the inner radius of CNTs and \( G_m \) is the shear modulus of matrix.

The interfacial shear stress reaches its maximum value at the two ends of a tube and is zero at the middle, as shown in Figure 2.34. Figure 2.35 indicates that the tensile stress starts to build up from the two ends of the nanotube and reaches its maximum value, \( \sigma_{i,\text{max}} \), at the middle. When \( L \) is greater than 500nm, \( \sigma_{i,\text{max}} \) becomes uniform and reaches nearly \( E_i e \), suggesting the critical length is about 500nm.
2.5 Comparison of the Above Three Methods for Interfacial shear stress Evaluations in CNT Nanocomposites

The above three methods including the experimental method, computational simulation method and continuum media method are frequently used to analyze the load transfer mechanisms in CNT composites. The difference between these three methods is their CNT pull-out process. In experimental methods and continuum media methods, at the beginning of pullout, the matrix will have an elastic deformation and yield, which means, the matrix near the CNT surface will stick to the CNTs and move together, so there is no relative movement between the matrix and CNTs during analysis. The interfacial shear stress will increase during the displacement of CNTs and reaches the maximum value before the interface failure. However, in simulation methods, the relative movement will happen as soon as the beginning of CNT pullout, which means the models assume interface de-bonding already happened and the interfacial shear stress reached the maximum point and will keep constant during the whole pull-out process. This difference is illustrated in Figure2.36.
When the pull-out process is completed, there are three possible failure modes. Each mode demonstrates the quality and strength of interfacial bonding. Figure 2.37 shows these three failure modes. In Figure 2.37 (a) the CNT surface is covered by some resin and in Figure 2.37 (b) the CNT is subjected to rupture; both modes suggest the interface is strong enough to sustain the shear force caused by CNT pullout. However, Figure 2.37 (c) implies a weak interfacial bonding because the CNT is pulled out with a clean surface.

Experimental methods such as SEM and TEM could offer direct observation of the interface deformation and properties; however, it is difficult to measure actual interfacial shear stress due to
nanoscale sizes of CNTs and difficulty in getting an individual CNT properly isolated for the measurement. There are still some research quantitatively analyzing the interfacial shear stress using AFM and SPM methods for providing direct measurement of interfacial properties; but these methods are usually very costly and time consuming, and have large variations in measurements.

The computational simulation method is an effective research technique at the atomic-scale level; however the interfacial shear stress happens at molecular level, so even after millions of simulation steps, the interfacial thermal, mechanical or physical events could not start yet, and hence the results are questionable. In addition, due to the scaling problem, the CNT length could only be 1-100 nm long in simulations, however, the length is a critical factor in influencing the interfacial shear stress; hence this method is difficult to calculate the interfacial shear stress value with an adequate CNT length.

As mentioned above, both the experimental methods and computational simulation methods have their limitations, hence the continuum media method is relatively appropriate to study interface property in CNT nanocomposites.

Among the five continuum media models discussed, the modified Cox’s model will be selected to study the interfacial shear stress in this research, because this model is well developed in traditional fiber composites and all of the parameters in this model can be obtained from actual tensile test results of our experiments.
CHAPTER 3

EXPERIMENTS

According to the literature review, the modified Cox’s model was selected to study the interfacial shear stress in the nanocomposites developed in our experiments. The calculations are expressed as Equation 3.1-3.3 as discussed in section 2.4.5.

\[
\tau = \frac{E_i ed \beta}{4} \times \frac{\sinh \beta L/2}{\cosh \beta L/2} \quad (3.1)
\]

\[
\sigma_i = E_i e \left[1 - \frac{1}{\cosh \beta L/2}\right] \quad (3.2)
\]

\[
\beta = \sqrt{\left(\frac{G_m}{E_i}\right) \left(\frac{8}{d^2 \ln\left(\frac{\pi}{4V_r}\right)}\right)} \quad (3.3)
\]

The parameters used in the model are obtained from our actual experimental results.

3.1 CNT Nanocomposites Fabrication

Epon 862 epoxy and curing agent W (diethyltoluenediamines) were purchased from E.V. Rubber Inc. M-chloromethaneperoxybenzoic (m-CPBA) acid was purchased from Sigma Aldrich. All raw materials were used as received. m-CPBA was dissolved in dichloromethane solvent and the pristine CNTs were immersed in the solution at room temperature (22-25°C) to conduct functionalization. The CNTs were then removed from the solution and washed for several times. Finally, the functionalized CNTs (F-CNT) were transferred to a vacuum oven for drying at 80°C for 2 hours.

The F-CNT powder was mixed with epoxy resin by using three-roller machine for 30 minutes. The mixture was then poured into a mold. Finally, the sample was cured in a hot press at 190F for 30
minutes and 350F for 4 hours under the pressure of 15.7MPa. The procedure of this fabrication was demonstrated in Figure3.1.

