Reinforcement Efficiency of Carbon Nanotubes – Myth and Reality

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Different micromechanical models for the prediction of mechanical properties of CNT/polymer composites, taking into consideration filler percolation throughout the matrix, are considered. It is demonstrated that the critical filler volume fraction, where a percolating network of CNTs is forming, marks a “turning point” in the reinforcement efficiency. Expectations for the reinforcing effect of CNTs at concentrations above a percolating threshold with the current technology are in general unrealistic.

1. Introduction

Due to their outstanding electrical, thermal, and mechanical properties, carbon nanotubes (CNTs) have many potential applications and are considered to be ideally suited for the next generation of composite materials.[1] Probably the most widely used application of CNTs is as reinforcing agents for polymers. The key issues for transferring the CNT properties to composites are: (i) homogeneous dispersion and distribution of CNTs in the matrix; and (ii) interaction between CNTs and the surrounding medium.[2,3] Due to their large specific surface area, CNTs tend to agglomerate, making their dispersion a real challenge. As a consequence, the reported results on mechanical properties of polymer composites are still far from satisfactory and are for the most part below expected simulated values. Commonly used micromechanical models such as the widely known Halpin-Tsai model or the simple rule of mixtures predict a continuous increase of the composite modulus with the addition of CNTs.[4] However, experimental results have shown that the enhancement of properties takes place up to a certain filler concentration, above which the reinforcement efficiency decreases.[5,6] One such example is shown in Figure 1 which compares experimental data for the elastic modulus of an epoxy system at various loadings of multiwalled carbon nanotubes (MWCNTs) with predicted values using the Halpin-Tsai model and the rule of mixtures. There is an obvious “turning point” at a volume fraction of CNTs of 0.00521 which is not predicted by the models.

There are numerous examples in literature which suggest that above a critical concentration of CNTs, the properties either drop or the reinforcement efficiency decreases considerably.[7–10] It is well known that nanotubes tend to aggregate and above a critical concentration will form a 3D network inside the polymeric matrix. The volume fraction of CNTs at which this 3D network forms is called the percolation threshold ($V_c$). The “turning point” in the reinforcement efficiency usually takes place at volume fractions coincident with the percolation threshold. To the best of our knowledge, there are no micromechanical models accounting for the turnaround in mechanical properties of CNT reinforced composites at concentrations above a threshold value.

In this study, we derive and compare different micromechanical models which account for the presence of dispersed and agglomerated CNTs in the polymeric matrix and consider the effect of a percolation threshold on the elastic modulus of the composite. The suitability of these models is verified by comparing simulated values with...
Experimental data from literature. The results show that some models are able to predict mechanical properties over a wide range of testing conditions. Overall the findings of this study strongly suggest that, despite of the exceptional properties of CNTs, their efficient use may be bound to limited concentrations.

2. Model Development

When using CNTs into a polymeric matrix, it is reasonable to assume that some of these nanotubes will form agglomerates. At low concentrations of filler, and considering adequate dispersion procedures, most of the nanotubes will be well dispersed into the matrix (Figure 2A). However, even at such low concentrations, some of the nanotubes will be agglomerated. At a critical volume fraction of the filler, the nanotubes will form a 3D network. We label this critical concentration the percolation threshold, $V_c$. At this point the concentration of nanotubes in the system enables the formation of a 3D network (Figure 2B). At filler concentrations exceeding the percolation threshold, the system will primarily engage all filler into the 3D network, although there still may be some nanotubes well dispersed or agglomerated present into the matrix (Figure 2C).

In view of the discussion above, one can conceptually formulate a simple mechanical model comprised of three constituents/phases: the matrix, the well-dispersed CNTs, and the agglomerated nanotubes. All these constituents have different mechanical properties and they will contribute to the overall mechanical behavior of the composite system. For simplicity, we will consider that all three constituents exhibit a linear elastic behavior and are isotropic. The well-dispersed CNTs encompass all non-entangled units characterized by an average aspect ratio $\eta$. Agglomerated CNTs consist of the percolated network (at overall concentration in the system exceeding the threshold value) and all other entangled nanotubes present in the system. The models presented here do not account for nanotube/matrix debonding, slippage at the interface matrix/nanotube, or any voids or cracks present in the system. No residual stresses are present in the system.

