Reinforcing efficiency of nanoparticles: A simple comparison for polymer nanocomposites

Hua Liu a, L. Catherine Brinson a,b,*

a Department of Mechanical Engineering, Northwestern University, Evanston, IL 60208, USA
b Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA

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Abstract

The mechanical reinforcing efficiencies of two types of nanoparticles, nanotube and nanoplatelet, are compared from a micromechanics perspective. Additionally, the interphase zone created by altered dynamics of host polymer molecules in the vicinity of the nanoparticles is addressed. The results indicate that nanotubes generally have superior mechanical reinforcement potential beyond that of nanoplatelets for aligned orientations, while the high in-plane isotropic modulus of nanoplatelets allows better reinforcing in random orientations. However, at the same volume fraction, under the assumption of identical degree of dispersion and extent of influence on the surrounding polymer molecules, the nanotubes generate a significantly larger amount of interphase than the nanoplatelets. The interphase effects can then overwhelm the basic nanoparticle influence and lead to higher stiffnesses for all configurations of nanotube composites. These simple yet insightful comparisons may provide guidance in the design of nanocomposites.

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1. Introduction

Nanoparticles, including nanospheroidal particles, nanoplatelets, and nanotubes, have received intense attention and research in the past decade. The addition of these nanoparticles into polymer matrix materials has been observed to dramatically change the properties of the host polymers, promising a novel class of polymer matrix composite materials with superior properties and added functionalities [1–4]. By adding a few weight percent of nanoparticles, it is possible to substantially improve the mechanical properties, decrease permeability, increase thermal stability and heat distortion temperature, improve chemical resistance, and enhance electrical conductivity and optical clarity, while preserving many advantages of the parent polymer systems, such as low density and high processibility. Such polymer nanocomposites are ideal candidate materials in many applications, including aerospace applications, automobile manufacturing, medical devices, and sporting goods.

Many different nanoparticle and host polymer combinations have been investigated [1,3,4]. To the best of authors’ knowledge, however, efforts to systematically examine the reinforcing effect of different nanoparticles in the same polymer matrix have not been reported. Lacking this information, the choices of nanoparticles are made based on concerns such as cost and availability. In this regard, the present paper compares the reinforcing efficiency of two types of frequently used nanoparticles, nanotubes and nanoplatelets, based on a micro-mechanics perspective. Our analysis considers only static micro-mechanical response and small strain behavior. While micro-mechanics models have been applied to traditional micro-scale composites to examine differences in particle shape [5], the purpose of this paper is to compare the reinforcing efficiency of
different types of particles (tube vs. platelet) in a nanoscale context including appropriate volume fractions and surface area factors that arise due to the nanoparticle size.

The applicability of continuum mechanics to nanocomposites has been subjected to intensive debate [2,6]. It should be noted, however, that in spite of the fact that continuum theory loses direct applicability at the atomic scale, many recent works directly applying continuum mechanics to nanostructures and nanomaterials have reported meaningful results and helped elucidate many issues [7–12]; for example, in the paper by Arroyo and Belytschko, different deformation patterns, such as twisting and bending, of nanotubes, were studied using a finite deformation continuum theory; the continuum simulation results not only reproduced the experimental observation and full scale atomistic simulation results but also allowed some matters not fully identifiable by the experiments (limited by 2D nature), e.g., the complex buckling pattern of multiwalled carbon nanotubes, to be studied [8]. Additionally, simulations that are based on atomic or molecular structure also contain inherent assumptions and difficulties in the extrapolation to address thermo-mechanical response at the continuum scale. Thus, in this work we remain fully within the realm of continuum mechanics while incorporating important nanoscale morphological features of polymer nanocomposites. For analysis, we use the Mori–Tanaka method, which is widely regarded as a powerful micromechanical model for conventional micro-particle reinforced polymers [13,14] and has effectively been utilized in modeling nanocomposites [11,15–17]. The details of this method are not presented here, but can be found in many sources [18,19].