Several types of CNTs were used to fabricate the nanocomposites and they were defined in the following table for short. The pristine SWNT were purchased from Thomas Swan & Co. Ltd. The pristine DWNT were supplied by Cnano Company. The pristine LMWNT, LSWNT BP and LMWNT BP were offered by Nanocomp (Concord, NH).
Table 3.1 Definition of CNT types

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Fullname</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-SWNT</td>
<td>Pristine Single Walled Nanotubes</td>
</tr>
<tr>
<td>F-SWNT</td>
<td>Functionalized Single Walled Nanotubes</td>
</tr>
<tr>
<td>P-DWNT</td>
<td>Pristine Double Walled Nanotubes</td>
</tr>
<tr>
<td>F-DWNT</td>
<td>Functionalized Double Walled Nanotubes</td>
</tr>
<tr>
<td>P-LMWNT</td>
<td>Pristine Long Multi-walled Nanotubes</td>
</tr>
<tr>
<td>F-LMWNT</td>
<td>Functionalized Long Multi-walled Nanotubes</td>
</tr>
<tr>
<td>P-LSWNT BP</td>
<td>Pristine Long Single Walled Nanotube Buckypaper</td>
</tr>
<tr>
<td>F-LSWNT BP</td>
<td>Functionalized Long Single Walled Nanotube Buckypaper</td>
</tr>
<tr>
<td>P-LMWNT BP</td>
<td>Pristine Long Multi-walled Nanotube Buckypaper</td>
</tr>
<tr>
<td>F-LMWNT BP</td>
<td>Functionalized Long Multi-walled Nanotube Buckypaper</td>
</tr>
</tbody>
</table>

3.2 CNT Nanocomposites Characteristics

3.2.1 Raman Spectra

An inVia Raman Microscope (Renishaw Inc.) was used for Raman spectrum analysis. The major parameters were laser wavelength: 785nm, laser gate: 1200 l/mm, exposure time: 100s, and laser power level: 0.2%. The Raman Spectra of F-SWNT and F-DWNT are shown in Figure 3.2 and 3.3 respectively. For both cases, the D band increased significantly after the functionalization. This indicated the functionalization successful changed the structures of CNTs.
Figure 3.2 Raman spectra of P-SWNT and F-SWNT

Figure 3.3 Raman spectra of P-DWNT and F-DWNT
3.3.2 TGA Analysis

Thermogravimetric analysis (TGA) was conducted using a Q50 machine (TA instrument Inc.) from 50°C to 800°C in a nitrogen atmosphere to evaluate the functionalization results. The TGA curves in Figure3.4 and 3.5 show some weight losses caused by the decomposition of the molecules functionalized on CNT surfaces for F-SWNT and F-DWNT compared with the P-SWNT and P-DWNT samples. Based on the TGA results the functionalization degree can be calculated. The calculation was reported by Wang [36].

Figure3.4 TGA curves of P-SWNT and F-SWNT samples

Figure3.5 TGA curves of P-DWNT and F-DWNT samples
3.3.3 Tensile Tests

According to ASTM D 638-03, the tensile properties were tested by a Shimadzu machine (Kyoto, Japan) under a crosshead speed of 1mm/min with a gauge length of 20mm at room temperature. The tensile test results are shown in Figure3.6 and Figure3.7 for SWNT nanocomposites and DWNT nanocomposites respectively. All of these data were used in the Cox’s model to analyze the interface properties of the SWNT and DWNT nanocomposites recently. The percentage numbers are the weight percentages of CNTs in the samples.

![Stress-strain curves of SWNT nanocomposites and pure resin](image)

Figure3.6 Stress-strain curves of SWNT nanocomposites and pure resin
Figure 3.7 Stress-strain curves of DWNT nanocomposites and pure resin
CHAPTER 4

MODEL CALCULATION

The interfacial shear stress is expressed as Equation 4.1, also seen in section 2.4.5.

\[
\tau = \frac{E_t e d \beta}{4} \times \frac{\sinh \beta L / 2}{\cosh \beta L / 2}
\] (4.1)

The parameters in this equation could be obtained as shown in the Table 4.1.

Table 4.1 Parameters input for ISS calculation using the modified Cox’s model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Data Input</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_t)</td>
<td>Tensile Test</td>
</tr>
<tr>
<td>(e)</td>
<td></td>
</tr>
<tr>
<td>(d)</td>
<td>SEM image</td>
</tr>
<tr>
<td>(\beta)</td>
<td></td>
</tr>
<tr>
<td>(L)</td>
<td>Tensile Test</td>
</tr>
</tbody>
</table>

\[
\beta = \sqrt{\frac{G_m}{E_t}} \left[ \frac{8}{d^3 \ln \left( \frac{\pi}{4V_r} \right)} \right]
\]

\[
\alpha_t = E_t e \left[ 1 - \frac{1}{\cosh \frac{\beta L}{2}} \right]
\]

In the following sections, the procedure of model calculation is demonstrated by the calculation of interfacial shear stress for 6.83% P-LMWNT nanocomposites samples.
4.1 Model Parameter Determination

4.1.1 Approach to Determine $E_t$

$E_t$ is the tensile modulus on CNT ropes. It can be calculated by Krenchel’s model for three-dimensional randomly dispersed short-fiber composites as expressed in Equation 4.2 [3]. This model has been proven to have a good agreement with the experimental results for short fiber composites.

$$E_c = \frac{1}{5} E_t V_t + E_m (1 - V_t) \quad (4.2)$$

Where $E_c$ is the Young’s modulus of CNT nanocomposites; $E_t$ is the Young’s modulus of CNT rope; $E_m$ is the Young’s modulus of matrix and $V_t$ is the volume fraction of CNTs.

For 6.83% P-LMWNT nanocomposites, $E_c$ and $E_m$ can be directly obtained from the actual tensile test results as shown in Figure 4.1.

