

# Polymer Nanocomposites: A Small Part of the Story\*

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*Polymer nanocomposites are polymer matrix composites in which the fillers are less than 100 nm in at least one dimension. These composites have exhibited extraordinarily interesting properties. A defining feature of polymer nanocomposites is that the small size of the fillers leads to a dramatic increase in interfacial area as compared to traditional composites. This interfacial area creates a significant volume fraction of interfacial polymer with properties different from the bulk polymer even at low loadings. The properties and structure of this interfacial region are not yet known quantitatively, presenting a challenge both for controlling and predicting the properties of polymer nanocomposites. This paper provides a brief overview of polymer nanocomposites with emphasis on the impact of the interfacial region.*

## INTRODUCTION

Polymer nanocomposites can be defined as polymers containing fillers with one dimension smaller than 100 nm (Figure 1a). In contrast to traditional polymer composites with high loadings (60 vol.%) of micrometer-sized filler particles, polymer nanocomposites are being developed with very low loadings (less than 5 vol.%) of well-dispersed nanofillers. While elastomeric composites with nanoscale spherical fillers have been in use for more than 100 years,<sup>1</sup> in the last 15 years new fillers have emerged, providing an opportunity for the development of high-performance multifunctional nanocomposites. For example, transparent conducting polymer/nanotube composites are under development as solar cell electrodes,<sup>2</sup> nanoparticle-

filled amorphous polymers are being used as scratch-resistant, transparent coatings in cell phone and compact-disc technology,<sup>3</sup> and nanoparticles are being considered for enhancing matrix properties of traditional composites to increase out-of-plane properties and add conductivity and sensing capabilities.<sup>4</sup>

The recent resurgence of interest in polymer nanocomposites has emerged for several reasons. First, nanoscale fillers often have properties that are different from the bulk properties of the same material. For example, as the size of silicon nanoparticles decreases, the band gap changes, and the color of the particles changes.<sup>5</sup> As another example, single-wall carbon nanotubes can exhibit stiffness, strength, and strain-to-failure that substantially exceeds that of traditional micrometer-diameter carbon fiber. These features of nanoparticles provide an opportunity for creating polymer composites with unique properties. Second, nanoscale fillers are small defects. Micrometer-scale fillers are similar in size to the critical crack size causing early failure<sup>6,7</sup> while nanofillers are an order of magnitude smaller. This can prevent early failure, leading to nanocomposites with enhanced ductility and toughness.<sup>8,9</sup> Similarly it has been shown that nanoparticles can increase the electrical breakdown strength and endurance<sup>10,11</sup> and are small optical scattering defects.<sup>12</sup> Third, due to the large surface area of the fillers, nanocomposites have a large volume of interfacial matrix material with properties different from the bulk polymer. Figure 1b shows the large volume of interfacial material for spherical nanoparticles and nanotubes. In this paper, this region will be called the interfacial region and even at small filler volume fractions, less than 5 vol.%, almost the entire matrix can be

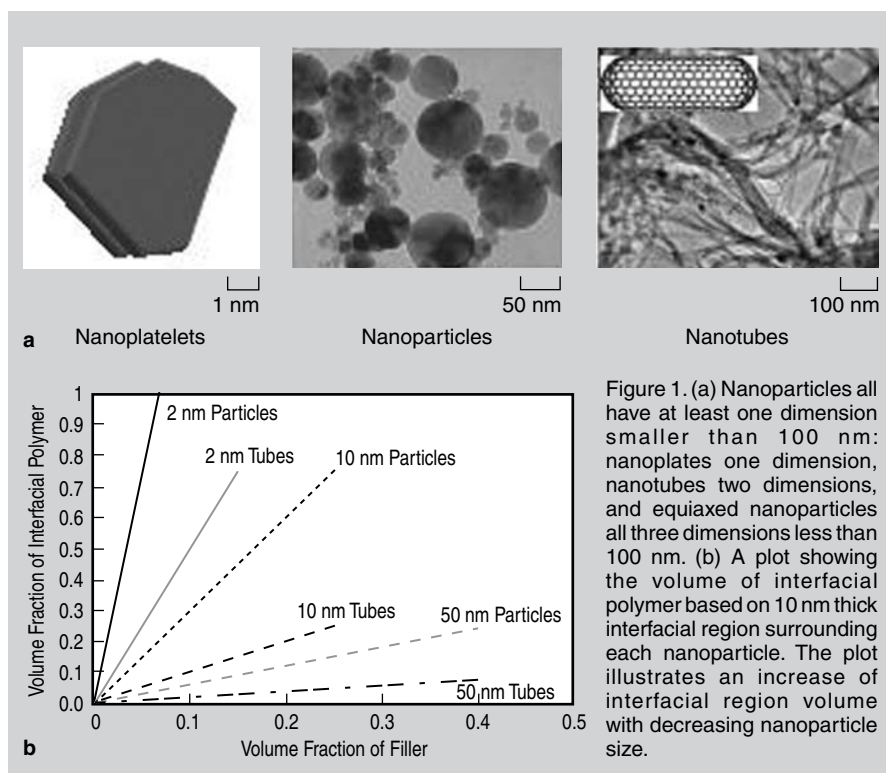


Figure 1. (a) Nanoparticles all have at least one dimension smaller than 100 nm: nanoplates one dimension, nanotubes two dimensions, and equiaxed nanoparticles all three dimensions less than 100 nm. (b) A plot showing the volume of interfacial polymer based on 10 nm thick interfacial region surrounding each nanoparticle. The plot illustrates an increase of interfacial region volume with decreasing nanoparticle size.

interfacial polymer. This interfacial polymer can dramatically change the thermal, mechanical, and electrical properties of the overall composite.

