Original Article

Tensile modulus prediction of carbon nanotubes-reinforced nanocomposites by a combined model for dispersion and networking of nanoparticles

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A B S T R A C T

In this work, two models for the tensile modulus of composites and blends are joined, assuming the dispersion and networking of carbon nanotubes (CNTs) and the interphases around CNTs in polymer nanocomposites after the percolation threshold. Equations are given to express the percolation threshold, the network fraction, and the fractions of interphases in the nanocomposites. The suggested model predicts the tensile modulus in several samples, and the roles and efficiencies of all parameters in the nanocomposite modulus are determined. CNT radius (\( r \)) and interphase thickness (\( t \)) as well as the modulus (\( E_0 \)) and volume fraction (\( \phi_0 \)) of the interphase surrounding the CNT network have the most important influences on the modulus; \( R = 10 \text{ nm} \) and \( t = 35 \text{ nm} \) produced a 400% improvement in the modulus of nanocomposite compared to the neat polymer matrix.

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1. Introduction

A substantial effort currently focuses on the production of new polymer composites and nanocomposites, due to their excellent properties and the development of novel applications [1–10]. Among the nanofillers, carbon nanotubes (CNTs) have shown outstanding properties amenable to numerous potential applications [11–19], including one or several cylindrical whiskers made from in-plane graphite construction [20,21]. The Young’s modulus of CNTs is estimated in the range of 1 TPa (1000 GPa). The CNT architecture can be created in a polymer matrix to fabricate polymer/CNT nanocomposites (PCNTs). It has been reported that the thermal cycling process can increase the hardness of PCNTs, while it can quickly decrease the hardness of pure polypropylene (PP) and PP/Kenaf composites [22]. Moreover, the poly (ether ether ketone) (PEEK)/multi-walled CNT (MWCNT) nanocomposite containing 6.5 wt% MWCNT showed an average tensile strength and modulus of 388.66 MPa and 6.52 GPa, respectively, which were higher than those of the bulk sample [23].

The main factors for optimization of the reinforcing effects of CNTs in PCNTs include the dispersion quality of the CNTs and the interfacial adhesion between the polymer host and the CNTs [24,25]. CNTs commonly form aggregates/agglomerates due to their high aspect ratio and strong van der Waals attraction, resulting in an inhomogeneous dispersion in polymer matrices. Moreover, the surfaces of CNTs
cannot provide strong interfacial adhesion with a polymer matrix, which restricts the effective load transfer from the matrix to the filler. Some techniques to improve these factors, such as surface modification of CNTs, have been described in the literature [26,27].

Almost all polymers made on a large scale are insulators. Thus, the electrical properties in polymer materials can be improved by preparing the nanocomposites with conductive fillers, as has been shown in various applications in biomaterials, electronics, sensors, and optics [28–35]. CNTs can cause high conductivity at lower fractions compared to carbon black or carbon fibers. The conductive PCNTs commonly display a percolation-type behavior, where the charge transports take place at a critical volume fraction of the CNTs, known as the percolation threshold [36,37]. In fact, a conducting network forms in a polymer matrix upon percolation, which rapidly increases the conductivity. The mechanical properties of polymer nanocomposites have also shown a percolation-like behavior, which is referred to as the mechanical percolation of high-aspect-ratio nanofillers [38,39]. Similar to electrical percolation, the mechanical percolation of nanocomposites can also take place at very low levels of filler concentration.

Particles at the nanoscale have a huge interface area, giving nanocomposites more interface opportunities with a polymer matrix, compared to usual composites [40–42]. The specific surface area of CNTs with a diameter of 20 nm is on the order of 100 m² per gram. Thus, a significant interfacial area is produced in nanocomposites, which affects their overall properties. In the past studies, it was assumed that the interfacial effects yield a different phase in nanocomposites, called the interphase, which displays different properties from the host matrix and the nanoparticles. Previous investigations have shown the reinforcing role of the interphase in polymer nanocomposites by modeling techniques for mechanical behavior [43,44]. Moreover, the size and stiffness of the interphase have been well characterized by models developed for the mechanical properties of nanocomposites, such as tensile modulus and yield strength [45–47]. The interphase can also produce a positive effect on the percolating level of nanoparticles. It can create a network structure in nanocomposites sooner than the networking of nanoparticles, which shifts the percolation threshold to a lower filler concentration [37,48]. Accordingly, the interphase improves the mechanical properties of nanocomposites in terms of reinforcing and percolating.