Recently, experimental data has led to the conclusion that the dramatic property changes of polymer nanocomposites beyond the pure matrix polymer result significantly from the formation of an interphase region in the vicinity of the nanoscale fillers [15,20–22]. The existence of the interphase is strongly supported by molecular dynamics simulation results [23,24] and experimental observations that the viscoelastic behavior of the host polymer is significantly changed upon the incorporation of nanoparticles [21,22]. Due to the enormous specific surface area (SSA) of nanoparticles, the amount of interphase generated by the addition of a small volume fraction of nanoparticles can be extensive and thus can have a remarkable impact on the bulk properties of the nanocomposite. In our discussion, we first consider the reinforcing efficiency of nanoparticles based on geometrical features and orientation alone, and then extend the model to include regions of altered behavior of polymer molecules near the nanoparticles, i.e., the interphase.

2. Theoretical set-up

In our discussion, the nanotubes will be considered as isotropic straight solid cylinders with a diameter of $d$ and a length of $l$, shown in Fig. 1a. Nanoplatelets will be considered as isotropic solid round disks with a thickness of $t$ and a diameter of $D$, as shown in Fig. 1b. For both materials we assume isotropic properties with an elastic modulus of 1TPa and a Poisson’s ratio of 0.3. Thus the properties chosen reflect moduli appropriate for individual single walled nanotubes or individual graphene sheets. Ideally, both nanoparticles should have different out of plane properties, but lacking reliable data for these transverse properties we adopt the common isotropy assumption.

Consider two polymer nanocomposites, one reinforced with nanotubes and the other with nanoplatelets, referred to subsequently as NT nanocomposites and NP nanocomposites, respectively. We model the nanocomposites as two-phase materials consisting of nanoparticles and matrix (without interphase) to evaluate the stiffness increment of the composite brought by the incorporation of nanoparticles. Only three important parameters, i.e., the volume fraction, the aspect ratios of the particles, and the particle orientation enter the calculation. The extent and influence of the interphase is considered later. In all cases, we assume ideal dispersion for both systems to the single tube and single platelet level. The results are also generalizable to other dispersions so long as consistency is maintained between the two morphologies. (e.g., dispersion down to NT bundles of radius $d_1$ and dispersion of NP down to stacks of thickness $t_1$, where $d_1$ and $t_1$ are comparable magnitudes.)

We consider several orientations of the nanoparticles; first, the case where the particles are ideally dispersed and aligned, as shown in Fig. 2a and b. However, the orientation...
of nanoparticles is strongly affected by the processing methods, e.g., compression molding on thin samples or layer-by-layer assembly (i.e., alternative deposition of nanoparticles and polymers onto substrates) which may result in an in-plane random orientation of the nanoparticles. Thus, we further calculate the modulus of the nanocomposites with randomly oriented, in-plane (2D random), and complete 3D randomly oriented nanoparticles, shown in Fig. 2c and d, and 3D randomly oriented nanoparticles, shown in Fig. 2e and f.

To facilitate our discussion, the following brief descriptive notation is used for each nanocomposite:

(a) **Aligned NT** refers to a composite with aligned nanotubes.
(b) **Aligned NP** refers to a composite with aligned nanoplatelets.
(c) **2D random NT** refers to a composite with in-plane randomly oriented nanotubes.
(d) **2D random NP** refers to a composite with in-plane randomly oriented nanoplatelets. Note that this case is the same as the aligned NP nanocomposite case.
(e) **3D random NT** refers to a composite with 3D randomly oriented nanotubes.
(f) **3D random NP** refers to a composite with 3D randomly oriented nanoplatelets.

