- A THEORITICAL MODEL TO DESCRIBE THE REINFORCING OF POLYMERS WITH CARBON NANOTUBES

Chris Krystia, Chad Gentes, Alireza Naghash, Department of Chemical and Materials Engineering, University of Alberta, Edmonton, T6G 2G6, AB, Canada

Introduction

Carbon nanofibers (CNFs) have been made and studied since 1960's. In 1991, Sumio Iijima (Iijima, 1991) observed hollow nanofibes during arc discharge production of CNFs. These fibers were subsequently known as carbon nanotubes (CNTs). His discovery was that the highly graphitized CNTs consist of coaxial tubes and a hollow core. Ideal CNTs are composed of entirely sp^2 bonds like graphite. The sp^2 bonding gives the CNT significant strength.

Carbon nanotubes are currently being made using three main methods which are arc discharge, laser ablation and chemical vapor deposition (CVD). Are discharge and laser ablation can be considered as high temperature (>1500 ^oC) and short time reactions (Teo K.B.K. et al, 2003). Owing to high reaction temperature, straight crystalline CNTs can be produced using these two methods. Chemical vapor deposition method requires medium temperatures of 600 to 900 ^oC and long reaction times. During CVD, a hydrocarbon gas is supplied to the surface of the metal catalyst and decomposes to form hydrogen and CNTs. CVD is the most attractive method to produce CNTs in large scale.

Because of the exceptional mechanical properties and low weight of CNTs and CNFs, they are being considered as the ultimate filler materials for polymer composites (Teo K.B.K., 2003). Carbon Nanotubes should be the ideal reinforcing materials for composites due to their high aspect ratio and high in-axis strength. The size of the CNTs are also important because it allows them to flow through conventional polymer processing equipment so that complicated shapes or small parts can be moulded from their composites. Because of the improvement of physical properties that the addition of CNTs adds to polymers there is an increased of possible applications for these materials, such as aerospace and space sector and automotive industry.

Polymer Matrix-Carbon Nanotubes Integration

The sp^2 configuration of the carbon atoms in a nanotube makes bonding to another substance difficult. Two possible ways of bonding the CNTs to a polymer matrix are through the use of a binding agent and through the manipulation of the electron configuration of the carbon atoms. If an evenly distributed fraction of the carbon atoms within the nanotube had an sp^3 configuration, similar to that in diamond, a polar functional group, such as a hydroxyl or an amide group, could be attracted to the extra bond, as only three bonds are needed to connect to the nanotube structure. This would then allow hydrogen bonding to polymers with polar functional groups, such as nylons or polyesters.

There are some difficulties with this method of bonding. To be effective, an even distribution of sp^3 configured carbon atoms would have to be obtained over the surface of the nanotube to maintain even bonding and to ensure that the nanotube remains relatively straight. A curved CNT provides less linear reinforcing strength than a straight nanotube. Moreover, a sp^3 oriented carbon atom has different bond angles than one with a sp^2 orientation. This would lead to defects in CNTs. Instead of a uniform hexagonal array pentagonal or heptagonal arrangements would likely be found near the sp^3 carbon atom. These defects are the primary cause for the reduction in the strength of the CNTs, so increasing the CNT-matrix interface bond decreases the reinforcing strength of the CNTs.

It should be considered, however, that CNTs produced by today's means typically only have purities of 40 to 95%. By far the most common impurity of a CNT is in the form of a defect, not a substitution of another atom into the structure. Moreover, CNTs with higher levels of defects cost significantly less than those of higher purity, while maintaining mechanical properties substantially larger than those of other reinforcing materials.

This method of binding the CNTs to the polymer matrix would only work for polymers with polar functional groups. For non-polar polymers, such as polyethylene and polypropylene a different approach must be taken, as the only bonding possible would be based on Van Der Waals forces acting between the CNTs and the matrix. This might be accomplished through the use of coupling agents, such as epoxies. Unfortunately, most coupling agents tend to also rely on functional groups to bond to the polymer matrix, and unfortunately no references regarding the extent of their usefulness for bonding to non-polar polymers could be found.