2.1. Three-Phase Model in Series and Parallel

The composite system contains three phases, namely the matrix of volume fraction $V_m$ and tensile modulus $E_m$, the dispersed CNTs of volume fraction $V_{\text{dis}}^{\text{NT}}$ and modulus $E_{\text{dis}}^{\text{NT}}$ and the agglomerated CNTs of volume fraction $V_{\text{agg}}^{\text{NT}}$ and modulus $E_{\text{agg}}^{\text{NT}}$. The three phases can be arranged in series or in parallel as shown schematically in Figure 3A and B.

The mechanical properties of the agglomerated nanotubes will differ significantly from the ones of the well-dispersed ones. In fact, the properties of large diameter CNT bundles are dominated by shear slippage of individual nanotubes within the bundle.[11] This inter-tube slippage within bundles lowers to a great extent their intrinsic mechanical properties and may partially explain the decrease in the modulus of a polymer composite at high volume fraction of CNTs. Experimental measurements on films of CNTs show values of elastic modulus orders of magnitude lower than the ones reported for individual CNTs.[12] Moreover, CNTs are not linked by strong hydrogen bonds, as is the case with other nanofillers, such as cellulose whiskers, and consequently, the formation of a percolating network can be detrimental for the mechanical properties of the composite system. We will explore this concept in predicting the decrease in mechanical properties of the system at nanotube concentrations above a critical value.

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can be calculated from:

\[ E_c = \frac{V_{agg}^{NT} E_{agg}^{NT} + V_{dis}^{NT} E_{dis}^{NT} + (1 - V_{agg}^{NT} - V_{dis}^{NT}) E_m}{V_{agg}^{NT}} \]  

(1)

For the case of a parallel arrangement of the three phases (Figure 3B), the strain is identical in all three phases, whereas, the stress is additive. In this case the composite modulus is given by:

\[ E_c = V_{agg}^{NT} E_{agg}^{NT} + V_{dis}^{NT} E_{dis}^{NT} + \left(1 - V_{agg}^{NT} - V_{dis}^{NT}\right) E_m \]  

(2)

Equation 1 and 2 will predict a lower and upper bound of the modulus in the composite system.

One can differentiate between the well dispersed and the agglomerated CNTs present in the system using the percolation theory. Chatterjee\(^{[13]}\) employed the concept of a “switching function”, \(f_s\), to emulate the percolation behavior in the vicinity of the percolation threshold. The switching function is defined as:

\[ f_s(V_{NT}) = \begin{cases} 0 & V_{NT} < V_c \\ 1 & V_{NT} \geq V_c \end{cases} \]  

(3)

where \(A\) is an adjustable parameter which modulates the width of the transition. In other words, the domain within which the percolation probability exhibits power-law behavior can be appropriately confined to the vicinity of the threshold by a suitable choice of the parameter \(A\).\(^{[13]}\)

For filler volume fractions exceeding the percolation threshold, a fraction \(V_{agg}^{NT} = f_s V_{NT}\) of the filler particles in the system belongs to the percolating network, whereas, the remaining rods, \(V_{dis}^{NT} = V_{NT}(1 - f_s)\) are treated as being uniformly dispersed within the matrix material.

The percolation threshold, \(V_c\) depends on the CNT aspect ratio. Based on the excluded volume concept, Celzard et al.\(^{[14]}\) and Balberg et al.\(^{[15]}\) estimated the percolation threshold to be:

\[ V_c = \frac{0.5}{\eta} \]  

(4)

where \(\eta = l/d\) is the aspect ratio of the CNTs, and \(l\) and \(d\) are the average length and diameter of the nanotubes, respectively. In systems with large distributions of aspect ratios, the percolation threshold can be lower than the value predicted by Equation 4.