To facilitate our discussion, specific note must be taken regarding our definition of the aspect ratio of the particles. For nanotubes, it is defined as the ratio of length to the diameter of the cross-section, that is, \(l/d\), referring to Fig. 1a. For nanoplatelets, on the other hand, the aspect ratio is defined as the ratio of the planar diameter to thickness, i.e., \(D/t\) (Fig. 1b). In such a context, it is appropriate to compare \(E_{11}\) of aligned NT nanocomposites (Fig. 2a) with \(E_{11}\) of aligned NP nanocomposites (Fig. 2b) in which the nanotubes and nanoplatelets have the same aspect ratio.

3. Results and discussion of nanoparticle geometry effects

In this section we consider predictions for composites containing nanoparticles in the arrangements shown in Fig. 2 with two phases only: the nanoparticles and the matrix. Fig. 3a shows such a comparison of the longitudinal stiffness as predicted by the Mori–Tanaka model. We note that the influence of aspect ratio on the reinforcement provided by the individual type of nanoparticles is similar to previously observed for micro-size particles [5], that \(E_{11}\) of aligned nanocomposites increases with the increase of nanoparticle aspect ratio. As can be seen in the figure, at the same loading levels of nanoparticles, \(E_{11}\) of aligned NT nanocomposites is larger than \(E_{11}\) of aligned NP nanocomposites with corresponding aspect ratio of nanoparticles, for all volume fractions. Note that because of the interphase issues to be further discussed, nanocomposites typically contain less than 5% nanoparticles. Thus, calculations were performed up to 5% nanoparticle volume fraction in most cases. Insets are shown in each figure with the results at higher nanoparticle loadings.

To consider the transverse properties, the normalized \(E_{22}\) of aligned NT nanocomposites is compared with the normalized \(E_{22}\) of aligned NP nanocomposites in Fig. 3b. The transverse properties of both aligned NT and NP nanocomposites are only modestly affected by the particle geometry or the particle aspect ratio. In the low to medium volume fraction region (up to \(\sim 45\%\)), \(E_{22}\) of aligned NT nanocomposites is lower than \(E_{22}\) of aligned NP nanocomposites for the high aspect ratio cases. Additional simulations indicate that this behavior is material property dependent, in particular on the Poisson’s ratio of the matrix: when the Poisson’s ratio of the matrix is small, \(E_{22}\) of aligned NT nanocomposites exceeds \(E_{22}\) of aligned NP nanocomposites, with the exception of the very low volume fraction area; when the Poisson’s ratio of the matrix is fairly high (approaching 0.5), \(E_{22}\) of aligned NP nanocomposites is higher than \(E_{22}\) of aligned NT nanocomposites, persistently through all volume fractions. In Fig. 3b, we include into the plot normalized out of plane modulus, \(E_{22}\) of 2D random NT nanocomposites. Interestingly, it is seen to be nearly equivalent to \((a = 1000 \text{ aligned NP})\) or slightly higher than (all other cases) the transverse moduli of both aligned systems.

Also plotted in Fig. 3a is the normalized in-plane modulus, \(E_{11}\), of 2D random NT nanocomposites (also see Fig. 2c). As expected, \(E_{11}\) of 2D random NT nanocomposites is significantly smaller than \(E_{11}\) of aligned NT nanocomposites at the same volume fraction of tubes. It is interesting to notice that this \(E_{11}\) of 2D random NT nanocomposites is larger than for the corresponding NP
Fig. 3. The normalized nanocomposite modulus vs. the volume fraction, as predicted by the Mori–Tanaka model: (a) normalized (w.r.t. Young’s Modulus of bulk polymer matrix, which is set to 2.1 GPa in all simulations; the Poisson’s ratio of the matrix is set to 0.3) longitudinal modulus, $E_{11}$, of aligned NT nanocomposites (referring to Fig. 2a) vs. normalized $E_{11}$ of aligned NP nanocomposites (referring to Fig. 2b) with the same aspect ratios (a) of nanoparticles. Also plotted is normalized in-plane modulus of 2D random NT nanocomposites (referring to Fig. 2c). Inset figure shows high volume fraction region, (b) normalized transverse modulus, $E_{22}$, of aligned NT nanocomposites (referring to Fig. 2a) is plotted in comparison with normalized $E_{22}$ of aligned NP nanocomposites (referring to Fig. 2b) with the same particle aspect ratios of nanoparticles. Normalized out of plane modulus $E_{22}$ of 2D random NT nanocomposites (referring to Fig. 2c) is also included. Little difference with aspect ratio is observed so that some curves overlay each other. Inset figure shows high volume fraction region and (c) normalized modulus of nanocomposites with 3D randomly oriented nanoparticles (referring to Fig. 2e and f) at low to intermediate inclusion loading levels. Inset figure shows high volume fraction region.
nanocomposites \( (E_{11} \text{ of 2D random NP nanocomposites}) \) at lower aspect ratios \( (a = 10 \text{ and } a = 100) \) but it is smaller at high aspect ratio \( (a = 1000) \).

