SWCNT COMPOSITES, INTERFACIAL STRENGTH AND MECHANICAL PROPERTIES

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1 Introduction
Single-Walled Carbon Nanotubes (SWCNT) have despite the superior mechanical properties not fully lived up to the promise as reinforcement in SWCNT composites. The strain transfer from matrix to carbon nanotubes (CNT) is poorly understood and is caused by both fewer localized strong bondings and frictional forces generated by residual compressive forces acting on the nanotubes. The interphase area i.e. size of CNT and bundles also play a crucial role. In this paper the strain transfer of SWCNT in a polymeric matrix is evaluated by monitoring the Raman 2D band shift as a tensile strain is applied to the composite materials. [1-4] The effect of polymer matrix, modification and concentration of the CNTs are discussed. The strain transfer i.e. 2D band shift under tension is compared to the mechanical properties of the SWCNT composite material.

2 Experimental

2.1 Materials

2.1.1 Carbon nanotubes
2.1.1.1 Carbolex Grade A
The Carbolex Grade A single walled carbon nanotubes were synthesized by arc-discharge method. The purity of the as received nanotubes was 50-70% and impurities mainly consist of amorphous carbon and catalyst particles. Average diameter of individual tubes was 1.4 nm, bundle size was approximately 20 nm and the length was 2-5 μm. These SWCNT were always purified by annealing in air at 275°C for 1 h and followed by refluxing in 6M hydrochloric acid for 6 h to remove the amorphous carbon and the metal catalysts particles. The suspension was washed with water and dried at 100 °C for 24 h. Weight loss was around 50%. The purified nanotubes were also used for the subsequent modifications.

2.1.1.2 Cheaptubes
The SWCNTs were purchased from Cheaptubes, Inc. and were produced by CCVD method with >90% purity and 1-2 nm in diameter (supplier information). The purchased tubes were purified by 3M HNO3 treatment by the supplier. These nanotubes did not undergo any purification before use.

2.1.2 Modification
2.1.2.1 Nitric acid functionalization
500 mg of non-modified SWCNTs were refluxed in 50 ml 5 M nitric acid for 1 h. Then the SWCNTs were washed with de-ionized water and dried at 100°C for 24 h.

2.1.2.2 Octadecylamine (ODA) functionalization
230 mg of Nitric acid functionalized-SWCNTs and 2 g of Octadecylamine (ODA) was mixed and heated at 125 °C for 4 days, during which ODA melted and reacted with the nanotubes. Hereafter the mixture was washed several times by ethanol in ultrasonic bath and filtered; the temperature was kept above 50 °C during the ultra-sonication and filtration. Finally the SWCNTs were dried at 100 °C for 24 h.

2.1.2.3 Dodecylamine (DDA) functionalization
2 g dodecyl amine (DDA) was added to 200 mg HNO3 functionalized SWCNTs, and the mixture was held at 90°C for 4 days. Then the mixture was washed with ethanol to remove the remaining DDA and filtered through 0.45μm filter. And finally the powder was dried at 100°C for 24 h.

2.1.2.4 Dichlororcarcene functionalization
100 mg of as received SWCNTs were dried at 110°C for 8 h to remove the absorbed water, then ultrasonicated in 6ml chloroform for 1 h, 40g of potassium tert-butoxide is dissolved in 60ml Tetrahydrofuran (THF), and surrounded by dry ice-ethanol solution with temperature around -75°C. Then the purified SWCNTs/chloroform suspension was added into the potassium tert-butoxide /THF drop by drop. Hereafter, the mixture was poured in
to ice and the mixture was washed with water to removed potassium chloride and washed with ethanol 3 times and once with THF to remove butanol and other chemicals. Finally the powder was dried at 100°C for 24h.