Whereas, the inclusion of the percolation concept in the three phase model in series and parallel can give some guidelines in terms of predicting the mechanical behavior of CNT filled systems, in order to better account for the effect of a percolating network on the mechanical properties a more advanced model is required. Such a model may be the Takayanagi model described below.

### 2.2. Takayanagi Model

Takayanagi et al.\(^{[16]}\) developed a two-phase mechanical model to predict the modulus of a crystalline polymer, taking into consideration the crystalline and non-crystalline phases of a polymer and the fact that different parts of the crystalline phase can undergo different deformation under the application of stress. A schematics for the series-parallel (model I) and parallel-series (model II) models is shown in Figure 3C and D. The Takayanagi model was used successfully to analyze tensile properties for polymer blends and for composite systems with diverse filler morphologies.\(^{[17,18]}\) Ouali et al.\(^{[19]}\) extended the parallel-series model of Takayanagi by introducing a percolating concept. This enabled the authors to apply the model to
predict mechanical properties for polymer composites reinforced with cellulose nanowhiskers and polymer blends.\[17\] Parameters $\lambda$ and $\phi$ or their combinations reflect volume fractions of the system components. So far, the series-parallel model of Takayanagi has not been extended to include a percolating concept.

Following the concept put forward by Ouali et al.,\[19\] we used the percolation concept in the series-parallel and parallel-series models of Takayanagi to predict mechanical properties of our three-phase system consisting of the matrix, the agglomerated CNT phase, and the well-dispersed CNT phase. Schematics of our models are shown in Figure 3C and D. In our models, $1 - \lambda$ is the volume fraction of the percolating phase, mostly comprised of agglomerated nanotubes, and $\lambda \phi$ is the volume fraction of the dispersed CNTs. It follows that the volume fraction of the CNTs is given by:

$$V_{\text{NT}} = 1 - \lambda + \lambda \phi$$

The volume fraction of the percolating phase varies between 0, at CNT concentrations below a percolation threshold, and 1 when the volume fraction of CNTs approaches 1. Using the percolation theory, one can relate the volume fraction of the percolating phase to the overall CNT concentration in the system through:

$$1 - \lambda = V_{\text{NT}} = \frac{V_{\text{NT}} - V_c}{1 - V_c}$$
$$1 - \lambda = 0 \quad V_{\text{NT}} < V_c$$
$$1 - \lambda = 1 \quad V_{\text{NT}} = 1$$

In Equation 6 above, $V_c$ is the critical volume fraction to reach a geometrical percolation of nanotubes and $b$ is the percolation exponent believed to be 0.4 in a 3D geometrical system.\[20\]

In addition, the amount of well dispersed and agglomerated CNTs present in the system can be related to the overall CNT concentration by applying the concept of a switching function ($f_0$) described above (Equation 3).

Considering model I (Figure 3C), the elastic modulus of the composite $E_c$ can be written as:

$$E_c = \frac{(1 - \lambda)(1 - V_{\text{NT}})E_{\text{NT}}^{\text{agg}} + (V_{\text{NT}} + \lambda - 1)E_{\text{m}} + \lambda E_{\text{NT}}^{\text{dis}}}{(1 - V_{\text{NT}})E_{\text{NT}}^{\text{agg}} + (V_{\text{NT}} + \lambda - 1)E_{\text{m}} + \lambda^2 E_{\text{NT}}^{\text{dis}}}$$

where $E_{\text{NT}}^{\text{agg}}$ and $E_{\text{NT}}^{\text{dis}}$ are the Young's moduli of the percolated CNT network and of the dispersed nanotubes, respectively, and $E_m$ is the Young's modulus of the matrix phase. Below the percolation threshold ($1 - \lambda = 0$), Equation 7 simply reduces to the rule of mixtures,

$$E_c = (1 - V_{\text{NT}})E_m + V_{\text{NT}}E_{\text{NT}}^{\text{dis}}$$

For model II (Figure 3D) the modulus of the composite is given by

$$E_c = \frac{E_{\text{m}}E_{\text{NT}}^{\text{dis}}}{(1 - V_{\text{NT}})E_{\text{NT}}^{\text{agg}} + V_{\text{NT}}E_{\text{m}}}$$