One of the challenges in developing polymer nanocomposites for advanced technology applications is a limited ability to predict the properties. While the techniques exist to tailor the surface chemistry and structure of nanoparticle surfaces<sup>13,14</sup> using a myriad of methods, the impact of the nanoscale filler surface on the morphology, dynamics, and properties of the surrounding polymer chains cannot be quantitatively predicted. Therefore, the properties of a significant volume fraction of the polymer, the interfacial polymer, are unknown making it difficult to predict bulk properties. Other challenges include predicting the impact of heterogeneous filler distribution and filler geometries (e.g., wavy fibers). The solutions to this predicament are focused experimental and multiscale modeling efforts which are ongoing and too broad to address here. Instead, the goal of this paper is to briefly introduce polymer nanocomposites and describe the impact of the interfacial region on both composite properties and the ability to model behavior

### IT'S ALL INTERFACE

"It's all interface" refers to the large volume fraction of interfacial polymer compared to the volume fraction of filler as indicated in Figure 1b. By taking advantage of this large interfacial area and interfacial volume, unique combinations of properties have been achieved.<sup>15</sup> Figure 2 shows select examples. In Figure 2a the electrical endurance strength of crosslinked polyethylene (XLPE) nanocomposites is shown.<sup>16</sup> The endurance strength of XLPE increased by more than an order of magnitude due to the addition of 5 wt.% (about 2.5 vol.%) untreated nanosilica. Further improvement was found due to the incorporation of a vinylsilane treatment of the silica to promote a covalent linkage with the XLPE. Similar behavior has been observed in titania/epoxy nanocomposites.<sup>17</sup> In both cases, the interfacial region created local conduction and scattering that partly explained the nanocomposite performance.

Figure 2b shows a plot of the modulus data along with several two-phase predic-

tions as a function of filler content for carbon nanotube filled polymers.<sup>18-21</sup> It should be noted that these commonly used, simple predictions are all upper bounds for two-phase composite behavior as the models all assume straight nanotubes, perfect nanotube-matrix

bonding, and ideal nanotube properties; relaxing any of these assumptions would decrease the predictions. Nevertheless, in some cases it is clear that the modulus from the data exceeds that predicted by both the rule of mixtures (ROM) and a Mori-Tanaka method for randomly or-