Some power-law models have been developed for the tensile modulus of blends and composites above the percolation threshold, because the percolating effect rapidly improves the modulus. Kolarik [49] expressed a model for the tensile modulus of co-continuous polymer blends above the percolation threshold. Additionally, Ouali et al. [50] developed a “rule of mixtures” by percolation effect and proposed a model for the modulus of polymer composites. These models were also used to study the modulus of polymer nanocomposites above percolation threshold, even though they cannot be applied in practice because they ignore the interphase as an important term. In our previous paper [51], we used the Ouali model to simplify and develop the Kolarik model for the tensile modulus of CNT nanocomposites by assuming the presence of CNT networks. Specifically, we only focused on the CNT networks in that previous article.

In this study we coupled two Kolarik systems, assuming the dispersion and networking of nanoparticles, to predict the tensile modulus in PCNTs above the percolation threshold. Since those two models do not consider the interphase region, we added interphases around the dispersed and networked nanoparticles to the developed model. We applied this new model to predict the tensile modulus as well as the interphase and network properties in certain PCNTs taken from the literature. Further, the effects of the parameters in our new model on the modulus are clarified and their efficiencies are debated.

### 2. Equations

Kolarik [49] suggested a cubic orthogonal skeleton or three perpendicular plates (3PP) system (Fig. 1a) for the tensile modulus of particulate composites, which can be applied for polymer nanocomposites containing dispersed nanoparticles. He suggested the following equation based on this structure:

\[
E = E_m f(2-f) + \frac{(1-f)^2}{f/E_m + (1-f)/E_f} \tag{1}
\]

\[
f = 1 - \phi_f^{1/3} \tag{2}
\]

where \(E_f\) and \(E_m\) indicate the tensile modulus of the filler and the polymer matrix, respectively, and \(\phi_f\) is the filler volume fraction. Due to the outstanding modulus of the CNTs (1000 GPa), the term \((1-f)/E_f\) can be neglected, which results in:

\[
E = E_m f(2-f) + \frac{E_m(1-f)^2}{f} \tag{3}
\]

The relative modulus of the nanocomposites can be expressed by \(E/E_m\) as:

\[
E_R = f(2-f) + \frac{(1-f)^2}{f} \tag{4}
\]

In addition, Kolarik suggested a cross-orthogonal skeleton model (COS), including three orthogonal bars of filler surrounded by a matrix in a unit cube (Fig. 1b), for polymer blends with a co-continuous structure. This model can be applied for PCNTs above the percolation threshold, where the network of CNTs is presumed as a continuous phase in polymer matrix. Kolarik proposed the initial form of the model according to COS as:

\[
E = E_m(1-f^2) + E_f f^2 + \frac{2f(1-f)E_m}{\frac{1}{f} + \frac{E_m}{E_f}} \tag{5}
\]

\[
1 - \phi_f - (1-f)^2(1+2f) = 0 \tag{6}
\]
Fig. 1 – (a) Cubic orthogonal skeleton or three perpendicular plates (3PP) model for polymer particulate composites, and (b) cross-orthogonal skeleton (COS) system consisting of three orthogonal bars as reinforcement [49].