![Figure 4.1 Tensile test results of LMWNT nanocomposites and pure resin](image)

Figure 4.1 Tensile test results of LMWNT nanocomposites and pure resin
The volume fraction of CNTs, $V_i$, can be calculated by Equation 4.3.

$$V_i = \frac{W_i}{\rho_i} \times 100\% = \frac{6.83}{\frac{1.8}{6.83} \times 100\% + \frac{1.2}{6.83} \times 100\%} = 4.7\% \quad (4.3)$$

Where $W_i$ is the weight percentage of CNTs; $W_m$ is the weight percentage of matrix; $\rho_i$ is the density of CNTs and $\rho_m$ is the density of matrix.

With the $E_c$, $E_m$ and $V_i$ known, $E_t$ can be computed based on actual tensile test results, rather than assumed value. For 6.83% P-LWMNT nanocomposites, the calculated $E_t$ is 267GPa. It is critical important to properly determine $E_t$ in the model since a reliable database of CNTs and CNT rope properties is lacking.

4.1.2 Approach to Determine $\varepsilon$

$\varepsilon$ is the elastic strain of nanocomposites. Both nanocomposites and neat epoxy resin samples underwent the elastic deformation at the beginning stage, and then the stress-strain curves became nonlinear. Based on the boundary conditions of Cox’s model, the interfacial shear stress was calculated at only the linear portion. At the nonlinear stage, the deformation of nanocomposites and possible interface slippage between CNTs and resin matrix became very complicated.

For 6.83% P-LMWNT nanocomposites, the linear strain was 1.7% as shown in the Figure 4.2:
4.1.3 Approach to Determine $d$

A JEOL JSM-7401F Field Emission Scanning Electron Microscope (JEOL USA, Inc.) was used. Samples for the SEM experiments were sputter-coated for 60s at a current of 5mA. The diameter of CNT ropes $d$, was measured from the SEM images as shown in Figure 4.3.
The measurement results are shown in Figure 4.4. Multiple ropes were measured to improve accuracy.

![Figure 4.4 Diameter distributions of the P-LMWNT ropes in the nanocomposites samples](image)

The average diameter is about 31nm.

### 4.1.4 Approach to Determine $\beta$

The calculation of $\beta$ is expressed as in Equation 4.5.

$$\beta = \sqrt{\frac{G_m}{E_t}} \left( \frac{8}{d^2 \ln\left( \frac{\pi}{4V_t} \right)} \right) \quad (4.5)$$

Based on the above calculations of 6.83% P-LMWNT nanocomposites; $E_t$ is 267GPa; $d$ is 31nm; $V_t$ is 4.7% and $G_m$ is a constant which is 1.2GPa, therefore $\beta$ is calculated to be $5.16 \times 10^6 m^{-1}$. 

49
4.1.5 Approach to Determine $L$

The calculation of $L$ is a little complicated. The Krenchel’s model for the tensile strength of three-dimensional randomly dispersed short-fiber composites was applied again as Equation 4.6.

$$\sigma_c = \frac{1}{5} \sigma_i V_t + \sigma_m (1 - V_t) \quad (4.6)$$

Where $\sigma_c$ is the tensile stress of CNT nanocomposites; $\sigma_i$ is the tensile stress on the CNT ropes when composite sample is broken; $\sigma_m$ is the matrix stress when composite is broken and $V_t$ is the CNT volume fraction which is already calculated before.

As shown in Figure 4.5, for the 6.83% P-LMWNT nanocomposites case, $\sigma_c$ and $\sigma_m$ were found to be 71MPa and 37MPa from the tensile test results of the P-LMWNT nanocomposites and neat epoxy composite respectively where the strain was 1.7%.

![Figure 4.5 Schematic of determining stresses of 6.83% P-LMWNT nanocomposites and neat resin samples at their linear stages](image)
\(\sigma_c\), \(\sigma_m\) and \(V_r(4.7\%)\) were submitted in the Krenchel’s model, so the stress level on the CNT ropes was calculated to be 3.8GPa.

In Cox’s model, \(\sigma_i\) is expressed as Equation 4.7.

\[
\sigma_i = E_i e \left[1 - \frac{1}{\cosh \beta L / 2}\right] \quad (4.7)
\]

By now, the only unknown parameter in this equation is \(L\), the load transfer length of CNT ropes. By solving this equation, \(L\) is calculated to be 969nm.

### 4.1.6 Calculation of \(\tau\)

With all of the five parameters (\(\sigma\), \(e\), \(d\), \(\beta\) and \(L\)) became known, the ISS was calculated as Equation 4.8.

\[
\tau = \frac{E_1 e d \beta}{4} \times \frac{\sinh \beta L / 2}{\cosh \beta L / 2} \quad (4.8)
\]

For 6.83% P-LMWNT nanocomposites, the ISS was calculated to be 182MPa.