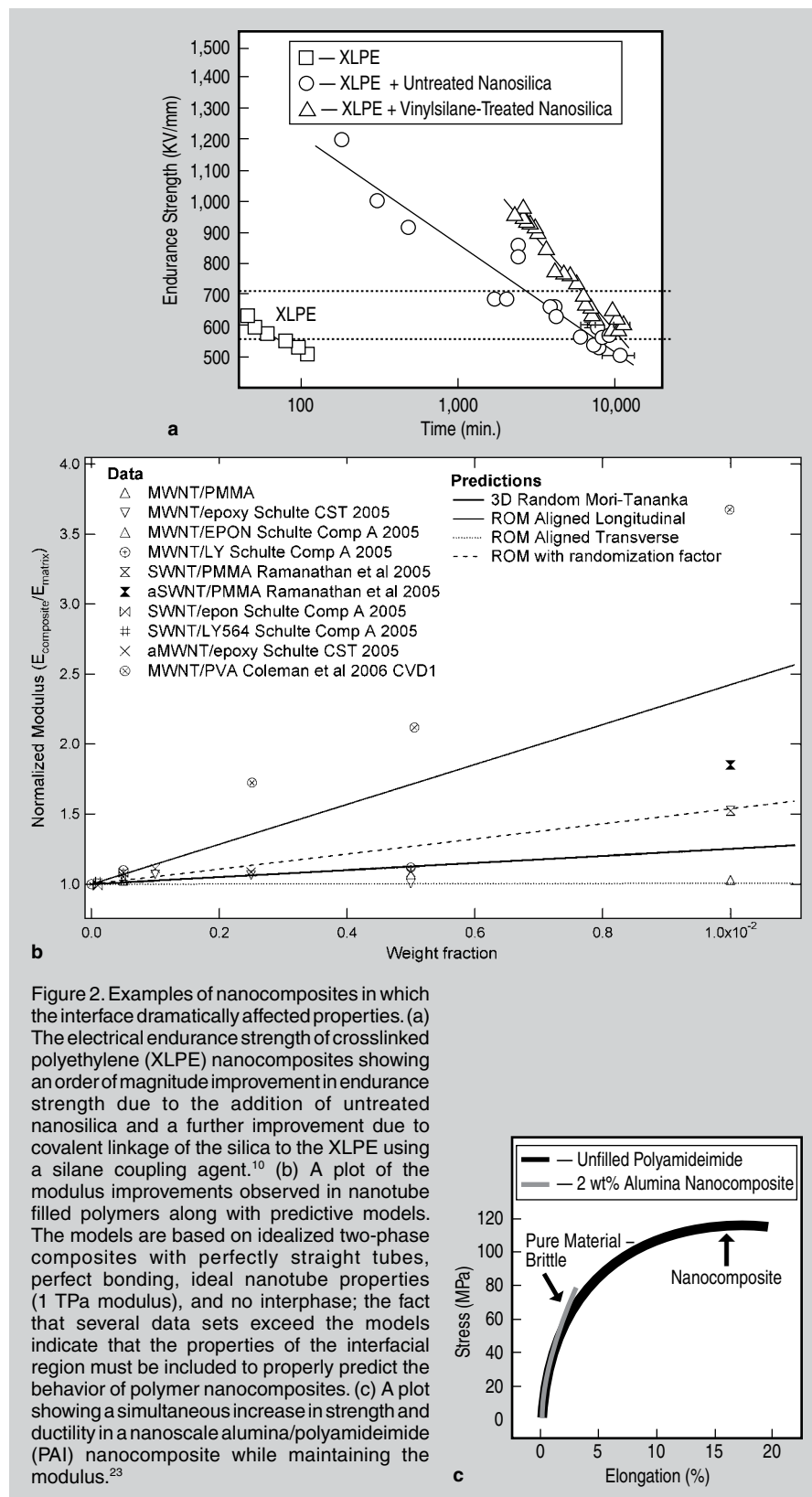


Figure 2. Examples of nanocomposites in which the interface dramatically affected properties. (a) The electrical endurance strength of crosslinked polyethylene (XLPE) nanocomposites showing an order of magnitude improvement in endurance strength due to the addition of untreated nanosilica and a further improvement due to covalent linkage of the silica to the XLPE using a silane coupling agent.<sup>10</sup> (b) A plot of the modulus improvements observed in nanotube filled polymers along with predictive models. The models are based on idealized two-phase composites with perfectly straight tubes, perfect bonding, ideal nanotube properties (1 TPa modulus), and no interphase; the fact that several data sets exceed the models indicate that the properties of the interfacial region must be included to properly predict the behavior of polymer nanocomposites. (c) A plot showing a simultaneous increase in strength and ductility in a nanoscale alumina/polyamideimide (PAI) nanocomposite while maintaining the modulus.<sup>23</sup>

ented tubes.

For this to be the case, it is believed that the interfacial region properties, which are not accounted for in these simple models, must play a significant role in increasing the composite modulus. For amorphous polymer matrices, it is hypothesized that the interfacial region in these nanotube composites is a region of polymer with reduced mobility and associated higher stiffness. The extent of the interfacial region and the reduction in mobility (increase in stiffness) can be tailored through functionalization of the nanotubes. For the polyvinylalcohol data, the matrices are semicrystalline and it has been shown that the nanotubes facilitate the formation of a highly ordered crystalline interfacial region. It is also in semicrystalline polymers that the addition of multi-walled carbon nanotubes (MWNT) has led to fibers with a higher specific energy to

fracture than Kevlar or Spectra 900.<sup>22</sup> Finally Figure 2(c) shows alumina/polyamideimide (PAI) nanocomposites exhibiting a simultaneous increase in strength and ductility while maintaining the modulus.<sup>23</sup> This has been observed in several systems and is found to be highly sensitive to the strength of the particle/matrix interaction.

These and many other results indicate that the structure and properties of the interfacial region are not only different from the bulk but are also critical to controlling properties of the overall nanocomposite. It is relevant, therefore, to explore the structure and properties of the interfacial region. In thermoplastics the interfacial polymer can exhibit changes in crystallinity,<sup>24,25</sup> mobility,<sup>26</sup> chain conformation,<sup>27</sup> molecular weight,<sup>28</sup> chain entanglement density,<sup>29</sup> and even charge distribution.<sup>30</sup> In crosslinked matrices, there is an additional compli-

cation of changes in crosslink density<sup>31</sup> due to small molecule migration either to or from the interface.

As one example, consider semicrystalline thermoplastic composites. In this case, the nanofiller surface can alter the degree of crystallinity, the phases present, the lamellae size and organization, and even the spherulite structure (Figure 3a).<sup>25,32,33</sup> This influence is important particularly in materials where the crystalline phase and spherulite structure significantly impact the mechanical and tribological behavior.<sup>34,35</sup> Figure 3 shows data from a study in nanoscale gamma-phase alumina polyethylene terephthalate (PET).<sup>24</sup> Figure 3b shows the percent crystallinity of the PET as a function of time under isothermal crystallization conditions. At loadings of 1 wt.%, the spherical particles were well dispersed and inhibited nucleation and growth compared to the unfilled PET. As the volume fraction of alumina was increased and agglomeration occurred, the filler acted as a heterogeneous nucleating agent increasing the nucleation and growth rates. In all cases the fillers altered the lamellar organization. Figure 3c and d shows tapping mode atomic force microscopy images of the unfilled and 1 wt.% nanofilled PET. The darker regions represent interspherulitic boundaries. Even 1 wt.% (less than 1 volume percent) of loading interrupted the spherulite structure significantly, resulting in smaller spherulites. Furthermore, by compatibilizing the filler with the matrix, the crystallization temperature could be altered by 6 degrees (not shown).<sup>36</sup> In this case, the changes in crystalline structure were important because they dramatically decreased the tendency of PET fibers to fibrillate and fail in wear applications.<sup>37</sup>