However, we simplified and developed this model for PCNTs assuming the percolation effect [51] as:

\[ E_R = 1 + \frac{E_f \psi_d^{1.4}}{E_m} + 2\psi_f^{0.7} \]

(7)

Kolarik equations can be applied when nanoparticles are dispersed or networked in nanocomposites. This status commonly occurs in PCNTs above the percolation threshold, where a fraction of the CNTs is dispersed in the polymer matrix, while others form a network structure. So, a model can be suggested for the tensile modulus of PCNTs, including the dispersed nanoparticles and the CNT network above the percolation threshold, by coupling Eqs. (4) and (7) as:

\[ E_R = f(2 - f) + \frac{(1 - f)^2}{f} + \frac{E_{N\phi_f}^{1.4}}{E_m} + 2\psi_f^{0.7} \]

(8)

\[ f = 1 - \psi_d^{1/3} \]

(9)

where \( \psi_d \) and \( \phi_f \) are the volume fractions of the dispersed and networked nanoparticles, respectively, and \( E_N \) is the modulus of the CNT network. The absence of CNTs in the sample \( (\phi_f = \phi_N = 0) \) results in \( E_R = 1 \), i.e., the modulus of the sample is equal to the modulus of the polymer matrix. Eq. (8) properly predicts this incident \( (f = 1) \). However, when 1 in Eq. (7) is added to Eq. (8), \( E_R = 2 \) is calculated at \( \phi_d = \phi_N = 0 \), which is incorrect. In fact, Eq. (8) considers the contributions of dispersed and networked CNTs in the nanocomposites using Eqs. (4) and (7).

This equation can be further developed by assuming an interphase surrounding the nanoparticles. This is a reasonable assumption because an interphase usually forms in polymer nanocomposites and expressly governs their mechanical behavior. When the effects of an interphase around dispersed particles and a filler network are assumed, Eqs. (8) and (9) become:

\[ E_R = f(2 - f) + \frac{(1 - f)^2}{f} + \frac{E_{N\phi_f}^{1.4}}{E_m} + 2\psi_f^{0.7} + \frac{E_{N\phi_f}^{1.4}}{E_m} + 2\psi_f^{0.7} \]

(10)

\[ f = 1 - (\psi_d + \psi_N)^{1/3} \]

(11)

where \( \psi_d \) and \( \phi_N \) are the volume fractions of the interphases surrounding the dispersed and networked nanofiller, respectively, and \( E_N \) is the modulus of the latter one. Eq. (11) only considers the interphase surrounding dispersed particles because this equation is derived from Eqs. (2) and (4) for the nanocomposites containing dispersed particles. However, Eq. (10) assumes an interphase around the CNT network by reformulating Eq. (7). In fact, both equations for dispersed and networked CNTs are reformulated assuming interphase regions, but Eq. (4) only considers the volume fraction of nanoparticles in the modulus, which is related to the volume fraction of the interphase region in Eq. (11). Additionally, since Eq. (7) for the modulus of nanocomposites above the percolation threshold reflects the concentration and modulus of the CNTs, it is recast into Eq. (10) considering the modulus and concentration of the CNT network and the interphase region.

We then developed some formulas to calculate the \( \phi_N, \phi_d \), \( \phi_f \) and \( \phi_N \) parameters. As was stated, the interphase area around nanoparticles forms a network in the PCNTs before being connected to the CNTs. The volume fraction at the percolation point of CNTs is given [36] as:

\[ \phi_f = \frac{\pi R^2 l + (4/3)\pi R^3}{\frac{2\pi}{3}(R + t)^3 \left[ 1 + \frac{2}{3} \left( \frac{1}{R + t} \right) + \frac{4}{27} \left( \frac{1}{R + t} \right)^2 \right]} \]

(12)

where \( R \) and \( l \) are the radius and length of the CNTs, respectively, and \( t \) is the interphase thickness.