### 4.2 Calculation Results

The same calculation procedure was applied to the other CNT nanocomposites cases. The results were summarized in the Table 4.2 to 4.6.
Table 4.2 Calculation of ISS values in short SWNT nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_t$ (GPa)</th>
<th>$e$ (%)</th>
<th>$d$ (nm)</th>
<th>$\beta$ ($\mu$m$^{-1}$)</th>
<th>$L$ (nm)</th>
<th>ISS($\tau$) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4% P</td>
<td>91</td>
<td>1.8</td>
<td>10</td>
<td>26.3</td>
<td>124</td>
<td>100</td>
</tr>
<tr>
<td>4% F</td>
<td>80</td>
<td>2.0</td>
<td>9</td>
<td>31.1</td>
<td>110</td>
<td>105</td>
</tr>
<tr>
<td>10% F</td>
<td>78</td>
<td>1.4</td>
<td>11</td>
<td>30.8</td>
<td>132</td>
<td>90</td>
</tr>
<tr>
<td>20% F</td>
<td>82</td>
<td>0.78</td>
<td>16</td>
<td>25.3</td>
<td>208</td>
<td>65</td>
</tr>
</tbody>
</table>

Table 4.3 Calculation of ISS values in short DWNT nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_t$ (GPa)</th>
<th>$e$ (%)</th>
<th>$d$ (nm)</th>
<th>$\beta$ ($\mu$m$^{-1}$)</th>
<th>$L$ (nm)</th>
<th>ISS($\tau$) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% P</td>
<td>26</td>
<td>2.0</td>
<td>15</td>
<td>35.8</td>
<td>176</td>
<td>70</td>
</tr>
<tr>
<td>5% F</td>
<td>35</td>
<td>1.8</td>
<td>11</td>
<td>42.1</td>
<td>124</td>
<td>72</td>
</tr>
<tr>
<td>10% F</td>
<td>37</td>
<td>2.1</td>
<td>15</td>
<td>31.9</td>
<td>156</td>
<td>92</td>
</tr>
</tbody>
</table>

Table 4.4 Calculation of ISS values in LMWNT nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_t$ (GPa)</th>
<th>$e$ (%)</th>
<th>$d$ (nm)</th>
<th>$\beta$ ($\mu$m$^{-1}$)</th>
<th>$L$ (nm)</th>
<th>ISS($\tau$) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.83% P</td>
<td>267</td>
<td>1.7</td>
<td>31</td>
<td>5.16</td>
<td>969</td>
<td>182</td>
</tr>
<tr>
<td>6.85% F</td>
<td>453</td>
<td>1.8</td>
<td>28</td>
<td>4.38</td>
<td>951</td>
<td>242</td>
</tr>
</tbody>
</table>
### Table 4.5 Calculation of ISS values in LSWNT BP nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_t$ (GPa)</th>
<th>$e$ (%)</th>
<th>$d$ (nm)</th>
<th>$\beta$ (µm$^{-1}$)</th>
<th>$L$ (nm)</th>
<th>ISS($\tau$) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.7% P</td>
<td>370</td>
<td>1.0</td>
<td>57</td>
<td>4.75</td>
<td>1644</td>
<td>251</td>
</tr>
<tr>
<td>45.5% F</td>
<td>580</td>
<td>0.69</td>
<td>48</td>
<td>4.93</td>
<td>1703</td>
<td>261</td>
</tr>
</tbody>
</table>

### Table 4.6 Calculation of ISS values in LMWNT BP nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_t$ (GPa)</th>
<th>$e$ (%)</th>
<th>$d$ (nm)</th>
<th>$\beta$ (µm$^{-1}$)</th>
<th>$L$ (nm)</th>
<th>ISS($\tau$) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42.7% P</td>
<td>442</td>
<td>1.2</td>
<td>74</td>
<td>3.03</td>
<td>1026</td>
<td>298</td>
</tr>
<tr>
<td>43.7% F</td>
<td>1080</td>
<td>0.86</td>
<td>34</td>
<td>4.29</td>
<td>1394</td>
<td>339</td>
</tr>
</tbody>
</table>
CHAPTER 5

DISCUSSION

5.1 Perfect Interface

To evaluate whether the ISS values are adequate or not, the desired ISS values should be calculated and compared with the calculation results. The desired interface is perfect interface. It is defined as where reinforcement (CNTs) can deform together with the matrix (epoxy resin) without any sliding until the matrix reaches its failure strain assuming CNTs have large failure strains (10%-30%) [37]. So the tensile strain of reinforcement and matrix should keep same until the matrix breaks.

There are two predictions to achieve a perfect interface. The first one is that the CNT length is larger than its critical length. The second one is the interaction between CNTs and resin matrix should be strong enough to avoid any CNT/resin slippage.

For 6.83% P-LMWNT, assumed perfect interface condition, the stress-strain curve is expected to keep going until the matrix breaks as shown in Figure 5.1.

![Figure 5.1 Schematic of stress-strain curve under the perfect interface for 6.83% P-LMWNT nanocomposites, the dotted line indicates the virtual elongation of CNT nanocomposites](image-url)
This assumed that the Young’s modulus of CNT ropes remains constant and CNT ropes do not rupture during the virtual stage. Under the perfect interface, the interfacial shear stress at the composite break point can be calculated by Equation 5.1 based on the modified Cox’s model.

\[ \tau = \frac{E_e d \beta}{4} \]  

(5.1)

For 6.83% P-LMWNT nanocomposites, the perfect interfacial shear stress (ISS*) was calculated to be 1068MPa. However, the actual ISS in the nanocomposites is just 182MPa, which is much lower than the perfect interfacial shear stress. Same procedure is also used to calculate the ISS* values for the rest cases. The results are summarized in Table 5.1 to 5.5.