In amorphous polymer matrices, it is qualitatively understood that an attractive interface will decrease the mobility of the polymer chains and a repulsive interface will increase the mobility.<sup>38</sup> One method for probing this change in mobility of the polymer chains in the interfacial region is to measure the glass transition temperature, using either differential scanning calorimetry (DSC) or rheology—typically, dynamic mechanical analysis (DMA).<sup>39,40</sup> Studies using these methods show that the glass transition temperature of a polymer nano-

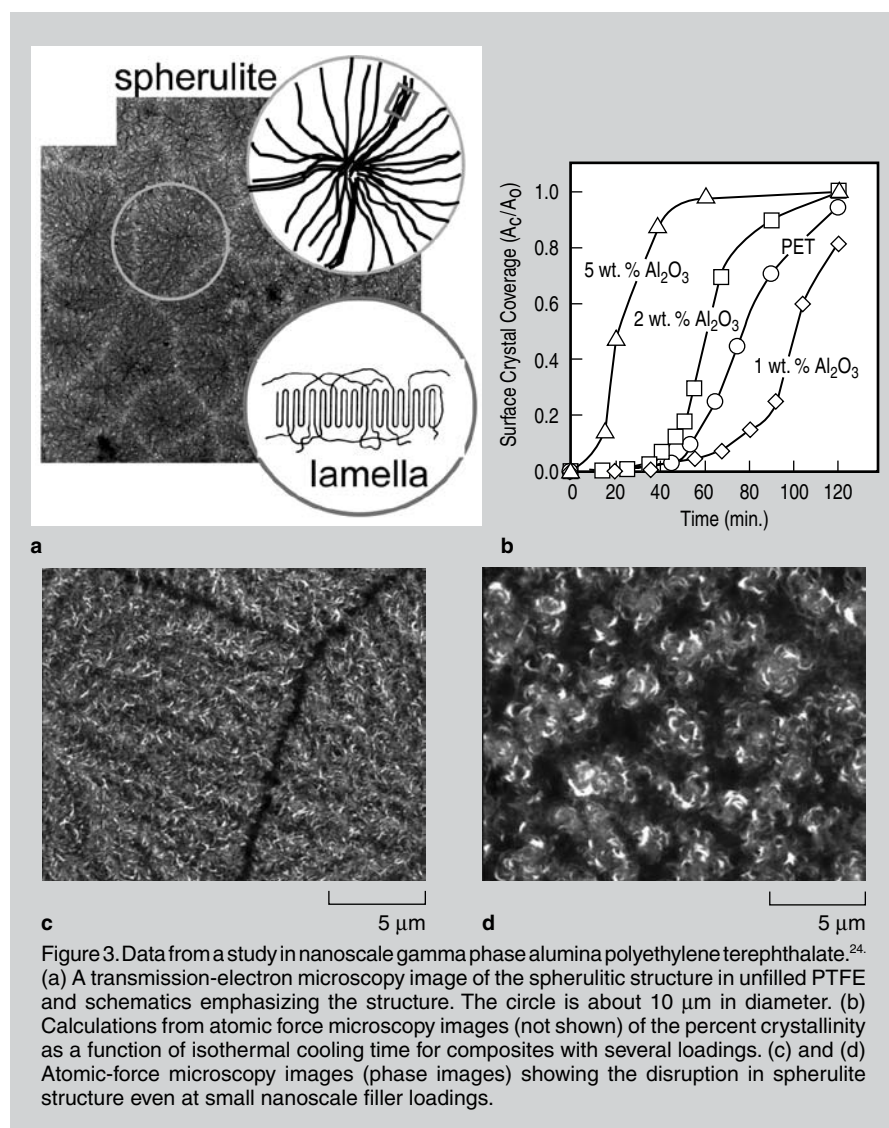


Figure 3. Data from a study in nanoscale gamma phase alumina polyethylene terephthalate.<sup>24</sup> (a) A transmission-electron microscopy image of the spherulitic structure in unfilled PET and schematics emphasizing the structure. The circle is about 10 μm in diameter. (b) Calculations from atomic force microscopy images (not shown) of the percent crystallinity as a function of isothermal cooling time for composites with several loadings. (c) and (d) Atomic-force microscopy images (phase images) showing the disruption in spherulite structure even at small nanoscale filler loadings.