The comparison of the normalized moduli of NT and NP nanocomposites with 3D randomly oriented nanoparticles is shown Fig. 3c. At \( a = 10 \), the moduli of the two nanocomposites are both small and nearly the same. At increasing aspect ratios however, initially the NT nanocomposites are stiffer than the NP composites but by \( a = 1000 \), the modulus of NP nanocomposites significantly exceeds that of NT nanocomposites. Results for 1% nanoparticle loading are shown in bar graph form in Fig. 4 for easier comparison, where data is separated into results at aspect ratios of 1000, 100, and 10.

To understand these results, two competing mechanisms are involved. First, a rather simple explanation can be used to explain better NT results: considering a nanotube and a nanoplatelet of the same aspect ratio \( a \), if the thickness of the nanoplatelet \( (t \text{ in Fig. 1b}) \) is comparable to the diameter of the nanotube \( (d \text{ in Fig. 1a}) \), the volume of the nanoplatelet is significantly larger than that of the nanotube; thus, at the same volume fraction of reinforcing particles, the number of reinforcements in NT nanocomposite is significantly larger than the number of reinforcements in NP nanocomposite. As the stiffening effect happens through the interaction between the reinforcing phase and the host matrix, a larger number of particles should offer better reinforcing effect.

Competing with this first mechanism of more reinforcing particles however is the second mechanism of the nanoplatelet’s capability to provide multidirectional reinforcement. The geometry of the nanoplatelet allows it to offer uniform reinforcement isotropically in the 1–3 plane, while the nanotube offers only superior reinforcement as the loading approaches the 1 direction. Reinforcement potential for the nanotube in the 3 direction (same as in the 2 direction) is two orders of magnitude lower (see Fig. 3a and b). Thus, for nanocomposites with randomly oriented nanoparticles, the nanoplatelet’s capability of offering significant reinforcing in more than one direction comes into play.

Combining these two effects, when the particle aspect ratio is low, the influence of the nanoplatelet’s transverse isotropy is relatively small and the modulus of random NT composites exceeds that of random NP nanocomposites. However, when the particle aspect ratio increases, the influence of the nanoplatelet’s high stiffness in the 1–3 plane becomes significant and the results for the NP nanocomposites exceed those for the NT nanocomposites. The aspect ratio at this transition differs for the 2D (Fig. 3a and b) and 3D (Fig. 3c) randomly oriented composites, as well as for longitudinal, \( E_{11} \), and transverse, \( E_{22} \), properties. The change in the weighting of these influence factors with aspect ratio is seen by the different bar heights for the aspect ratios in Fig. 4.

In summary, these simulations demonstrate that from a micro-mechanics perspective the reinforcing efficiency of nanotubes is higher than that of the same aspect ratio nanoplatelets for longitudinal properties in aligned nanoparticle cases. For transverse loadings and nanocomposites with randomly oriented nanoparticles, the nanoplatelet’s ability to provide isotropic reinforcement in a plane yields superior results over the nanotube, when the particle aspect ratio is sufficiently high. As the aspect ratio of nanotubes and sufficiently exfoliated graphite can be on the order of 1000, this result is relevant for these systems.