2.1.3 Composite fabrication
All composites were prepared by solution blending.

2.1.3.1 Epoxy composites fabrication
The nanocomposites were fabricated by the respective SWCNTs and a commercial epoxy Proset-117 / 229PF. The epoxy resin Proset 117 contains 30-60% Bisphenol A Diglycidyl Ether (BADGE), 30-60% Epoxy Bisphenol F resin, and 10-30% butane-diol-diglycidyl ether. The epoxy hardener Proset 229PF contains 60-100% Polyoxypropyleneamine and 10-30% Methylene-dicyclohexylamine.

Certain amount of SWCNTs (0.05 wt-% and 0.5 wt-%) were dispersed in DMF for 0.5 h using an 80 W ultrasonic rod generator to form a stable suspension; an ice bath was used to keep the suspension cold during sonication. The nanotube suspension was then poured into 100 parts by weight of epoxy resin, and sonicated for 5 min. Afterwards solvents were evaporated at 45 °C. 34 parts by weight of hardener was then added to the mixture of SWCNTs / resin mixture and stirred under vacuum to prevent introduction of air bubbles. Dog bone test specimens (ISO 527-2, specimens type 1BA) was obtained by casting the resin/hardener mixture in a silicon mold, specimens was pre-cured at 40 °C for 24 h and post cured at 80 °C for 16 h. For comparison, the neat epoxy was prepared using the same procedure.

2.1.3.2 PC composites
Cyclohexanone (CH-ONE) was ultrasonically mixed with 1wt-% SWCNTs with a dr. Heischel UP400s ultrasonic processor set at 80 W for 2 h. Hereafter, 17–18 g of polycarbonate (PC) purchased from Bayer (Trade name: Makronol Grade M2405F) was added and stirred at 80–90 °C until the PC was dissolved. Furthermore, the compound was heated under vacuum at 130 °C for 3 days to remove CH-ONE. Injection molding (by a custom made injection molding machine) was carried out at 223 °C and the mold was heated to 75 °C.

2.1.3.3 PVDF composites
1wt-% SWCNTs were ultrasonically dispersed in N, N-dimethylformamide (DMF) for 30 min using an 80 W ultrasonic rod generator Heischel UP400s to form a stable suspension. At the same time, PVDF (Sigma-Aldrich 427144-100G) supplied by Aldrich Chemistry, Inc. was dissolved in DMF at 60 °C with constant stirring for 2 h. The CNT/DMF suspension was added to the PVDF solution and shear mixed for 30 min at the speed of 5000-6000 rpm. Afterwards, the compound was poured into a large tray to form a very thin layer and dried at 60 °C to remove DMF. TGA measurements showed no traces of DMF. Subsequently, dog bone test specimens (ISO 527-2) were obtained by injection molding (Thermo HAAKE Minijet II) at 260 °C as the melt temperature, the mold was heated to 90 °C, holding at 95 MPa for 10 s.

2.2 Techniques

2.2.1 Dynamic Light Scattering
The dispersion of SWCNT after 5 min rod sonication in various solvents was characterized by dynamic light scattering (DLS) performed on Malvern Zetasizer Nano ZS with a glass cell, using a detection angle of 173°. The test temperature was 20°C or 25°C, the viscosity of the solvent at the measuring temperature were provided to the software.

2.2.2 Dynamic mechanical analysis (DMA)
The glass transition temperature (Tg) of the SWCNT reinforced epoxy composites were measured with Dynamic mechanical analysis (DMA) with TA Q800 instrument operating in the three point bending mode at an frequency of 1.0 Hz. The data were collected from ambient to 80 °C at a scanning rate of 3 °C /min. The glass transition temperature was measured on the onset of change in the storage modulus.

2.2.3 Raman spectroscopy
The strain transfer from epoxy to the SWCNTs was evaluated by measuring the second order Raman peak (2D band) shift under tension. The position of the Raman 2D peak of SWCNTs at around 2630 cm$^{-1}$ is sensitive to the mechanical deformation. Composites were tested in Renishaw Invia Raman Microscope with 632.8nm excitation focused through an X20 objective lens. The small dog-bone specimens were loaded in a custom-made tensile test rig placed on the microscope table. The laser was parallel to the loading direction and an analyzer also parallel to the load direction was also used the so called VV geometry. The specimen was gradually loaded up to different strains and Raman spectra were taken at each strain level.
2.2.4 Tensile testing
The tensile properties of the polymer composites were measured by a Zwick100 tensile testing machine. The strain rate was 5 mm/min. The reported data of tensile strength Young’s modulus and failure strain were the average values of five samples.