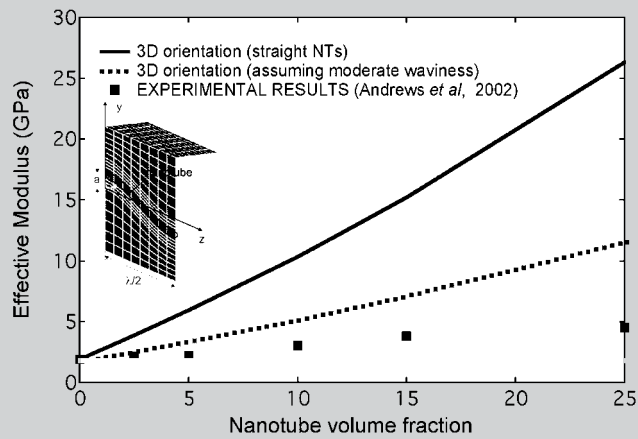


Figure 4. The effect of nanoparticle waviness. In this continuum approach, the inherent curvature of nanotubes in-situ in the composite are taken into account and shown to dramatically affect the overall stiffness enhancement potential of the nanotubes.<sup>57</sup> The light gray line at ~2 GPa is the baseline unmodified polymer modulus. Inset figure shows the finite element unit cell used to capture the effect of nanotube curvature.

and morphology of the polymer interacting with nanoscale surfaces is still developing.

## CHALLENGES FOR PREDICTING THE THERMOMECHANICAL RESPONSE

Predicting the mechanical properties of nanocomposites is quite challenging. Not only are the properties and geometry of the interfacial region unknown as discussed in the previous section, the dispersion, filler curvature (for tube and plate structures), and the exact properties of the nanofiller are also not well quantified for any given system. Thus, at the moment, models predicting macroscopic response are best used to elucidate how changes in constituent properties and morphology affect the overall material response. What is required to both aid in understanding interfacial polymer behavior and to create models appropriate for materials design is a coupled multiscale approach. Currently, the methods used to simulate nanocomposite behavior can be roughly categorized as:

- Molecular-scale approaches, such

composite can be raised or lowered with the addition of nanoparticles with attractive and repulsive interaction with the matrix, respectively.<sup>41–43</sup> Changes in glass transition temperature as large as 30°C have been observed.<sup>21,44</sup> While the correlation between interactions at the interface and changes in glass transition temperature are understood qualitatively, a quantitative understanding is required in order to design nanocomposites. Attempts to quantify this correlation using the differences in surface energy between the polymer and the nanoparticle filler have had limited success.<sup>45,46</sup> Rheological experiments can be used to probe the properties of the interfacial region more specifically. The loss modulus is sensitive to the distribution of relaxation times (relaxation spectra) of the polymer matrix. As nanofiller is added, if the mobility of the polymer chains is altered, the relaxation spectra can either shift (if the interface causes global changes in the polymer relaxation times) or broaden (if the interface creates only local changes in polymer relaxation behavior). Thus rheology has been used in nanoscale composites to probe the extent, structure, and properties of the interfacial region<sup>29</sup> and it has been found that the extent and properties of the interfacial region depend on the nanofiller/matrix interaction.

Direct measurements of the properties of the interfacial region are extremely difficult. Wagner et al. have used tests developed for traditional composites and downsized them using an atomic force microscope to measure interfacial shear

strength for nanotube/polymer composites using fragmentation tests<sup>47</sup> and pullout tests.<sup>48</sup> In most cases, their results show that the interfacial shear stress values for nanotubes are similar to those predicted for traditional composites.

Thus, while it is clear that the interfacial region has a significant impact on the properties of nanocomposites, quantitative understanding of the structure