The fraction of nanoparticles in the network phase \( (g) \) above the percolation threshold was also estimated [52] by:

\[ g = 1 - \exp\left[-A\phi_f^{0.474} \right] \]

(13)

where \( A \) is a constant parameter as \( A = 0.02 \). By the \( g \) parameter, the volume fraction of the networked nanoparticles is given by:

\[ \phi_N = g\phi_f \]

(14)

which can estimate the \( \phi_d \) parameter by:

\[ \phi_d = \phi_f - \phi_N \]

(15)

Application of these equations indicates that the percolation threshold of CNTs determines the fraction of nanoparticles in the dispersed and networked phases.
The volume fraction of the interphase ($\phi_i$) was defined by the radius of the CNTs and interphase thickness [53] as:

$$\phi_i = \phi_f \left(1 + \frac{t^2}{R} \right) - 1$$  \hspace{1cm} (16)

When the concentrations of the dispersed and networked nanoparticles in PCNTs are considered, the $\phi_d$ and $\phi_{IN}$ parameters can be calculated by:

$$\phi_d = \phi_d \left(1 + \frac{t^2}{R} \right) - 1$$  \hspace{1cm} (17)

$$\phi_{IN} = \phi_N \left(1 + \frac{t^2}{R} \right) - 1$$  \hspace{1cm} (18)

Now all the parameters in the suggested model (Eqs. (10) and (11)) can be calculated by the properties of the nanoparticles, the interphase, and the network. In the next section, all of these expressed equations are applied to predict the modulus of PCNTs.

3. Results and discussion

3.1. Evaluation of model by experimental results

We applied the developed model to predict the modulus for some reported samples in the literature. Fig. 2 exhibits the experimental results and the predicted moduli by the model for poly (styrene-co-butyl acrylate) (PSBA)/MWCNT [54], polyyacrylonitrile (PAN)/MWCNT [55], polypropylene (PP)/MWCNT [56], ultrahigh-molecular-weight polyethylene (UWPE)/MWCNT [57], polyamide 6 (PA6/MWCNT) [58], and poly (vinyl alcohol) (PVA)/MWCNT [59] samples. These samples were randomly chosen from relevant articles. This model is certainly applicable for other PCNT systems. The characteristics of the polymer matrix and the nanoparticles were extracted from the original references, as reported in Table 1. Fig. 2 illustrates that the theoretical values calculated by our model properly agree with the experimental results, which indicate the formation of interphases and CNT networks in these samples. Therefore, this model can predict the tensile modulus of PCNTs above the percolation threshold.

When our model is applied to the experimental results of the modulus, it can predict the average levels of the interphase and network properties based on the experimental data of the modulus. However, the typical techniques for calculating the interphase and network properties are very difficult because they analyze the interphase and network at the nanoscale. Therefore, it is better to focus on the predictions of the interphase and the network characteristics. The modeling methods for predicting interphase and network properties are normally usable, as stated in Refs. [38,44,48].

We calculated the interphase characteristics for the reported samples using our model; they are reported in Table 1. As is known, the interphase thickness cannot exceed the gyration radius of polymer chains. Furthermore, the interphase modulus changes from the modulus of the matrix to the nanofiller modulus. Thus, we calculated the correct values for the interphase properties in the reported samples. The poorest interphases around dispersed and networked CNTs formed in the PSBA/MWCNT sample, while the strongest ones developed in the UWPE/MWCNT nanocomposite. Since the extents of the interphase thickness and modulus depend on interfacial interaction/adhesion between the polymer and nanofillers, these calculations reflect the different levels of interfacial properties in the samples. This means that the strongest interfacial bonding formed in the UWPE/MWCNT sample, while the poorest one was observed in PSBA/MWCNT. The interfacial adhesion is correlated to the compatibility between the polymer matrix and the nanoparticles, which can be enlarged by modification of the components [60,61].

Besides the interphase properties, our new model can also predict the network modulus. The calculations show the highest and the lowest $E_N$ values in the UWPE/MWCNT and PSBA/MWCNT samples, respectively. These results are similar to those for the interphases, because these parameters consistently cause a reinforcing effect in nanocomposites. We calculated the percolation threshold, assuming an interphase region in PCNTs, according to Eq. (12), and it is included in Table 1. The lowest level of $\phi_f$ was observed in the PA6/MWCNT nanocomposite, whereas the highest levels were calculated for the PSBA/MWCNT and UWPE/MWCNT samples. Generally, the samples containing thin and long CNTs as well as a thick interphase showed the smallest percolation threshold values in PCNTs. Accordingly, although the UWPE/MWCNT sample contained the longest CNTs and the thickest interphase, thick CNTs worsened its percolation threshold. On the other hand, PA6/MWCNT showed the lowest level of percolation threshold among the reported samples, due to having the thinnest CNTs. This demonstrates that the application of this model can give some valuable results, such as the interphase and network properties, as well as percolation level for PCNTs.