4. Results and discussion of nanoparticle-interphase effects

As mentioned previously, the improved properties of nanocomposites are due not only to the morphology and intrinsic properties of the nanoparticles alone, but also to...
the extensive interphase created from polymer molecules of altered mobility in the vicinity of the nanoparticles. Thus a second important consideration beyond pure geometrical reinforcement of the nanoparticle is the potential extent and influence of this interphase when comparing the two nanoparticle morphologies. An important indicator when considering the interphase is the effective surface area per unit particle volume, which is denoted as \( \beta \) below.

Now let us consider a nanotube with a diameter of \( t \) and a length of \( D \) and a nanoplatelet with a thickness of \( t \) and a diameter of \( D \) (please refer to Fig. 1; note that to facilitate quantitative comparison, we replace \( d \) with \( t \) and \( l \) with \( D \) for the nanotube).

The particle volume and effective surface area for the nanoplatelet are

\[
V_{\text{NP}} = \frac{\pi D^2}{4} t
\]

\[
S_{\text{NP}} = \frac{\pi D^2}{2} + \pi D t
\]

which give the effective surface area per unit particle volume of nanoplatelet as

\[
\beta_{\text{NP}} = \frac{S_{\text{NP}}}{V_{\text{NP}}} = \frac{2\pi D^3 + 4\pi D t}{\pi D^2 t}
\]

Similarly, for the nanotube, we have

\[
V_{\text{NT}} = \frac{\pi t^2}{4} D
\]

\[
S_{\text{NT}} = \frac{\pi t^2}{2} + \pi D t
\]

and

\[
\beta_{\text{NT}} = \frac{S_{\text{NT}}}{V_{\text{NT}}} = \frac{2\pi t^3 + 4\pi D t}{\pi t^2 D}
\]

The ratio between the two is then

\[
\frac{\beta_{\text{NT}}}{\beta_{\text{NP}}} = \frac{2\pi t^2 + 4\pi D t}{\pi t^2 D}. \frac{\pi D t}{2\pi D^2 + 4\pi D t} = \frac{t + 2D}{D + 2t}
\]

If \( D \gg t \), which is exactly the dimensional feature of these nanoparticles,

\[
\frac{\beta_{\text{NT}}}{\beta_{\text{NP}}} \approx 2
\]

Thus, the effective surface area per unit particle volume of the nanotube is nearly two times that of the nanoplatelet. Based on surface area alone, nanotubes therefore have higher potential than nanoplatelets to generate interphase, assuming identical surface chemistries and identical dispersions. This result is consistent with the earlier simple explanation for the micro-mechanics calculations: at the same particle volume fractions, the nanotube can have a stronger interaction with the matrix and therefore can result in better reinforcement than the nanoplatelet.

The extent of the interphase zone is not governed merely by surface area per unit volume, but also by the morphology of the particle itself and the nature of the volume of the surrounding interphase polymer. To further elaborate on this concept, we introduce \( t_i \), the range of influence of the nanoparticle into the surrounding polymer. It should be noted that although the interphase is a zone with a gradient in properties away from the nanoparticle surface, to simplify the discussion we use this \( t_i \) to provide a finite bound for each interphase. The extent of the influence of the nanoparticle on polymer chain dynamics can be several times the radius of gyration of the host polymer long chain molecules [20,24,25] (also indirectly from thin film literature [26,27]). Results indicate that the density and the glass transition temperature, \( T_g \), of the polymer within this interphase region have changed as compared to the bulk, implying changes in other thermomechanical properties and/or electric properties as well. Thus the length scale of the interphase can be significantly larger than the nanoparticle thickness/diameter, \( t \), and can even approach the length of nanotube and the diameter of nanoplatelet in some circumstances.