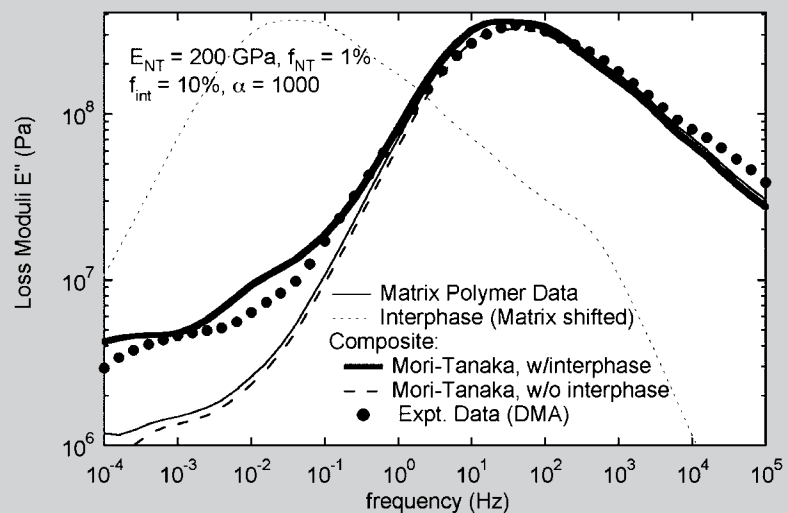


Figure 5. (a) The normalized elastic modulus prediction from Mori-Tanaka micromechanics models for two-phase (no interphase) and three-phase (with interphase) nanocomposites. Properties of the interfacial region are taken to be twice that of the bulk matrix polymer and interphase volume fraction is determined by 1 nm × 1 μm<sup>2</sup> nanoplates individually dispersed with interfacial region of 17 nm surrounding each plate. For the highest volume fraction shown, 2% nanoplates and 68% interfacial region is present. (b) Data and prediction of viscoelastic loss modulus from a hybrid approach considering a restricted mobility interfacial region surrounding 2 wt.% multi-wall nanotubes in polycarbonate. Here, due to the larger diameter of multiwall tubes and imperfect dispersion, a 10% volume fraction of interfacial region is used; viscoelastic properties of the interfacial region are based on those of the matrix but with relaxation times shifted to 3 decades slower. The prediction for the composite with interfacial region then captures the experimental data at low frequencies accurately.<sup>61</sup> Loss modulus predictions for a composite without interphase mimic the matrix properties and are not shown.

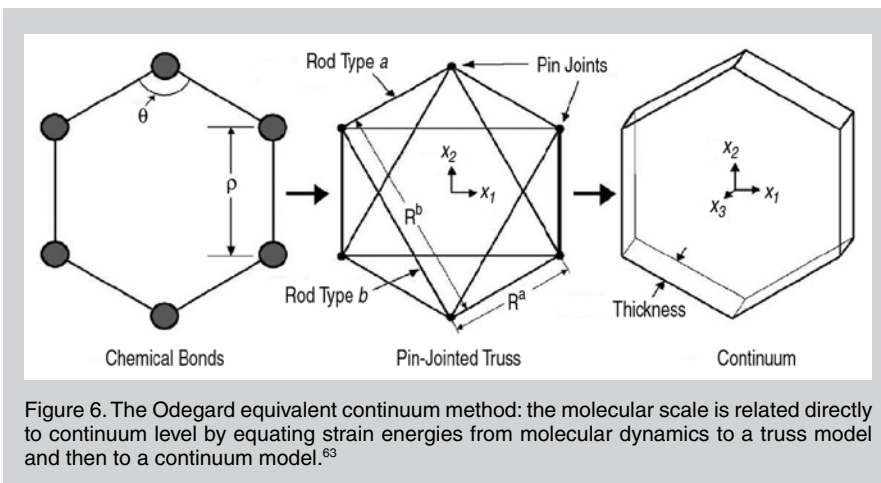


Figure 6. The Odegard equivalent continuum method: the molecular scale is related directly to continuum level by equating strain energies from molecular dynamics to a truss model and then to a continuum model.<sup>63</sup>

- as molecular dynamics
- Continuum approaches, such as traditional micromechanics and finite elements
- Hybrid methods, which aim to combine aspects of the small- and large-scale approaches

Each scale level carries with it a set of assumptions and approximations. In the following only a brief description is presented along with a few representative examples for the modeling strategies; a more extensive discussion can be found in Reference 49.

The molecular level approaches can, at present, only model short nanotube segments and small numbers of short polymer chains at elevated temperatures to obtain meaningful results in a realistic time scale. Thus, how the results scale to systems with molecular weights in the hundreds of thousands with micrometer-long nanotubes is unclear. Such models have been used very successfully, however, to understand the influence of nanoparticle functionalization or geometrical constraints on neighboring polymer chains.<sup>50,51</sup> They have shown that polymer density and diffusion is greatly impacted by nanoparticles and to distances on the order of the radius of gyration of the polymer chain.<sup>51,52</sup> Related work on polymer ultrathin films on substrates has indicated an even larger influence of the surface on polymer dynamics, over four times the radius of gyration away from the surface.<sup>53,54</sup> The mobility near the interface has also been probed and it has been shown that for repulsive interfaces, the mobility increases and for attractive interfaces mobility decreases, agreeing qualitatively with experiment. In addition, the heterogeneity of the surface has been

shown to affect the structure and mobility.<sup>55</sup> Quantitative numbers, however, with chemical specificity are not yet available.

At the opposite end of the spectrum, the continuum approaches treat the nanoscale objects with traditional continuum mechanics properties and thus lose all atomistic interaction detail. Efforts to bridge this wide gap between molecular and continuum models are being developed and are among the most promising areas of research. Meanwhile, continuum modeling approaches have been used successfully to help better understand nanocomposite behavior. For example, it was shown that the in-situ curvature of many nanotubes can have a significant impact on elastic stiffness (even greater than that of the interface).<sup>56,57</sup> Figure 4 illustrates how predictions for randomly oriented straight nanotubes lie far above experimental data. To account for nanotube curvature, a curvature distribution is assigned and the reduced effective stiffness of the curved nanotube can be determined either analytically or numerically for inclusion into the micromechanics prediction. Note that a curvature distribution of the nanotubes can impact the predicted stiffness by as much as 70%. A continuum finite element approach has also been used to elucidate the local strain shielding provided by high-aspect-ratio nanoparticles that can lead to nonlinear reinforcing effects.<sup>58</sup>

Hybrid and multi-scale approaches that specifically include interface properties are likely to have the largest impact on improving the ability to design polymer nanocomposites. One hybrid approach combines a finite element unit cell with traditional micromechanics to account for nanoparticle morphology

and the interfacial region in predictions of viscoelastic properties.<sup>59-61</sup> In this and similar approaches, the extent of the interfacial region and its properties must be given. The changes in properties can be based upon information from molecular dynamic simulations or local experimental data, or assumed based on knowledge of the chemical interaction between nanoparticle and polymer host. For nanotubes that interact strongly with the host polymer matrix, the interfacial region can reasonably be assumed to be stiffer and/or have slower relaxation mechanisms than the bulk polymer.