Table 5.1 ISS and ISS* values of SWNT nanocomposites

<table>
<thead>
<tr>
<th>SWNT</th>
<th>ISS (MPa)</th>
<th>ISS* (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4% P-SWNT</td>
<td>100</td>
<td>598</td>
</tr>
<tr>
<td>4% F-SWNT</td>
<td>105</td>
<td>561</td>
</tr>
<tr>
<td>10% F-SWNT</td>
<td>90</td>
<td>664</td>
</tr>
<tr>
<td>20% F-SWNT</td>
<td>65</td>
<td>826</td>
</tr>
</tbody>
</table>

Table 5.2 ISS and ISS* values of DWNT nanocomposites

<table>
<thead>
<tr>
<th>DWNT</th>
<th>ISS (MPa)</th>
<th>ISS* (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% P-DWNT</td>
<td>70</td>
<td>349</td>
</tr>
<tr>
<td>5% F-DWNT</td>
<td>72</td>
<td>405</td>
</tr>
<tr>
<td>10% F-DWNT</td>
<td>92</td>
<td>423</td>
</tr>
</tbody>
</table>
Table 5.3 ISS and ISS* values of LMWNT nanocomposites

<table>
<thead>
<tr>
<th>LMWNT</th>
<th>ISS (MPa)</th>
<th>ISS* (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.83% P-LMWNT</td>
<td>182</td>
<td>1068</td>
</tr>
<tr>
<td>6.85% F-LMWNT</td>
<td>242</td>
<td>1389</td>
</tr>
</tbody>
</table>

Table 5.4 ISS and ISS* values of LSWNT BP nanocomposites

<table>
<thead>
<tr>
<th>LSWNT BP</th>
<th>ISS (MPa)</th>
<th>ISS* (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.7% P-LSWNT BP</td>
<td>251</td>
<td>1122</td>
</tr>
<tr>
<td>45.5% F-LSWNT BP</td>
<td>261</td>
<td>1535</td>
</tr>
</tbody>
</table>

Table 5.5 ISS and ISS* values of LMWNT BP nanocomposites

<table>
<thead>
<tr>
<th>LMWNT BP</th>
<th>ISS (MPa)</th>
<th>ISS* (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42.7% P-LMWNT BP</td>
<td>298</td>
<td>1110</td>
</tr>
<tr>
<td>43.7% F-LMWNT BP</td>
<td>339</td>
<td>1763</td>
</tr>
</tbody>
</table>

Obviously, for all of the cases, the actual calculated ISS values are much less than the ISS* values of the defined perfect interface situation. There are two possible reasons for such low ISS values. One is weak interfacial bonding and the other one is possible CNT rope rupture, which is unique in CNT nanocomposites compared with fiber-reinforced composites.

5.2 Failure Modes

The following analysis and experiment evidences show that the failure mode is CNT rope rupture in the CNT nanocomposites. It is confirmed from three aspects: stress-strain curves, literature reports and SEM images of the fracture surfaces.
5.2.1 CNT Rope Rupture Analysis from the Stress-Strain Curves

For P-LMWNT, P-LMWNT BP and P-LSWNT BP nanocomposites, their stress-strain curves showed the onset points changing elastic linear behaviors to nonlinear behaviors as shown in Figure 5.2 and Figure 5.3.

![Figure 5.2 Stress-strain curves for P-LMWNT nanocomposites](image1)

![Figure 5.3 Stress-strain curves for P-LSWNT BP and P-LMWNT BP nanocomposites](image2)
For such changes, there are three possible reasons to cause those nonlinear deformations: (1) resin matrix yield; (2) interface failure; (3) CNT sliding within their ropes.

We can eliminate the effect of resin matrix yield because the linear strain of those nanocomposites has not reached the resin matrix yield strain yet. The linear strain for the P-LMWNT, P-LSWNT BP and P-LMWNT BP nanocomposites are 1.7%, 1.0% and 1.2% respectively. Those strains are much lower than the matrix yield strain, which is 2.3%.

The reason could not be interface failure because after that change point there was still a significant amount of load transferred to the CNTs as compared in Table5.6. This indicated there should not be many CNT/resin slippages at the change points.

Table5.6 Stress level on CNT ropes at the change points and break points

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_t$ (GPa) at the change point</th>
<th>$\sigma_t$ (GPa) at the break point</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.83% P-LMWNT</td>
<td>3.8</td>
<td>4.7</td>
</tr>
<tr>
<td>42.7% P-LMWNT BP</td>
<td>3.6</td>
<td>7.7</td>
</tr>
<tr>
<td>40.7% P-LSWNT BP</td>
<td>3.7</td>
<td>5.8</td>
</tr>
</tbody>
</table>

The only reason left is CNT sliding; hence the failure mode is CNT rope rupture. This is also supported by the values of $\sigma_t$, which are almost the same for those above three nanocomposites. For P-CNT rope, the interaction between CNTs are Van der Waals force and electrostatic interaction; the distance between the CNTs within bundles are almost the same, and the molecular structure and configuration of the MWNT and SWNT are similar. So the interaction within MWNT rope and SWNT rope are most likely to be the same, which means the sliding strength of the ropes should be close to each other. Our results of the $\sigma_t$ values at these onset points have a good agreement with this deduction, so the reason for the flexure should be the CNT sliding within rope.

For 6.85% F-LMWNT and 42.7% F-LMWNT BP nanocomposite samples, the stress-strain curves are almost linear until the nanocomposites failure at much small failure strain values and high stress levels as shown in Figure5.2 and Figure5.3. As was discussed before, the CNT rope rupture is the failure mode. Differently here, the CNT rope failure at a high stress level, 9.1GPa for both cases occurred.
because we used the same functionalization approach for both cases.