For example, consider a single-wall carbon nanotube (SWCNT) reinforced poly(methyl methacrylate) (PMMA) and a graphene sheet (GS) reinforced PMMA. The typical geometries for SWCNT are 1 nm in diameter and 1 \( \mu \) m in length and those for GS are 1 nm in thickness and 1 \( \mu \) m in planar diameter. If the molecular weight of PMMA is 350,000, an estimate of radius of gyration is 17 nm [28]. If the interaction between nanoparticle and the PMMA molecules is strong, \( t_i \) can be several times the radius of gyration, i.e., \( \sim \) 50 nm. Note that the range of influence predominantly depends on how the polymer molecules and particle surface interact. Functionalization of the surface to form covalent or secondary bonds with the host polymer will substantially increase the range of influence from the nanoparticle surfaces [22,29]. It is also probable that the extent of the influence region will depend on the geometry of the nanoparticle itself, however for this study we assume identical \( t_i \). While some molecular dynamic studies have been performed to indicate influence of surface geometrical features such as corrugation [24], no comparison between nanoplatelets and nanotubes has been done from which to base another assumption.

Using these concepts, we define a simple extended volume around each nanoparticle for the interphase and directly compare the interphase volume generated per unit nanoparticle volume, denoted as \( \gamma \), for nanotube and nanoplatelet. Fig. 5 illustrates schematically the extent of the interphase surrounding a nanoparticle. As nanotube ends (and nanoplatelet edges) may be differently functionalized than the side walls and the extent of the influence domain into the polymer may differ between the ends and the walls, cases with and without significant interphase at the ends are considered.

For the nanotube with diameter \( t \) and length \( D \), at certain range of influence \( t_i \), the volume of interphase generated, as schematically shown in Fig. 5a, is given by
The volume of the tube is

\[ V_{NT} = \frac{\pi t^2}{4} D \]  

Hence the ratio between the two is

\[ \gamma_{NT1} = \frac{V_{NTint1}}{V_{NT}} \]  

Similarly, for the nanoplatelet with diameter \( D \) and thickness \( t \) at the same range of influence \( t_i \), the volume of interphase generated is given by

\[ V_{NPint1} = \left[ \frac{\pi t^2}{4} + \frac{\pi D^2}{4} - \frac{\pi t^2}{4} \right] \left[ t + 2 \cdot \frac{\pi t^2}{4} \cdot t_i + 4 \cdot \frac{1}{3} t_i^3 \right] + \frac{1}{2} \pi^2 t_i^4 D \]  

where it is noted that the same figure and expression may be used as for the nanotube, where the roles of \( D \) and \( t \) are reversed. The volume of nanoplatelet is

\[ V_{NP} = \frac{\pi D^2}{4} t \]  

And the ratio is

\[ \gamma_{NP1} = \frac{V_{NPint1}}{V_{NP}} \]  

Therefore, comparing the two, we have

\[ \frac{\gamma_{NT1}}{\gamma_{NP1}} = \frac{V_{NTint1}}{V_{NP}} \frac{V_{NP}}{V_{NT}} \]  

Note that for nanotubes and nanoplatelets, \( D \gg t \). And also, \( t_i \gg t \) but \( t_i \) is not comparable to \( D \). We then have (please see Appendix for detailed derivation)

\[ \frac{\gamma_{NT1}}{\gamma_{NP1}} \approx \frac{D}{t} \gg 1 \]  