3 Results and discussion
3.1 Raman 2D band shift measurements
In Figure 1 the 2D band shift is shown for different epoxy composite materials. Two observations can be done. One is that HNO₃ functionalization improves the strain transfer and the other is that low concentrations of SWCNT in the composite also improves the strain transfer. HNO₃ treatment is known to cause debundling of SWCNT bundles. A low concentration of SWCNT will possible also minimize the re-agglomeration in the polymers after dispersion and during the manufacturing of the composite. The highest 2D band shift rate we have observed is 18 cm⁻¹/% strain and is shown in figure 1. This is observed for a low concentration of SWCNTs, the low concentration will probably help the dispersion debundling of the SWCNTs. The observed shift rate is about half of the maximum 2D band shift rate observed for aligned and isolated SWCNTs in a polymeric matrix. [5] In the next section we will see how this compared to a theoretical shift rate.

3.2 Calculation of average Raman 2D band shift rate for a random 3D distribution of SWCNT
In this section we calculate the theoretical average 2D band shift rate for VV geometry and for a random 3D distribution of SWCNT i.e. an isotropic nanocomposite and it was compared with the obtained results in the previous section. For small strains the Raman 2D shift ($\Delta N_w$) is proportional to the mechanical strain ($\varepsilon$). [6] The slope ($m$) is also called the 2D peak shift rate:

$$\Delta N_w = m \cdot \varepsilon$$  (1)

For isolated and aligned SWCNTs the maximum shift rate has been found to be 35-40 cm⁻¹/% strain.[7] In the following calculation, we assume this shift is the actual shift rate when applying the strain on the nanotube and we call this shift rate $m_{\text{max}}$. So for an isolated SWCNT aligned with the tensile direction:

$$\Delta N_w = m_{\text{max}} \cdot \varepsilon$$  (2)

Depending on how the SWCNT is rotated from the principal tensile direction, the strain can be equal to the principal strain when the SWCNT is parallel to the tensile direction or be in compressive state when perpendicular to the tensile direction due to Poisson contraction. In this setup the SWCNT is first rotated $\theta$ along the x-axis and secondly $\phi$ along the new y-axis giving an angle $\beta$ to the z-axis as shown in Figure 2.

![Figure 2. Definition of the angles in the VV geometry.](image-url)
The strain is given by

\[ \varepsilon = \varepsilon_0 (\cos^2 \beta - \sin^2 \beta) \]  

(3)

Where \( \varepsilon_0 \) is the principal strain, \( \beta \) is the angle between the CNT (\( \pi \)) and the principal tensile direction which is the z-axis and \( \nu \) is Poisson’s ratio. [8,9] So for an isolated SWCNT at a given angle \( \beta \) to the tensile direction

\[ \Delta N_W(\beta) = m_{max} \cdot \varepsilon_0 (\cos^2 \beta - \sin^2 \beta) \]  

(4)

Again depending on the angle between the CNT and the polarization angle of the laser the Raman intensity will vary.

The scattered Raman intensity \( I^0_R \) is proportional to

\[ I^0_R \propto \left| \bar{e}^s \cdot \frac{d\alpha}{dq} \bar{e}^i_t \right|^2 \propto \left| \bar{e}_s \cdot \alpha \bar{e}_t \right|^2 \text{ or} \]

\[ I^0_R = I^0 \left| \bar{e}_s \cdot \alpha \bar{e}_t \right|^2 \]  

(5)

Where \( e_s \) and \( e_i \) are the polarization vectors of the scattered and incident laser light, \( \alpha \) is the polarizability tensor and \( I^0 \) is the Raman intensity when nanotube and laser polarization is aligned. For a simple shape like the SWCNT aligned along the z-axis the polarizability tensor \( \alpha_z \) has \( \alpha_{00} = 0 \) except for \( \alpha_{zz} = 1 \).[10]