### 5.2.2 CNT Rope Rupture Analysis from the Literature Reports

Besides the above analysis of actual stress-stain curves, the CNT rope rupture failure mode could also be understood based on some literature reports. The stress levels on CNTs in the CNT nanocomposites are listed in Table 5.7.

Table 5.7 Stress level on CNT ropes at the nanocomposite failure points

<table>
<thead>
<tr>
<th></th>
<th>Tensile Stress on CNT rope at the failure point</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SWNT</strong></td>
<td></td>
</tr>
<tr>
<td>4% P-SWNT</td>
<td>1.56</td>
</tr>
<tr>
<td>4% F-SWNT</td>
<td>1.39</td>
</tr>
<tr>
<td>10% F-SWNT</td>
<td>1.10</td>
</tr>
<tr>
<td>20% F-SWNT</td>
<td>0.48</td>
</tr>
<tr>
<td>40.7% P-LSWNT BP</td>
<td>5.83</td>
</tr>
<tr>
<td>45.5% F-LSWNT BP</td>
<td>4.71</td>
</tr>
<tr>
<td><strong>DWNT</strong></td>
<td></td>
</tr>
<tr>
<td>5% P-DWNT</td>
<td>0.57</td>
</tr>
<tr>
<td>5% F-DWNT</td>
<td>0.86</td>
</tr>
<tr>
<td>10% F-DWNT</td>
<td>1.07</td>
</tr>
<tr>
<td><strong>MWNT</strong></td>
<td></td>
</tr>
<tr>
<td>6.83% P-LMWNT</td>
<td>4.67</td>
</tr>
<tr>
<td>6.85% F-LMWNT</td>
<td>9.10</td>
</tr>
<tr>
<td>42.7% P-LMWNT BP</td>
<td>7.75</td>
</tr>
<tr>
<td>43.7% F-LMWNT BP</td>
<td>9.14</td>
</tr>
</tbody>
</table>

These values are in the range of tensile strength values of CNT ropes as reported in the literature and illustrated in Table 5.8. This indicated that the CNT ropes in the nanocomposites already reached their strength; therefore the CNT rope underwent rupture at the nanocomposites failure point.
Table 5.8 Tensile strength of CNT ropes reported from literature

<table>
<thead>
<tr>
<th></th>
<th>Tensile Strength</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>1 GPa</td>
<td>[38] Science</td>
</tr>
<tr>
<td></td>
<td>3-11 GPa</td>
<td>[40] Science</td>
</tr>
<tr>
<td>DWNT</td>
<td>0.62-2.6 GPa</td>
<td>[41] Carbon</td>
</tr>
<tr>
<td>MWNT</td>
<td>11-63 GPa</td>
<td>[42] Science</td>
</tr>
<tr>
<td></td>
<td>150-460 MPa</td>
<td>[43] Science</td>
</tr>
<tr>
<td></td>
<td>1.08-2.36 GPa</td>
<td>[44] Science</td>
</tr>
<tr>
<td></td>
<td>210 MPa</td>
<td>[45] Carbon</td>
</tr>
<tr>
<td></td>
<td>100-1000MPa</td>
<td>[46] Science</td>
</tr>
</tbody>
</table>

5.2.3 CNT Rope Rupture Analysis from SEM Images

In SEM images of fracture surface in our CNT nanocomposite samples, CNT sliding and peeling within rope were observed. These phenomena can be seen in Figure 5.4, 5.5 and 5.6.

Figure 5.4 SEM images of 6.85% F-LMWNT nanocomposites; the red circles indicate the CNT rope ruptures
Figure 5.5 SEM images of 5% F-DWNT nanocomposites; the red circles indicate the CNT rope ruptures.

Figure 5.6 SEM images of 45.5% F-LSWNT BP nanocomposites; the red circles indicate the CNT rope ruptures.

Some sharp ends of CNT ropes can be found at the spots B and C in Figure 5.4 and spot A in Figure 5.5. Especially in Figure 5.4, the CNT rope slippage fracture was discovered at spot A; this may be due to the inside sub rope being pulled out from the outer layers within CNT ropes. Figure 5.6 shows that many of the big CNT ropes were peeled into several sub ropes such as spots A and B. All of these spots indicated CNT ropes were ruptured in the samples.
5.3 Functionalization Effect on CNT Ropes

5.3.1 Functionalization Increased the Mechanical Properties of MWNT and DWNT Ropes

The Young’s modulus and sliding stress of DWNT rope in the F-DWNT nanocomposites and P-DWNT nanocomposites are shown in Figure 5.7. Figure 5.8 and 5.9 show the Young’s modulus and sliding stress of F-MWNT and P-MWNT ropes in the LMWNT nanocomposites and LMWNT BP nanocomposites.

Figure 5.7 Young’s modulus and strength of DWNT ropes in DWNT nanocomposites
Figure 5. Young’s modulus and strength of MWNT ropes in LMWNT nanocomposites
Figure 5.9 Young’s modulus and strength of MWNT rope in LMWNT BP nanocomposites

From the above figures, it is easy to notice that the Young’s modulus and strength of F-DWNT and F-MWNT are noticeably higher than those of P-DWNT and P-MWNT ropes. Hence, we demonstrated that the mechanical properties of DWNT and MWNT ropes were improved by functionalization.