Additionally, considering the case illustrated in Fig. 5b where the area around the nanotube ends (and the nanoplatelet edges) is not considered to generate an interphase of significantly altered mobility, the derivation is simplified. For the tube, diameter \( t \), length \( D \), range of influence \( t_i \), volume of the interphase becomes
Fig. 7. Comparison of properties of aligned SWCNT/PMMA nanocomposite (referring to Fig. 6a) and aligned GS/PMMA nanocomposite (referring to Fig. 6b); Also included is the comparison of properties of 3D random nanocomposites; aspect ratios of nanoparticles are 1000; interphase has been taken into account. Also plotted are results adopted from Fig. 3) for situations with no interphase: (a) normalized longitudinal modulus, \( E_{11} \), of aligned nanocomposites, (b) normalized transverse modulus, \( E_{22} \), of aligned nanocomposites and (c) normalized modulus of 3D random nanocomposites.
\[ V_{\text{NTint2}} = \left[ \frac{\pi (t + 2t_i)^2}{4} - \frac{\pi t^2}{4} \right] D \]  
(13)

For the nanoplatelet, diameter \( D \), thickness \( t \), range of influence \( t_i \), volume of the interphase when not considering end/edge functionality is

\[ V_{\text{NPint2}} = 2\cdot\frac{\pi D^2}{4}\cdot t_i \]  
(14)

Therefore (please see Appendix for detailed derivation)

\[ \gamma_{\text{NT}} \quad 2 \quad V_{\text{NTint2}} \quad V_{\text{NP}} \quad V_{\text{NPint2}} = 2\left(1 + \frac{t_i}{t}\right) \gg 1 \]

In other words, for polymer nanocomposites containing the same volume fraction of nanotubes and nanoplatelets, assuming the nanoparticles are ideally dispersed and have the same capability to interact with host polymer molecules, the amount of polymer with altered dynamics due to the nanoinclusions, i.e., the amount of the interphase is significantly larger in nanotube nanocomposites than that in nanoplatelet nanocomposites, as schematically shown in Fig. 6. A simple example is given here. Consider a 0.05 vol\% SWCNT (1 nm in diameter and 1 \( \mu \text{m} \) in length) reinforced PMMA (with a molecular weight of 350,000 and a radius of gyration of 17 nm) and a 0.05 vol\% GS (1 \( \text{nm} \) in thickness and 1 \( \mu \text{m} \) in planar diameter) reinforced PMMA. We assume perfect dispersion to the individual nanoparticle level and let the range of influence \( t_i \) (the thickness of interphase) be only one times the radius of gyration, i.e., 17 nm. Considering the case in Fig. 5b for simplicity yields 61.2 vol\% interphase in the SWCNT/PMMA nanocomposite, which is 36 times of the amount of interphase in GS/PMMA (1.7 vol\%). The enormous difference between these numbers alone calls our initial assumption of identical range of influence into question. Indeed, considering the concept of altered dynamics propagating via cooperative rearrangements through adjacent regions [30], the larger continuous surface of a nanoplatelet may give rise to a deeper penetration of the influence of the surface. Nevertheless, the results here provide an indication of the change in influence range required to elicit similar interphase extents with nanoplatelets as with nanotubes.

This example can be extended to determine the impact of the interphase on mechanical properties. Further assuming that the interphase is isotropic elastic and has a Young’s modulus twice that of the matrix (hence, 4.2 GPa) and a Poisson’s ratio same as that of the matrix (0.3), we calculated the properties of aligned as well as 3D random SWCNT/PMMA and GS/PMMA nanocomposites using a three phase Mori–Tanaka model and nanoparticles of high aspect ratio (\( a = 1000 \)). The results are shown in Fig. 7. The effect of this interphase on the stiffness of the nanocomposites is clearly observed. Particularly, we find that in the absence of an interphase, the moduli of composites with randomly oriented NPs as well as the transverse moduli of composites with aligned NPs are higher than those of the corresponding NT nanocomposites. With the consideration of the interphase, however, these moduli of NT nanocomposites greatly exceed those of aligned NP nanocomposite, consistently through all loading levels. Although just elastic stiffness is illustrated here, the interphase can have dramatically different thermomechanical and electrical properties from the matrix. Consequently, the considerable difference in the amount of interphase between nanoplatelets and nanotubes can lead to markedly different properties of the nanocomposites.