As one example, consider the elastic stiffness properties of a nanocomposite with and without an interfacial region surrounding well-dispersed nanoplates. Figure 5a illustrates that as the volume fraction of perfectly dispersed nanoplates approaches 2%, the stiffer interfacial region overwhelms the bulk matrix and dominates the overall response. Moving beyond simple stiffness, Figure 5b shows the loss modulus in frequency space of multiwall nanotubes in a polycarbonate matrix. The pure matrix polymer loss modulus lies significantly below the nanocomposite (black circles) at low frequencies, as does the predicted composite modulus if no interfacial region is considered (not shown). To better represent the nanocomposite, an interfacial region was modeled and assumed to be only 10% of the volume fraction for this unfunctionalized system and to have properties of the matrix polymer shifted to longer relaxation times. The prediction from the simulation with a restricted mobility interfacial region agrees well with the experimental data. In contrast to this example with unconnected interfacial regions, in many cases with good dispersion, the interfacial region will be percolated throughout the composite. In such cases, the loss moduli and tan delta shift dramatically to the value of the interfacial region polymer.<sup>62</sup>

Another hybrid approach is the equivalent continuum method pioneered by G.M. Odegard and coworkers.<sup>63-65</sup> In this approach the strain energies of a fully molecular dynamics system are equated to those of a truss system, which is then equated to those of a continuum, as illustrated in Figure 6. Via this approach, Odegard and coworkers have been able to study the mechanical properties of

nanocomposites where the anisotropy of the nanotubes is accounted for, as well as the effect of a crosslinking network polymer chains between functionalized nanotubes. A similar hybrid structural-mechanics/molecular-mechanics approach has been developed by C.Y. Li and T.W. Chou.<sup>66</sup>

Although many unresolved issues remain to address the relatively simple realm of stiffness, there is an even greater need for understanding and modeling of higher-level properties such as fracture toughness. These problems are beginning to be approached by molecular-level pull-out simulations<sup>67,68</sup> as well as continuum efforts to account for the influence of curvature and interfacial region on pull-out and crack bridging.<sup>69</sup> Thus, while there are still many challenges remaining to successfully model and understand polymer nanocomposites, significant strides are being made. Coupled with focused experimental study, the ongoing modeling efforts are helping to elucidate the physical mechanisms that underlie nanocomposite bulk performance and ultimately will enable efficient design of nanocomposites.

### TRIBOLOGY OF NANOPARTICLE-FILLED PTFE

One area in which nanofilled polymer composites are likely to have a significant technical impact is as solid lubricants for tribology applications. Homogeneous polymers are commonly used in bearing applications where the use of fluid lubricants is precluded. The major advantage of using homogeneous polymers in such dry-sliding applications is their ability to provide a non-abrasive and a moderately low friction surface. The primary limitation of using homogeneous polymers is their poor wear resistance. To solve this problem, hard micrometer-scale filler particles are frequently incorporated into a polymer matrix to increase the wear resistance, bulk hardness, yield strength, and elastic modulus. Unfortunately, these hard particle reinforced polymers tend to increase the abrasive wear to the counterface (the surface on which the polymer systems wear) and the dry sliding coefficient of friction. Lubricous fillers (such as graphite) added to polymers can reduce the wear rate primarily through a reduction in the

sliding friction coefficient, but require a favorable balance between the supply and removal of lubricant from the surface. Thus, these composites are sensitive to load, sliding speed, counterface roughness, and environment. Because of these shortcomings, research efforts continue in the search for hard and inert filler materials that can simultaneously improve the wear resistance and reduce the dry sliding coefficient of friction.

One common solid lubricant is polytetrafluoroethylene (PTFE) because of its low dry sliding friction coefficient ( $\mu < 0.2$ ), resistance to chemical attack in a wide variety of solvents and solutions, high melting point, and biocompatibility. A hypothesis for the low friction of PTFE is that the fluorine atoms are close enough to form a smooth cylindrical surface against which other molecules can easily slide (Figure 7a). At a somewhat larger scale, the long chains of PTFE orient on the counterface surface during sliding creating a transfer film. The transfer film creates a low shear-strength interface with the bulk PTFE material.

Unfortunately, however, PTFE suffers from poor wear resistance. The addition of micrometer-scale fillers to PTFE can result in a 2-orders-of-magnitude improvement in wear rate

at filler weight percents on the order of 15 wt%.<sup>70</sup> In PTFE systems this wear rate reduction typically comes at the expense of increases in dry sliding friction coefficient.<sup>71</sup> For nanoscale fillers, however, the wear rate can be reduced by up to 3 orders of magnitude (Figure 7b) using gamma-phase nanoscale alumina (10 wt.%) and 4 orders of magnitude for filler loadings as low as 1 wt.% of alpha-phase alumina nanoparticles.<sup>72,73</sup> The alpha alumina had a stronger interfacial interaction with the PTFE leading to improved dispersion and a further reduction in wear rate. In all cases, the friction coefficient remains relatively low when compared to micrometer-scale composites ( $\mu < 0.25$ ), and the nanocomposites were not particularly abrasive to the steel counterfaces (the pre-test polishing marks were still visible after many kilometers of sliding).