Mechanical Properties of Carbon Nanotube-Reinforced Polymers

In order to simplify the analysis of CNTs reinforced polymers, some basic assumptions are required to be made:

1) It should first be assumed that the CNTs are distributed homogeneously throughout the polymer matrix. This is necessary in order to consider that the volume fraction of CNTs is equal to the area fraction of CNTs for a cross-section of the composite material perpendicular to the loading axis;

2) For reinforcement in one dimension, it is assumed that CNTs are lined up with the direction of axial loading;

3) For reinforcement in two dimensions it is assumed that the CNTs provide reinforcement only in those two dimensions. No reinforcing strength is lost due to CNTs being oriented in directions with a component perpendicular to the plane of interest.

4) For reinforcement in two or three dimensions, it is assumed that CNTs components transverse to the axis of loading do not significantly contribute to either the Young's Modulus or the stress-bearing capacity of the composite material.

5) Due to the large aspect ratio of CNTs, it can be assumed that the length of the nanotubes is substantially longer than the critical length (I_c). Typical CNTs can be up to 1 mm or greater in length. By definition

$$I_c = \frac{\sigma_f^* \times d}{2 \times \tau^*_i} \qquad (1)$$

Where σ^*_f is the CNT's tensile strength, d is the diameter of the CNT, and τ^*_i is the strength of the polymer-nanotube interface (McCrum, N.G., et al., 2000). Assuming CNT tensile strength of up to 150 GPa and a diameter of 50 nm, the shear strength of the polymer-CNT interface could be as low as 15 MPa for a nanotube greater than or equal of 0.5 mm in length. This demonstrates that the polymer-CNT interface is likely to be sufficiently strong that the nanotube will break before it is ripped out of the polymer matrix, and thus that it contributes its full tensile strength to the composite material.

6) It should be assumed, again, due to the large aspect ratio of CNTs, even though CNTs in a composite are typically discontinuous their effect on the composite material can be accurately reflected by a continuous fiber model. For discontinuous fibers, a correction factor (η_i) is applied to the tensile property contribution of fibers from a continuous fiber model (McCrum, N.G., et al., 2000).

$$\eta_i = 1 - \frac{\tanh(na)}{na} \qquad (2)$$

For equation (2), a is the aspect ratio (l/d) of the CNT and n is:

$$n = \left[\frac{4 \times G_m}{E_f \times \ln\left[\frac{\pi}{4 \times \phi_f}\right]}\right]^{1/2} \qquad (3)$$

The shear modulus (G_m) of some common polymers ranges from 80 MPa for nylon 6 to 1 GPa for polypropylene. The Young's Modulus of CNTs (E_f) is in the order of 900 GPa (Demezyk, B.G., et al, 2002). By inspection of equation (3), it can be seen that by reducing the volume ratio of fibers (ϕ_f) the value of n will be reduced.

Assuming a polymer shear modulus of 100 MPa, a nanotube's Young's Modulus of 900 GPa, and a volume fraction of 1% fibers, an estimated of N = 0.0101 is obtained for polymer-CNT composites. When this value is used in equation (2), along with an assumed aspect ratio of 50000 (1 mm long/20 nm diameter) a correction factor of $\eta_1 = 0.998$ is obtained. Based on the assumption that the estimates of n and of the aspect ratio accurately reflect a polymer-CNT composite, the resultant 0.2% deviation from a continuous fiber scenario can be regarded as negligible. Given that the above six conditions are true, a continuous fiber model should fairly accurately produce theoretical Young's Moduli and stress capacities for polymer-CNT composite materials.

Linear reinforcement model

Linear reinforcement of polymers would usually apply to rope-like products, where the expected stress is primarily tensile. Ropes are typically made of nylon, polyester, polyethylene, or polypropylene. In this case, it would be most beneficial to align the reinforcing CNTs with the tensile loading direction. The theoretical Young's Modulus for CNT-reinforced rope can be estimated using continuous fiber reinforcement formula:

$$E = \phi_f E_f + (1 - \phi_f) E_m \qquad (4)$$

Where ϕ_f is the volume fraction of reinforcing fibers and E, E_f, and E_m are the Young's Moduli of the composite, the fibers, and the polymer matrix, respectively. Likewise, the theoretical yield stress of the composite rope can be estimated with:

$$\sigma = \phi_f \sigma_f + (1 - \phi_f) \sigma_m \qquad (5)$$

Where σ, σ_f, and σ_m are the yield strengths of the composite, the fibers, and the polymer matrix, respectively. It is important to note that composite material mechanical properties calculated by these means assume that the CNTs lie directly parallel to the axis of tensile stress. As polymer fibers used to make rope almost always wound or woven, the carbon fibers encased in the polymer matrix would not lie totally parallel to the axis of tensile stress. Therefore the values obtained through (4) and (5) should be multiplied by a factor less than 1 that accounts for the average angles of the CNTs (and the polymer fibers) in relation to the tensile loading.

Tow or three dimension reinforcement model

For two or three dimension objects, the polymer matrix is more likely to possess bulk, as opposed to fibrous properties. An example of the reduction of mechanical properties of polymers in bulk form is shown for nylon and polyester in Table 1. While it may be possible to somewhat control the polymer fiber and CNT orientation during fabrication of two and three dimensional objects, the polymer provides an insignificant contribution to overall composite properties.

Table. Mechanical properties of some common rope-making materials.

Material	Young's modulus (Gpa)	Density (Kg/m^3)	Strength (Mpa)
Cotton	7.9	1,540	225
Hemp	32	1,490	300
Bulk Polyester	2.9	1,300	50
Bulk nylon	2.5	1,090	63
Carbon Fiber	300	1,770	3,430
Aramid Fiber	124	1,450	3,930
Polyester Fiber	13.2	1,390	784
Nylon Fiber	3.9	1,140	616
Alloy Steel	210	7,800	1,330
CNTs	Up to 1,000	500-2,500	Up to 63,000

The equations describing the Young's Modulus and yield strength of a two or three dimensional object are basically the same as those for the case of linear reinforcement. An additional factor has to be introduced in order to account for the fact that only a fraction of the CNTs provide reinforcement in the direction of interest. The equations are modified as follows:

$$E_n = X_n \phi_f E_f + (1 - \phi_f) E_m \qquad (6)$$

$$\sigma_n = X_n \phi_f \sigma_f + (1 - \phi_f) \sigma_m \qquad (7)$$

Where the subscribed n represents the direction of interest and X_n represents the fraction of nanotube reinforcement in that direction.

For isotropic materials the fraction X_n would have a value of 0.5 in the two dimensional case and a value of one third in the three dimensional case. It can be seen that the two dimensional case could be considered as an anisotropic three dimensional situation where one of the principle axes has zero reinforcement. For both the two and the three dimensional cases, regardless of whether the material is isotropic or anisotropic, the one condition that must be met is that

$$X_x + X_y + X_z = 1 \qquad (8)$$

The effect of the addition of CNTs into a nylon matrix is shown in Figures 1 and 2. Fig. 1 shows the theoretical Young's Modulus obtained for linear, two and three dimensional reinforcement while Fig. 2 shows the theoretical effect on the composite yield stress.

From Fig. 1 it appears that a significant portion of the composite material would have to be CNTs in order to attain a Young's Moldulus equal to that of the alloy steel, especially in the multidimensional cases. This result indicates that a nanotube reinforced polymer would tend to be significantly more elastic than steel. Fig. 2 however, indicates that very little reinforcement would be necessary to give the composite material a higher strength than steel, especially in one dimensional reinforcement case.