3.2. Analysis of parameters

We produced 3D and contour plots to evaluate the model predictions at various ranges of all the parameters. Fig. 3 demonstrates the effects of the $\phi_f$ and $l$ parameters (the volume fraction and length of the nanoparticles, respectively) on the predicted modulus at average values of the other factors ($E_m = 2$ GPa, $R = 10$ nm, $t = 10$ nm, $E_d = 200$ GPa, $E_N = 1500$ GPa, and $E_N = 2000$ GPa). The highest modulus is estimated by the highest levels of these parameters, while a very low level of $\phi_f$ causes the smallest modulus. As displayed, $E_R = 2.8$ is reported at $\phi_f = 0.02$ and $l = 30$ $\mu$m, but $\phi_f < 0.006$ cannot reinforce the PCNTs. Accordingly, very low concentrations of short or long CNTs cannot improve the modulus of PCNTs, which demonstrates the important role of nanoparticle concentration in the behavior of nanocomposites. Nanoparticles with excellent mechanical properties can significantly reinforce the nanocomposites, but their concentration should be higher than a critical value, which is reported here as 0.006.

Although a high concentration of nanoparticles mainly increases the modulus, the improvement level depends on the length of nanoparticles. As observed in Fig. 3, the longest nanotubes can result in the highest modulus because the length of CNTs determines the level of reinforcement. In fact, long CNTs can involve a large number of polymer chains, which positively increases the stiffness [62], while short nanotubes cannot be in contact with many polymer chains, which weak-
ens the reinforcing effect. Moreover, Eq. (12) shows that the CNT length has a good effect on the percolation threshold, i.e., long CNTs lower the level of percolation, which raises the network fraction of the nanoparticles (Eq. (14)) and the modulus of the PCNTs). As a result, finding a better modulus by seeking long CNTs is well justified, which shows the correct application of our model.

Fig. 2 – The experimental data and the estimated moduli for (a) PSBA/MWCNT [54], (b) PAN/MWCNT [55], (c) PP/MWCNT [56], (d) UWPE/MWCNT [57], (e) PA6/MWCNT [58] and (f) PVA/MWCNT [59] samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_m$ (GPa)</th>
<th>$R$ (nm)</th>
<th>$l$ (µm)</th>
<th>$t$ (nm)</th>
<th>$E_d$ (GPa)</th>
<th>$E_l$ (GPa)</th>
<th>$E_N$ (GPa)</th>
<th>$\phi_p$</th>
</tr>
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<tr>
<td>PSBA/MWCNT [54]</td>
<td>0.520</td>
<td>10</td>
<td>10</td>
<td>2</td>
<td>50</td>
<td>1700</td>
<td>800</td>
<td>0.0008</td>
</tr>
<tr>
<td>PAN/MWCNT [55]</td>
<td>2.200</td>
<td>9</td>
<td>10</td>
<td>11</td>
<td>5000</td>
<td>3700</td>
<td>2700</td>
<td>0.0004</td>
</tr>
<tr>
<td>PP/MWCNT [56]</td>
<td>0.773</td>
<td>8</td>
<td>10</td>
<td>11</td>
<td>300</td>
<td>3500</td>
<td>2600</td>
<td>0.0003</td>
</tr>
<tr>
<td>UWPE/MWCNT [57]</td>
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<td>25</td>
<td>20</td>
<td>14</td>
<td>700</td>
<td>5000</td>
<td>3300</td>
<td>0.0008</td>
</tr>
<tr>
<td>PA6/MWCNT [58]</td>
<td>2.450</td>
<td>6</td>
<td>10</td>
<td>10</td>
<td>400</td>
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<td>0.0002</td>
</tr>
<tr>
<td>PVA/MWCNT [59]</td>
<td>1.950</td>
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<td>10</td>
<td>7</td>
<td>200</td>
<td>2000</td>
<td>1600</td>
<td>0.0006</td>
</tr>
</tbody>
</table>
Fig. 3 – The roles of “$\phi_f$” and “l” parameters in the predicted modulus at average $E_m = 2$ GPa, $R = 10$ nm, $t = 10$ nm, $E_{id} = 200$ GPa, $E_{iN} = 1500$ GPa and $E_N = 2000$ GPa: (a) 3D and (b) contour plots.