Below the percolation threshold ($1 - \lambda = 0$), Equation 9 reduces to the series model (lower bound)

$$E_c = \frac{E_{\text{m}}E_{\text{NT}}^{\text{dis}}}{(1 - V_{\text{NT}})E_{\text{NT}}^{\text{agg}} + V_{\text{NT}}E_{\text{m}}}$$

In some studies using the Takayanagi equations with the percolation concept, it has been suggested that the formation of a percolating network of fillers is the mechanism responsible for improving the composite mechanical properties.\[21\] In such cases, fillers like, for example, cellulose whiskers are linked by strong hydrogen bonds and model II with percolation captures well the system mechanical behavior. However, in the case of CNTs which form a geometrical percolating network without strong hydrogen bonds, the network formation can be detrimental to the system mechanical properties. Such behavior is better described using the Takayanagi model I with the percolation concept.

3. Application

3.1. Model Comparison

In this section we compare the various models described above for predicting the elastic modulus of polymer composites containing CNTs. We consider a composite system with CNTs of average aspect ratio of 333, rendering a percolation threshold of 0.0015. We employ Chatterjee's switching function with $A = 1.2$ to describe percolation behavior. The modulus of the agglomerated phase is considered to be $E_{\text{NT}}^{\text{agg}} = 50$ GPa, whereas, the Young's modulus of the matrix and dispersed CNTs are assumed to be 3 and 900 GPa\[12\] respectively. Figure 4 compares the moduli calculated from the Takayanagi models I and II with the three phase model in series and parallel.

Takayanagi model I predicts an increase in the composite modulus with the amount of CNTs in the system up to the percolation threshold ($V_c = 0.0015$). Once a percolating network is formed, the modulus drops continuously when
further increasing the CNTs amount. As Figure 4 illustrates, the reinforcement effect is significantly higher before reaching the percolation threshold but it deteriorates considerably afterwards. The results obtained for the three phase model in parallel are identical to the Takayanagi model I up to the threshold concentration, not surprisingly since both models consider the matrix and dispersed CNTs to be arranged in series below the percolation threshold. Once the CNT network is formed the reinforcement efficiency decreases instantly.

The three phase series model gives a lower bound for the composite modulus considering that all three phases experience the same stress and the strain is additive. Takayanagi model II closely follows this lower bound up to the percolation threshold, followed by a slight increase in the composite modulus once the CNT network is formed. The three phase parallel model is based on the assumption that all three phases can deform to the same extent upon the application of stress, which will render an upper bound to the composite modulus. However, a more realistic picture can be obtained if one differentiates between the deformation of the dispersed and percolated CNTs, which is achieved by employing Takayanagi model I.

### 3.2. Fitting Experimental Data

In order to analyze the suitability of the various mechanical models for predicting system properties, experimental data from literature are compared with model predictions. Figure 5A shows the experimental data obtained by Wu et al.\cite{7} for silane-modified MWCNT/epoxy composites. The MWCNTs have been treated 24 h in a mixture of HNO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4}, which may explain the rather low aspect ratio further increasing the CNTs amount. As Figure 4 illustrates, the reinforcement effect is significantly higher before reaching the percolation threshold but it deteriorates considerably afterwards. The results obtained for the three phase model in parallel are identical to the Takayanagi model I up to the threshold concentration, not surprisingly since both models consider the matrix and dispersed CNTs to be arranged in series below the percolation threshold. Once the CNT network is formed the reinforcement efficiency decreases instantly.

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reported by the authors. We have employed Takayanagi I model with Chatterjee’s percolation function to fit the experimental data. Our fitting parameters are the modulus of the dispersed CNT and the modulus of the percolated network, as well as the parameter A of the switching function. The model fits very well the experimental data. We also show the three phase parallel model with Chatterjee’s percolation function employing the same material parameters. Noteworthy, are the rather low values for the CNT modulus which may be due to their rather low aspect ratio, low interfacial shear strength, integrity, possible waviness,[22] as well as sliding between tube interfaces in MWCNTs.[23]

Omid et al.[24] prepared MWCNT/ epoxy composites using a high power tip sonication method for the CNT dispersion and reported experimental values for the composites’ moduli for CNT concentrations as high as 10 wt%. In Figure 5B we compare Omid’s experimental results with model predictions. Note that Takayanagi model I captures well the change in CNT reinforcing efficiency once the percolation concentration is reached. The three phase parallel model does not fit well the experimental data.