5.3.2 Functionalization Decreased the Mechanical Properties of SWNT Ropes

The Young’s modulus of SWNT ropes in F-SWNT nanocomposites is compared with that in P-SWNT nanocomposites in Figure 5.10. It clearly shows that the Young’s modulus of SWNT rope dropped after functionalization.
The strength of SWNT rope was also decreased. This is illustrated in Figure 5.11; This is true because at the break point of nanocomposites the stress on F-SWNT rope is only 4.2 GPa. This value is lower than that on P-SWNT and F-MWNT rope which are 5.7 and 9.1 GPa respectively.
5.3.3 Mechanism of Functionalization Effect on the Mechanical Properties of CNT Ropes

For DWNT and MWNT, the functionalization may form some crosslink between CNTs so the individual CNTs were integrated in the ropes with covalent bonding as shown in Figure5.12. Although the functionalization may degrade mechanical properties of the outmost layer of DWNT and MWNT ropes, the inner layers are still available to sustain the external force. Thus the mechanical properties of DWNT ropes and MWNT ropes get increased. Some experimental research using a tunneling electronic microscopy and scanning electronic microscopy (SEM) have validated the enhancement of mechanical properties of an individual nanotube rope, due to the inter-tube covalent bonding formation [36] [47] [48].

![Diagram showing crosslink within CNT bundle formed by functionalization](image)

Figure5.12 Schematic of crosslink within CNT bundle formed by functionalization

For SWNT, the functionalization damaged the structure of the nanotube too much, so it degraded the mechanical properties of individual SWNT and, therefore, degraded the mechanical properties of SWNT ropes.

5.4 Functionalization Effect on the Failure Behavior for LSWNT BP and LMWNT BP Nanocomposites

For F-LSWNT BP and F-LMWNT BP nanocomposites, the failure is very brittle and there is no yield stage as shown in P-LSWNT BP and P-LMWNT BP nanocomposites as shown in Figure5.13.
In F-LSWNT BP and F-LMWNT BP nanocomposites, the nanocomposites failure was actually the CNT rope failure. Since CNT ropes were much stronger than resin when they were broken, there was a huge amount of energy released and the samples suddenly broke.

In P-LSWNT BP and P-LMWNT BP nanocomposites, the samples at first yielded and then broke. At the yield point, the CNTs were sliding within the rope and had some possible interface sliding; hence the samples have these mechanisms to dissipate the energy and gradually fractured.

5.5 Influential Factors for ISS

5.5.1 Functionalization Effect

Functionalization improved the interfacial shear stress as shown in Figure5.14. Here only DWNT, LMWNT and LMWNT BP nanocomposites were analyzed because functionalization decreased the
properties of SWNT; thus the SWNT nanocomposites and LSWNT BP nanocomposites were not taken into consideration.

![Graphs showing ISS for different nanocomposites](image)

Figure 5.14 ISS for pristine and functionalized DWNT, LMWNT and LMWNT BP nanocomposites

5.5.2 Volume Fraction Effect

The interfacial shear stress values also increase when the volume fraction increases as illustrated in Figure 5.15. High CNT content may lead to less spacing distance among functionalized CNTs and high covalent bonding density in interface zones.
This relationship has a good correlation with the Cox’s model prediction. In Cox’s model, the interfacial shear stress is calculated by Equation 5.2.
\[ \tau = \frac{E \epsilon d \beta}{4} \times \frac{\sinh \beta L/2}{\cosh \beta L/2} \] (5.2)

The parameter \( \beta \) is calculated by Equation 5.3.

\[ \beta = \left( \frac{G_m}{E_i} \right) \left( \frac{8}{d^2 \ln\left( \frac{\pi}{4V_t} \right)} \right) \] (5.3)

From these two equations, it is easy to see that when volume fraction \( V_t \) increases, \( \beta \) will increase, and therefore interfacial shear stress \( \tau \) increases.

5.5.3 CNT Length Effect

The longer the CNTs are, the higher the ISS are as shown in Figure 5.16. This also agrees with the Cox’s model prediction according to Equation 5.2 and load transfer mechanism or critical length principle in composites. But this result may couple with CNT volume fraction effect.

Figure 5.16 ISS for short SWNT and long SWNT nanocomposites
5.5.4 CNT Type Effect

For short CNTs, the SWNT are better than DWNT for load transfer, and for long CNTs, the MWNT are better than SWNT. This is demonstrated in Figure 5.17.

![Figure 5.17 CNT type effect on ISS values](image)

5.6 Effective Length of Load Transfer

The effective length of load transfer is much lower than the actual CNT length as compared in Table 5.9.
Table 5.9 Comparison of effective length of load transfer vs. actual CNT length

<table>
<thead>
<tr>
<th></th>
<th>Effective Length (nm)</th>
<th>Actual Length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SWNT</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4% P-SWNT</td>
<td>124</td>
<td></td>
</tr>
<tr>
<td>4% F-SWNT</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>10% F-SWNT</td>
<td>132</td>
<td>2000</td>
</tr>
<tr>
<td>20% F-SWNT</td>
<td>208</td>
<td></td>
</tr>
<tr>
<td>40.7% P-LSWNT BP</td>
<td>996</td>
<td>10^6</td>
</tr>
<tr>
<td>45.5% F-LSWNT BP</td>
<td>961</td>
<td></td>
</tr>
<tr>
<td><strong>DWNT</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% P-DWNT</td>
<td>176</td>
<td></td>
</tr>
<tr>
<td>5% F-DWNT</td>
<td>124</td>
<td></td>
</tr>
<tr>
<td>10% F-DWNT</td>
<td>152</td>
<td>2000</td>
</tr>
<tr>
<td><strong>MWNT</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.83% P-LMWNT</td>
<td>969</td>
<td>10^6</td>
</tr>
<tr>
<td>6.85% F-LMWNT</td>
<td>951</td>
<td></td>
</tr>
<tr>
<td>42.7% P-LMWNT BP</td>
<td>1563</td>
<td></td>
</tr>
<tr>
<td>43.7% F-LMWNT BP</td>
<td>1104</td>
<td></td>
</tr>
</tbody>
</table>