Fig. 4 – (a) 3D and (b) contour plots for the effects of “$E_m$” and “$\phi_p$” parameters on nanocomposite modulus at $\phi_f = 0.01$, $R = 10$ nm, $t = 10$ nm, $E_{id} = 200$ GPa, $E_{iN} = 1500$ GPa and $E_N = 2000$ GPa.

Fig. 4 plots the variation of the nanocomposite modulus with respect to the $E_m$ and $\phi_p$ parameters. The highest modulus is observed at the lowest levels of the $E_m$ and $\phi_p$ parameters, while increasing these parameters lowers the modulus. This suggests that the modulus of nanocomposites containing a poorer matrix and smaller percolation threshold is improved by the addition of nanoparticles. The role of the matrix modulus may be interpreted by the “rule of mixtures,” wherein the modulus of a nanocomposite depends on the moduli of the polymer host and the nanoparticles. Obviously, the modulus of a poor matrix more closely approximates the nanoparticles modulus compared to a stronger one, due to the significant difference between the moduli of the polymer matrix and the nanoparticles. Additionally, a filler network quickly forms when the percolation threshold is slightly higher. The nanoparticles involved in the network (network fraction) are enlarged by a low percolation level. Both of these occurrences have positive influences on the modulus of nanocomposites. Several literature reports attempted to decrease the percolation threshold in nanocomposites to use its advantages in electrical conductivity and mechanical performance [63,64]. Therefore, our model shows the correct effect of the $\phi_p$ parameter on the modulus of PCNTs.

The impacts of the $R$ and $t$ parameters on the predicted modulus at average levels of other properties are depicted in Fig. 5. Thick nanotubes ($R>22$ nm) or a thin interphase ($t<13$ nm) produce $E_l = 1$, indicating that the modulus of the nanocomposite does not improve. Thus, the addition of thick nanoparticles or the formation of a thin interphase in PCNTs does not change the modulus of nanocomposites; in other words, nanocomposites do not benefit from thick CNTs or a thin interphase. However, $R = 10$ nm and $t = 35$ nm result in the highest modulus, a 400% improvement over the polymer matrix. This evidence shows the positive effects of thin CNTs and a thick interphase on the reinforcement of nanocomposites, which should be considered in the production of PCNTs.

Thin nanotubes produce a large interfacial area between nanoparticles and polymer chains, indicating that polymer macromolecules are well affected by thin nanoparticles. Therefore, thin nanoparticles can well perform a reinforcing role in nanocomposites. In addition, according to Eq. (12), thin CNTs lower the percolation threshold in comparison to thick ones, which benefits the network properties. Thus, thinner CNTs improve the reinforcing and percolation in polymer nanocomposites. The reinforcement of the interphase region in nanocomposites also depends on its thickness. A thick interphase implies the formation of a large interphase region in nanocomposites, which can promote the mechanical properties. Accordingly, it is reasonable to significantly improve the reinforcement by promoting a thick interphase. Based on these explanations, it is reasonable to seek a better modulus at the smaller and larger levels of the $R$ and $t$ factors, respectively. These observations agree well with previous studies [65,66], which confirm the estimations of our model at different parameters of nanoparticles and interphases.
Therefore, indicating a fraction of the filler network cannot generally improve the tensile modulus. It is essential to enhance the network fraction in PCNTs to obtain a high stiffness. The highest relative modulus of about 3.4 is obtained by the highest levels of $\phi_N = 0.005$ and $E_N = 3000$ GPa.