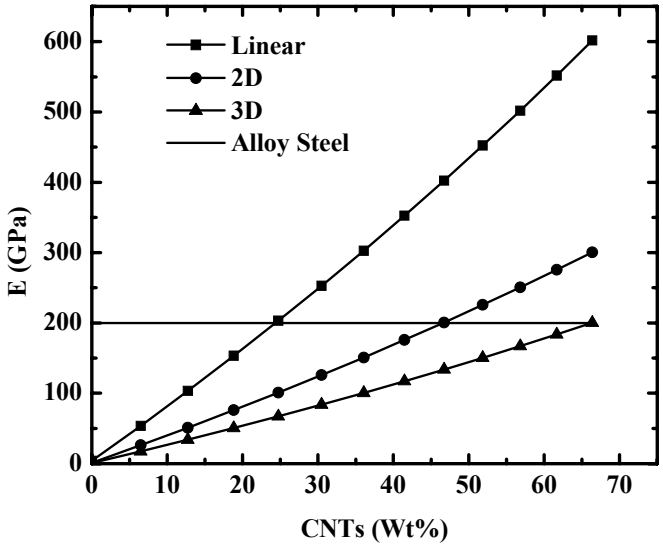

Figure 1. Effect of CNTs composition on the Young's Modulus for nylon with alloy steel data plotted for comparison.

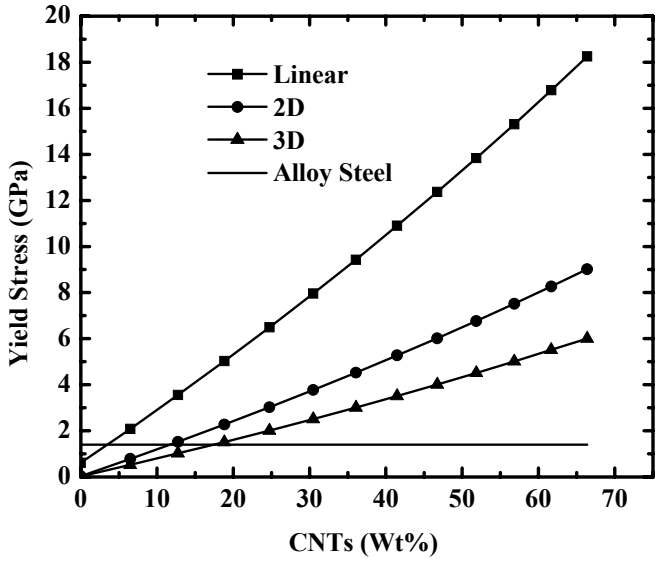

Figure 2. Effect of CNTs composition on the yield stress of nylon with alloy steel data plotted for comparison.

The density of any two-component reinforced composite material can be accurately predicted if the densities and volume fractions of the components are known through the formula (McCrum, N.G., et al., 2000).

$$\rho = \phi_f \rho_f + (1 - \phi_f)\rho_m \qquad (9)$$

Where ρ is the composite density, ρ_f is the density of the fibers, and ρ_m is the density of the reinforced matrix.

In order to obtain the weight percent amount of CNTs, the volume fraction of CNTs was multiplied by a density ratio and a factor of 100% as follows

$$Wt\% = \frac{\phi_f \rho_f}{\rho} \text{ x } 100 \qquad (10)$$

One final thing to note in regards to the mechanical properties of CNT reinforced polymer composites is that CNTs being hollow, will tend to buckle when compressive or flexural stress is applied to them. CNTs, however, are extremely resilient and can withstand severe deformation then return to their original configuration when the stress is removed.

Conclusions

Based on some basic assumptions the theoretical analysis of CNTs reinforced polymers was discussed. It was found that because of high aspect ratio of CNTs the continuous fiber model can be used to describe the CNTs' reinforcing effect of polymers. Given that the assumptions are a good estimate of the actual conditions, a continuous fiber model should fairly accurately produce theoretical Young's Moduli and stress capacities for polymer-CNT composite materials. Linear, two and three dimensional models were studied in this work. It was found that for a linear model, more than 25 wt% CNTs are required to increase the Young's Moduli of nylon fiber to that of alloy steel, whereas for two and three dimensional model a significant portion of the composite material would have to be CNTs in order to attain a Young's Modulus equal to that of the alloy steel.

References

Demczyk B.G. et al. *Materials Science and Engineering* A334: 173-178.

Iijima, S. 1991. *Nature* 354:56-7.

MacCrum, N.G. et al. 2000, Principles of Polymer Engineering. Pages 245-50, Oxford, New York.

Teo, K.B.K. et al. Catalytic Synthesis of Carbon Nanotubes and Nanofibers. Pages 1-22 in H.S. Nalwa ed., *Encyclopedia of Nanoscience and Technology,* American Scientific Publishers, USA.