When rotating the SWCNT the polarizability tensor can be calculated from

\[ \alpha = R^T \alpha_z R \]  

(6)

where \( R \) is the rotation matrix

\[ R = B \cdot A \]  

(7)

\[ A = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{bmatrix} \]

rotation along x-axis

\[ B = \begin{bmatrix} \cos \varphi & 0 & \sin \varphi \\ 0 & 1 & 0 \\ -\sin \varphi & 0 & \cos \varphi \end{bmatrix} \]

rotation along y’-axis

giving

\[ \left| \bar{e}_s \cdot \alpha \bar{e}_t \right|^2 = \cos^4 \phi \cos^4 \theta = \cos^4 \beta \]  

(8)

Combining equation (5) and (8) gives

\[ I^0_R = I^0 \left| \bar{e}_s \cdot \alpha \bar{e}_t \right|^2 = I^0 \cos^4 \beta \]  

(9)

The Raman intensity from all SWCNTs at an angle \( \beta \) from the tensile direction can be calculated by

\[ I_R(\beta) = I^0 \cdot f(\beta) \sin \beta d\beta \]  

(10)

Where \( f(\beta) \) is the distribution function of the SWCNTs. See Figure 3. Assuming a random distribution

\[ I_R(\beta) = I^0 \frac{1}{4\pi} \sin \beta d\beta \]  

(11)

and this gives for the Raman intensity

\[ I_R(\beta) = \frac{I^0}{4\pi} \cos^4 \beta \cdot \sin \beta d\beta \]  

(12)

An average 2D band shift rate (\( m_{average} \)) can be calculated by summing for all \( \beta \) the Raman intensity (equation 12) multiplied with the shift rate (equation 4) divided by the total Raman intensity.

Figure 3. Distribution of carbon nanotubes.
The shift rate from one individual SWCNT parallel to the principal tensile direction is found to be up to $37.3\,\text{cm}^{-1} /\%$. [7] Assuming a Poisson ratio of 0.4 in this case the calculated average shift rate for a random 3D is $22.4\,\text{cm}^{-1} /\%$. In the experiments the maximum shift is $19\,\text{cm}^{-1}$ showing that there is still some room for improvements in the de-bundling of the SWCNT bundles, but in the case of 10M HNO$_3$ functionalized SWCNT the shift rate is close to the theoretical maximum.

### 3.3 Influence of polymer matrix

Using different polymers causes differences in the strain transfer as seen in Figure 4. Generally the best strain transfer is observed in the epoxy matrix. Polymers with low creep strength generally give an inferior strain transfer. This might be explained by smaller residual compressive forces being developed during the cooling from the moulding temperature or stress relaxation after the manufacturing. Creep testing of the three neat polymers at room temperature and at a constant tensile load of 40 MPa and holding for 20 min, resulted in creep strains for the neat PC, PVDF, and epoxy that were 0.5%, 4.2%, and 0.6%, respectively. The inferior shift rate of PC compared to epoxy might be a result of smaller bundles as indicated by the DSL size in Table 1 or possibly covalent bonding taking place between the epoxy and the nanotubes.

As can be seen from Figure 4, the strain transfer is poor for the SWCNT-PVDF composites. Looking at the mechanical properties and especially the Young’s modulus in Table 2 the poor strain transfer is reflected in very small improvements in the stiffness.

![Figure 4. 2D band shift in different SWCNT(Carbolex A)-composites.](image)

#### Table 1. DLS results of SWCNTs (Carbolex) in the solvents used for composite fabrication.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Purified Carbolex</th>
<th>HNO3 treated Carbolex</th>
<th>ODA-treated Carbolex</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Z-Ave (nm)</td>
<td>Z-Ave (nm)</td>
<td>Z-Ave (nm)</td>
</tr>
<tr>
<td>Cyclohexanone (CH-ONE)</td>
<td>471</td>
<td>357</td>
<td>1390</td>
</tr>
<tr>
<td>Dimethylformamide (DMF)</td>
<td>193</td>
<td>176</td>
<td>465</td>
</tr>
<tr>
<td>Ethanol (EtOH)</td>
<td>322</td>
<td>261</td>
<td></td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>337</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Table 2. Mechanical properties of SWCNT (Carbolex A)-PVDF composites.