The positive effects of network concentration and modulus on the modulus of nanocomposites are thus confirmed, as a large and strong network provides high resistance against stress loading, which in turn prevents the deformation of PCNTs [38,67]. However, a poor network in a PCNT can only bear a minor force, which cannot resist considerable stress. Therefore, a good network can produce high reinforcing efficiency in PCNTs, while a poor one cannot significantly reinforce the polymer nanocomposites. In summary, this model fairly shows the benefits of network concentration and a high modulus on the stiffness of PCNTs.

Fig. 6 reveals the calculated moduli at different values of the $\phi_N$ and $E_N$ parameters. A very low level of $\phi_N$ only decreases the modulus of the nanocomposites, but the highest modulus is achieved by the highest ranges of the $\phi_N$ and $E_N$ parameters. The lowest relative modulus is 1.3, attained for $\phi_N = 0.001$ and indicating that a low fraction of the filler network cannot generally improve the tensile modulus. It is essential to enhance the network fraction in PCNTs to obtain a high stiffness. The highest relative modulus of about 3.4 is obtained by the highest levels of $\phi_N = 0.005$ and $E_N = 3000$ GPa.

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The effects of the volume fraction ($\phi_{id}$) and the modulus ($E_{id}$) of an interphase around dispersed nanoparticles on the modulus of PCNTs are shown in Fig. 7. The nanocomposite modulus only depends on the level of the $\phi_{id}$ parameter, and the different ranges of $E_{id}$ do not have an effect on the PCNT modulus. The relative modulus of 1.33 is obtained at $\phi_{id} > 0.045$, whereas the smallest relative modulus of 1.27 is estimated at $\phi_{id} = 0.01$. Consequently, the reinforcement of nanocomposites directly depends on the concentration of the interphase around dispersed CNTs. The properties of the interphase region in nanocomposites change as the characteristics of the polymer matrix and the nanoparticles change, as previously described. In other words, the interphase is usually stronger than the polymer matrix, so a high fraction of the interphase increases the stiffness of a nanocomposite.

Our calculations of the nanocomposite modulus show that the variations of both $\phi_{id}$ and $E_{id}$ parameters negligibly affect the nanocomposite stiffness. According to Fig. 7, the relative modulus only increases from 1.27 to 1.33 for the different levels of these parameters. Therefore, the interphase around the dispersed nanoparticles does not have a significant effect on the reinforcement of PCNTs, based on our model.

Fig. 8 depicts the dependence of the relative modulus on the $\phi_N$ and $E_N$ parameters. A poor modulus is associated with a low value of $\phi_N$, whereas the modulus rises as both $\phi_N$ and $E_N$ parameters increase. As shown, $\phi_N < 0.005$ results in the modulus of the matrix ($E_R = 1$), but $\phi_N = 0.03$ and $E_N = 1900$ GPa produce a relative modulus = 8, a 700% improvement over the matrix modulus. These results clearly demonstrate that a low fraction of the interphase around a CNT network eliminates the stiffening effect of nanoparticles in a polymer matrix. Thus, it is necessary to provide a high level of interphase between a polymer matrix and a filler network to improve the PCNT modulus. However, it should be noted that only having a high fraction of interphase is not adequate for signifi-
Fig. 7 – The effects of “$\phi_d$” and “$E_d$” factors on the modulus at $\phi_f = 0.01$, $E_m = 2$ GPa, $R = 10$ nm, $t = 10$ nm, $l = 10$ $\mu$m, $E_N = 2000$ GPa and $E_{Ni} = 1500$ GPa: (a) 3D and (b) contour schemes.