Martone et al.[5] reported results for epoxy/MWCNT composites prepared using a high energy sonicator. The experimental data for the bending modulus, as well as the simulated values are presented in Figure 5C. Noteworthy, the calculated percolation threshold of 0.0005 coincides with the experimental value obtained by the authors via electrical conductivity measurements. In addition, morphological studies revealed also the formation of a percolating network.

Figure 6A shows the modulus for ultrahigh-molecular-weight polyethylene/MWCNT composites prepared by Ko and Chang[25] The CNTs were treated in concentrated H2SO4 and functionalized. The results show that up to the critical percolation threshold, the CNTs reinforce the polymer matrix but at higher volume fractions of CNTs the modulus drops significantly, even below the modulus of the pristine resin. The Takayanagi model I can fit these unexpected results very well.

Phenolic/based composites reinforced with MWCNTs have been prepared by Yeh et al.[26] The CNTs were dispersed in the phenolic resin via sonication. The simulated modulus using Takayanagi model I satisfactorily matches the experimental data (Figure 6B).

Guojian et al.[27] reported the elastic modulus for poly(vinyl chloride)/MWCNT composites. Figure 6C shows these results as well as simulated values using Takayanagi I model and the three phase parallel model. Above the percolation threshold value, there is a decrease in the modulus which is well captured by the Takayanagi model I.

Hou et al.[28] reported results for reinforced poly(vinyl acrylonitrile) using few-walled CNTs. The CNTs were treated in HNO3 and dispersed using a tip sonicator. The experimental results (Figure 6D) show a reduction in the reinforcing effect of the CNTs after the formation of a percolating network throughout the matrix. This effect is well captured by the simulated curve using Takayanagi model I.

The suitability of the Takayanagi model I in predicting the elastic modulus of CNT composites is well demonstrated in the examples presented above. We have shown also the simplified three-phase model system to reveal the
differences between these two “upper bound” models. All the experimental data and the fitted curves presented in this paper point out to the unrealistic expectations for the reinforcing effect of CNTs at concentrations above a percolating threshold. The critical volume fraction where a percolating network of CNTs is developed marks a “turning point” in the reinforcement. This critical volume fraction depends on a number of factors such as the quality of CNTs, aspect ratio, polydispersity, CNT waviness effect, and CNT functionalization. Another important factor in attempting to predict mechanical properties of CNT reinforced composites is the interaction between the filler and the matrix. The models presented in this work do not account for nanotube/matrix debonding or slippage at the interface matrix/nanotube. In view of this, one may look at these models as predictive of an upper bound in the mechanical properties of composite materials. This reinforces the conclusion that in spite of the exceptional properties of CNTs, their efficient use is bound to limited concentrations.

4. Conclusion

Different micromechanical models which account for the presence of dispersed and agglomerated CNTs in a polymeric matrix and consider the effect of filler percolation on the elastic modulus of composites have been presented. The experimental data and the fitted curves have shown that significant enhancement of mechanical properties takes place up to a certain filler concentration, after which the reinforcement efficiency decreases dramatically. This “turning point” in the reinforcement efficiency usually takes place at volume fractions coincident with the percolation threshold. This behavior is well captured by the Takayanagi model I. The findings of this study point out that in spite of the exceptional properties of CNTs, their efficient use as reinforcing agents is bound to limited concentrations. Moreover these results suggest that expectations for exceptional reinforcement efficiency of CNTs at concentrations above a percolating threshold with the current technology are unrealistic. In order to use CNTs at their full potential, issues such as interfacial shear strength, purity, integrity, orientation, dispersion, and distribution/alignment will have to be carefully examined and addressed.

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