<table>
<thead>
<tr>
<th>Composite type</th>
<th>Neat PVDF</th>
<th>1 wt-% purified SWCNT/PVDF</th>
<th>1 wt-% HNO$_3$-SWCNT/PVDF</th>
<th>1 wt-% ODA-SWCNT/PVDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus (GPa)</td>
<td>1.14 ± 0.1</td>
<td>1.26 ± 0.03</td>
<td>1.18 ± 0.004</td>
<td>1.17 ± 0.003</td>
</tr>
<tr>
<td>Ultimate tensile strength (MPa)</td>
<td>41.8 ± 0.9</td>
<td>41.3 ± 1.0</td>
<td>41.1 ± 0.1</td>
<td>40.7 ± 0.2</td>
</tr>
<tr>
<td>Toughness (J/m$^3$)</td>
<td>12.3 ± 2.9</td>
<td>11.7 ± 1.1</td>
<td>10.8 ± 1.8</td>
<td>10.4 ± 1.4</td>
</tr>
<tr>
<td>Failure strain (%)</td>
<td>34.5 ± 7.5</td>
<td>32.3 ± 2.8</td>
<td>29.8 ± 4.9</td>
<td>28.9 ± 4.0</td>
</tr>
</tbody>
</table>
The other mechanical properties are degraded due to the inferior failure strain probably caused by agglomerates in the composite. This behavior is observed for all the different functionalized SWCNTs.

### 3.4 Influence of modification of SWCNT

shows the effect of modifications on the 2D band shift in an epoxy matrix. Generally the best strain transfer is observed with HNO$_3$-modification; this was also observed for other polymer matrixes. [11] The hydrodynamic sizes measured by DSL in the solvents that were used for fabrication of the composites is shown in Table 1. It is seen that generally the HNO$_3$ modification gives the smallest hydrodynamic size.

![Figure 5. 2D band shift in SWCNT(Carboxyl A)-epoxy composites with different modifications.](image)

The hydrodynamic size will normally be larger than sizes measured by other techniques as Transmission Electron Microscopy, BET surface area measurement or laser diffraction techniques. DLS size gives a single value for the size and a value for the polydispersivity and does not give information of morphology of the particles. It tend to measure agglomerate size. However it is a simple techniques capable of measuring very small particle sizes in solvent suspensions. In this case we need a value to characterize the dispersion. Dispersion of carbon nanotubes means both deagglomeration and de-bundling. These to phenomena are not independent. Despite the reservations it is believed that the DLS size is a measure of the dispersion in the solvent and also that size of CNT in the solvent will all things being equal also represent the size in the final composites or at least that the ranking of size between the different modification will be the same in the polymers as it is in the solvents. The HNO$_3$ modification helps the debundling of SWCNT and thus give the smaller hydrodynamic size. [12]. The better strain transfer for the HNO$_3$-modified SWCNTs can also be explained by stronger hydrogen bondings or even covalent bondings between the carboxylic groups on the nanotubes and the polymer matrix.

### 3.5 Influence of concentration

In Table 3 the mechanical properties of epoxy with 0.05 and 0.5 wt-% of SWCNT both untreated and with different functionalizations are shown. However, only the failure strain is improved. This behavior might be a combination of the lower Tg of the composites compared to the neat epoxy and a strengthening effect by the nanotubes. However, only the failure strain is improved. This behavior might be a combination of the lower Tg of the composites compared to the neat epoxy and a strengthening effect by the nanotubes.