5. Conclusion

In summary, the mechanical reinforcing efficiency of nanotubes are higher than that of nanoplatelets of the same aspect ratio for longitudinal properties of aligned composites, while the geometrical features of nanoplatelets allows better reinforcing for most cases of random orientation and higher aspect ratio nanoparticles. However, at the same volume fraction, assuming identical degree of dispersion and extent of influence on the surrounding polymer molecules, nanotubes can generate a significantly larger amount of interphase than nanoplatelets. This difference can effect a significant change in the bulk performance of the nanocomposites, depending on the nature of nanoparticle-polymer molecule interaction. It was illustrated that modest interphase extents of enhanced stiffness compared to the matrix (representative of composites with positive nanoparticle–matrix interaction) led to NT composites with higher stiffnesses for all cases, including random orientation and high aspect ratios. These results may explain why experimental systems using graphite nanoparticles (expanded graphite [31], e.g.), have not achieved the same level of improvement in properties as those for carbon nanotube reinforced samples [22].

It should be noted that although many complexities have been omitted, this simple comparison nevertheless may provide generalized guidance in analyzing experimental data and in designing nanocomposite systems using nanotubes or nanoplatelets as reinforcing nanoparticles. These results motivate and provide a basis for further experimental comparisons of different nanoparticles in the same polymer matrix, which are currently lacking in the literature. Many assumptions introduced in this comparison are not easily experimentally controllable and these factors should be carefully evaluated in future studies. One critical assumption is that of the same extent of the interphase zone for both particles. It is probable that the different geometries of the particles will influence the extent of the altered polymer region. For example, since the nanoplatelets extend for a micron in two dimensions, they may have an increased ability to alter a larger zone of polymer than nanotubes through percolation of cooperating regions of altered dynamics. Future molecular dynamics...
or experimental studies should attempt to elucidate this issue. Other factors may also affect choice of nanoparticle, such as easier dispersion with one form over the other or targeted desire of particular properties that favor one particle. For example, when better barrier properties are desired, or when the cost of the materials is a significant factor to be considered, platelet nanoparticles may be desirable over carbon nanotubes.

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Appendix

The detailed derivation of comparing the two γ’s are listed below:

i. 

\[ \gamma_{\text{NT1}} = \frac{V_{\text{NTint1}}}{V_{\text{NT}}} = \frac{\frac{\pi(D+2\ell)}{4} \cdot D}{\frac{\pi(D+2\ell)}{4} \cdot \ell} \]

\[ = \frac{(t + t_1)D + \frac{\ell^2}{2} + \frac{\ell \cdot D}{2} + \frac{D^2}{2}}{(D + t_1)D + \frac{t^2}{2} + \frac{t \cdot D}{2} + \frac{D^2}{2}} \]

Note that \( D \gg t \)

(1) If \( t_1 \) is comparable to \( D \) (strong interaction between the nanoparticles and host polymer molecules and lower aspect ratio nanoparticles),

\[ \frac{\gamma_{\text{NT1}}}{\gamma_{\text{NP1}}} \approx \frac{\frac{\ell^2}{2} + \frac{\ell \cdot D}{2} + \frac{D^2}{2}}{\frac{t^2}{2} + \frac{t \cdot D}{2} + \frac{D^2}{2}} \approx \frac{\ell^2}{t^2} \]

(2) If \( t_1 \) is remarkably larger than \( t \) but is not comparable to \( D \)

\[ \frac{\gamma_{\text{NT1}}}{\gamma_{\text{NP1}}} \approx \frac{\frac{\ell^2}{2} + \frac{\ell \cdot D}{2} + \frac{D^2}{2}}{\frac{t^2}{2} + \frac{t \cdot D}{2} + \frac{D^2}{2}} \approx \frac{\ell^2}{t^2} \]

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