The difference may be due to the waveness variations of CNTs in the nanocomposites. The effective length of load transfer is just the CNT length along the load direction and accounted for actual load transfer based on the modified Cox’s model. There will be less or no load transfer when CNT ropes are not aligned with load direction. As shown in Figure 5.18, the effective length is L1, L2, L3 and L4. These lengths are much shorter than the whole CNT length.
Figure 5.18 Schematic of CNT waveness and effective load transfer length in nanocomposites.
CHAPTER 6

CONCLUSIONS

In this research the interfacial shear stress for actual CNT nanocomposites was calculated based on the modified Cox’s model and tensile test results. This approach is an attempt to understand and quantify the relationships between load transfer efficiency and property in actual CNT nanocomposites. The major conclusions of this effort are summarized in the following.

- Interfacial shear stress can be directly calculated based on tensile test results and microstructure observation.
- Major failure modes in both pristine and functionalized CNT nanocomposites are CNT rope rupture due to weak rope properties rather than interface failure based on both modeling analysis and experimental observations.
- Functionalization can noticeably improve interfacial shear stress and load transfer.
- Functionalization can also significantly improve mechanical properties of CNT ropes and lead to higher stress levels on CNT ropes.
- Effective length of load transfer is much shorter than the actual CNT length due to the waveness and lack of alignment of CNTs in nanocomposites.

Since the failure mode of CNT nanocomposites is CNT rope rupture rather than the interface failure in our nanocomposite samples, the focus of functionalization study should be switched to improve the CNT rope strength first before emphasizing interface property improvement.
CHAPTER 7

FUTURE WORK

In the future, the following works should be done to further investigate the ISS in different matrices and improvement of CNT ropes.

1. ISS of CNT/PC (polycarbonate) nanocomposites

The interfacial shear stress of the nanocomposites in Table 7.1 should be studied to find out how matrix properties effect on the interfacial shear stress.

Table 7.1 ISS of CNT/PC nanocomposites

<table>
<thead>
<tr>
<th></th>
<th>ISS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/PC</td>
<td>X</td>
</tr>
<tr>
<td>DWNT/PC</td>
<td>X</td>
</tr>
<tr>
<td>MWNT/PC</td>
<td>X</td>
</tr>
</tbody>
</table>

2. ISS of CNF (carbon nanofiber)/epoxy nanocomposites

The interfacial shear stress of CNF/Epoxy nanocomposites in Table 7.2 should be calculated and compared with the CNT/Epoxy nanocomposites to explore how the reinforcement effect the interfacial shear stress and load transfer.

Table 7.2 ISS of CNF/Epoxy nanocomposites

<table>
<thead>
<tr>
<th></th>
<th>ISS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/PC</td>
<td>X</td>
</tr>
<tr>
<td>DWNT/PC</td>
<td>X</td>
</tr>
<tr>
<td>MWNT/PC</td>
<td>X</td>
</tr>
</tbody>
</table>

3. Covalent functionalization to improve CNT rope properties
CNTs easily slide within rope due to the smooth surface and weak interaction, which will cause CNT rope, ruptures and therefore the nanocomposites break. To improve the surface roughness of CNTs, some rigid molecules like benzene ring could be grafted to the sidewalls of CNTs. These grafted molecules may form the micromechanical interlock between the CNTs, so it could prevent the CNT sliding, therefore, the strength of CNT rope can be increased. A proposed mechanism of this functionalization is illustrated in Figure 7.1.

![Diagram](image)

**Figure 7.1** Schematic of covalent functionalization

4. Noncovalent functionalization

Some special chemical agents could be applied to attach to the sidewall of CNTs to realize non functionalization to avoid property degradation of SWNTs. Possible molecule structures of these kinds of chemical agents are shown in Figure 7.2. The amino group of the chemical agents could react with Epoxy resin or the hydroxyl group could react with the curing agent, so the wrapped CNTs will be integrated in the networks of epoxy matrix. This kind of functionalization has three advantages. First, it could prevent the CNT sliding within rope. Second, it could improve interfacial shear stress. Third, it could keep the intact structure of CNTs and won’t degrade the mechanical properties of CNTs themselves.
Figure 7.2 Molecule structures of the chemical agents for noncovalent functionalization
REFERENCES


BIOGRAPHICAL SKETCH

Xianping Wang received her Bachelor’s degree in Polymer Materials & Engineering at Zhejiang University in July 2006. Upon graduation, she moved to the United States of America where she started studying Industrial & Manufacturing Engineering at Florida State University.

Xianping Wang worked as the teaching assistant for Principals of Engineering Economics and the Manufacturing Processes and Materials Engineering. Since December 2006, she worked as a research assistant at High-Performance Materials Institute (HPMI). Her research interests are mainly focused on functionalization of carbon nanotubes (CNT) and manufacturing CNT nanocomposites. She has also conducted some theoretical studies about the mechanical properties and interfacial properties of CNT nanocomposites.