### Table 3. Mechanical properties and glass transition temperature of SWCNT (Cheaptubes)-epoxy composites.

<table>
<thead>
<tr>
<th></th>
<th>E [GPa]</th>
<th>R$_m$[MPa]</th>
<th>Failure strain [%]</th>
<th>Tg @ Peak loss modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>3.33 ±0.17</td>
<td>59.3 ±1.6</td>
<td>2.82 ±0.66</td>
<td>47.6</td>
</tr>
<tr>
<td>P-SWCNT 0.05 wt-%</td>
<td>3.40 ±0.13</td>
<td>53.5 ±3.7</td>
<td>3.07 ±0.48</td>
<td>45.7</td>
</tr>
<tr>
<td>P-SWCNT 0.5 wt-%</td>
<td>3.33 ±0.16</td>
<td>53.5 ±2.4</td>
<td>3.94 ±1.81</td>
<td>47.4</td>
</tr>
<tr>
<td>8M HNO$_3$ 0.05 wt-%</td>
<td>3.23 ±0.10</td>
<td>54.6 ±0.8</td>
<td>4.91 ±0.52</td>
<td>43.2</td>
</tr>
<tr>
<td>8M HNO$_3$ 0.5 wt-%</td>
<td>3.24 ±0.14</td>
<td>55.1 ±1.1</td>
<td>3.74 ±0.41</td>
<td>44.8</td>
</tr>
<tr>
<td>Concentrated HNO$_3$ 0.05 wt-%</td>
<td>3.43 ±0.03</td>
<td>64.2 ±1.8</td>
<td>4.96 ±1.15</td>
<td>45.6</td>
</tr>
<tr>
<td>Concentrated HNO$_3$ 0.5 wt-%</td>
<td>3.50 ±0.10</td>
<td>55.7 ±0.8</td>
<td>4.71 ±1.26</td>
<td>48.0</td>
</tr>
<tr>
<td>DDA 0.05 wt-%</td>
<td>3.54 ±0.19</td>
<td>64.5 ±1.5</td>
<td>5.76 ±1.74</td>
<td>44.4</td>
</tr>
<tr>
<td>DDA 0.5 wt-%</td>
<td>3.11 ±0.26</td>
<td>56.2 ±0.6</td>
<td>3.66 ±0.59</td>
<td>40.0</td>
</tr>
<tr>
<td>Dichlorocarbene 0.05 wt-%</td>
<td>3.44 ±0.00</td>
<td>64.2 ±1.5</td>
<td>5.31 ±0.90</td>
<td>46.0</td>
</tr>
<tr>
<td>Dichlorocarbene 0.5 wt-%</td>
<td>3.45 ±0.09</td>
<td>57.8 ±1.2</td>
<td>4.39 ±0.25</td>
<td>47.3</td>
</tr>
</tbody>
</table>
modulus and tensile strength might be balanced by the degrading effect caused by the lower Tg and the reinforcement effect from the nanotubes resulting in properties similar to the neat epoxy.

Generally the best mechanical properties are seen for the low concentration of SWCNT. In Figure 6 it is clearly evidenced that the low concentration results in the best strain transfer. This behavior was observed for all the different functionalized SWCNT. [13] The strain transfer is affected by the specific surface area which again is controlled by dispersion and de-bundling of the CNT in the polymer. The lower concentration will result in a better dispersion. The superior strain transfer is reflected in the mechanical properties. The better dispersion will also mean less agglomeration and agglomerates will deteriorate the toughness and the failure strain.

4 Conclusion

The strain transfer from matrix to SWCNT depends on the dispersion, bundle size and the polymer matrix. The dispersion and bundle size is again influenced by concentration of CNTs in the matrix and modification of the SWCNTs. Compressive stresses from the matrix is also important for the strain transfer. In polymers with low creep strength these compressive stresses might be relaxed during aging and lead to inferior strain transfer. Further on in polymers with high creep strength and also high glass transition temperature a high magnitude of compressive forces might build up during cooling at the manufacturing of the composites. The efficiency of the strain transfer is reflected in the mechanical properties of the composite.

5 Reference