Fig. 8 – (a) 3D and (b) contour plots for relative modulus as a function of “$\phi_{Ni}$” and “$E_{Ni}$” parameters at $\phi_f = 0.01$, $E_m = 2$ GPa, $R = 10$ nm, $t = 10$ nm, $l = 10$ $\mu$m, $E_d = 200$ GPa and $E_N = 2000$ GPa.

cant improvement of the PCNT modulus; a strong interphase should also be obtained.

The interphase causes a reinforcing efficiency in nanocomposites, as discussed. The connection of an interphase region around a filler network can speed up the percolation threshold, which has a positive effect on the mechanical properties of PCNTs; clearly, a higher concentration of interphase can improve the reinforcing and networking. Generally, the interphase region bears the stress, which is transferred from the polymer matrix to the nanoparticles. A strong interphase can allow a high level of stress to be transferred, while a poor interphase breaks in the stress loading. In this way, a strong interphase helps reinforce a PCNT, as a strong interphase is essential to gain the profits of nanoparticles in polymer nanocomposites.

The material, the interphase, and the network parameters have dissimilar effects on the modulus of a PCNT. Some parameters cannot meaningfully affect the nanocomposite modulus, such as $E_m$ and $\phi_f$ (see Fig. 6) as well as $\phi_d$ and $E_d$ (see Fig. 7). A number of parameters, such as $\phi_f$ and $l$ (Fig. 3) in addition to $\phi_N$ and $E_N$ (Fig. 6) can somewhat change the stiffness of a PCNT. However, the calculations demonstrate that the $R$, $t$, $\phi_{Ni}$, and $E_{Ni}$ parameters significantly affect the modulus of a PCNT (see Figs. 5 and 8). The latter parameters, which are attributed to the CNT thickness and the interphase surrounding the CNT network, should be well controlled to achieve a high-quality product. However, CNT size may be threatened by the agglomeration of nanotubes, while the interphase properties mostly depend on the similar chemistries of the polymer matrix and the CNTs.

4. Conclusions

We joined two Kolarik models, assuming the dispersion and networking of nanoparticles, to approximate the tensile modulus of PCNTs above the percolation threshold. We considered the effects of interphases around the dispersed and networked particles in our new model, and our predictions agreed well with our experimental results, which demonstrated the predictability of our model and the expected formation of interphases and CNT networks in those samples. Additionally, the model gave some valuable calculations for the interphase and network properties as well as the percolation level, which were estimated for the reported samples. $E_8 = 2.8$ was calculated at $\phi_f = 0.02$ and $l = 30$ $\mu$m, but $\phi_f < 0.006$ could not reinforce the PCNTs. Therefore, the highest modulus was associated with the highest levels of these parameters, but also with the lowest levels of the $E_m$ and $\phi_f$ parameters. Thick nanotubes ($R > 22$ nm) or a thin interphase ($t < 13$ nm) could not improve the modulus, while $R = 10$ nm and $t = 35$ nm resulted in the highest relative modulus ($E_8 = 5$), which revealed the positive effects of thin CNTs and a thick interphase on the reinforcement of nanocomposites. A very low level of $\phi_f$ decreased the modulus, but the highest stiffness was achieved by the highest ranges of the $\phi_N$ and $E_N$ parameters. $\phi_f < 0.005$ resulted in $E_8 = 1$, but the highest values of $\phi_{Ni} = 0.03$ and $E_{Ni} = 1900$ GPa predicted a relative modulus of 8. Among the studied param-
eters, R, t, \(\phi_N\), and \(E_N\) had significant positive impacts on the modulus of PCNTs, while the parameters \(\phi_p\), \(\psi_d\), and \(E_d\) showed the least effects and can thus be disregarded in this model. According to the calculations of our model, the radius of the CNTs and the interphase thickness surrounding the network (Fig. 5) mainly controlled the modulus. Generally, thin nanoparticles intensified the interfacial interaction between the polymer chains and the nanofillers thickening the interphase region.

**Conflict of interest**

The authors declare no conflicts of interest.

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