A 4-orders-of-magnitude decrease in wear rate at less than 1 volume percent of filler is a striking result! To understand this result, it is important to describe the structure of PTFE more fully and to understand the role of the interface on the structure. Figure 8a shows a schematic of the semicrystalline nature of PTFE. There are lamellae of crystalline layers with amorphous regions in between. As

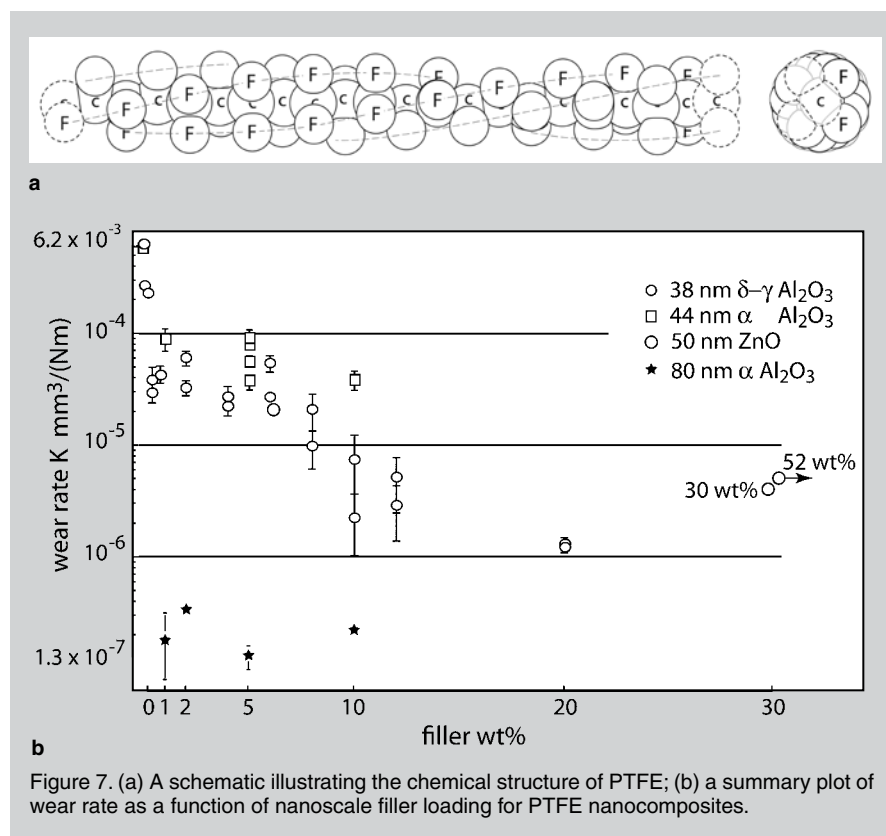


Figure 7. (a) A schematic illustrating the chemical structure of PTFE; (b) a summary plot of wear rate as a function of nanoscale filler loading for PTFE nanocomposites.

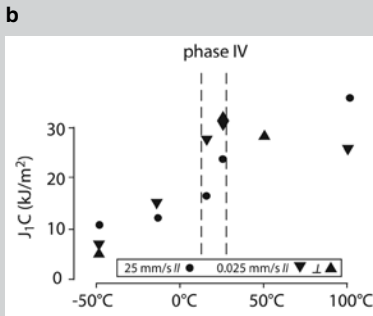
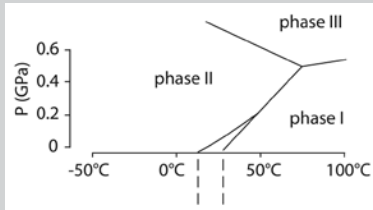
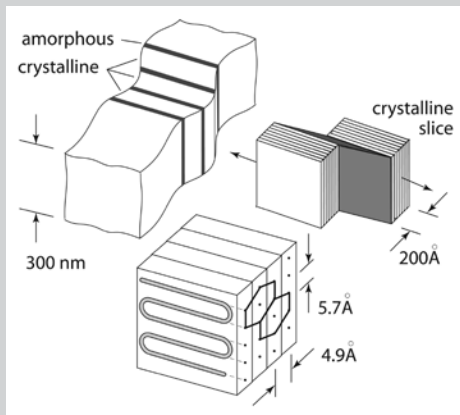


Figure 8. (a) A schematic illustrating the crystalline structure of PTFE; (b) the phase diagram of PTFE demonstrating that there are three phases present near room temperature at atmospheric pressure; (c) a figure from the work of E.N. Brown et al.<sup>75</sup> showing that the toughness of PTFE changes significantly due to changes in crystalline phase.

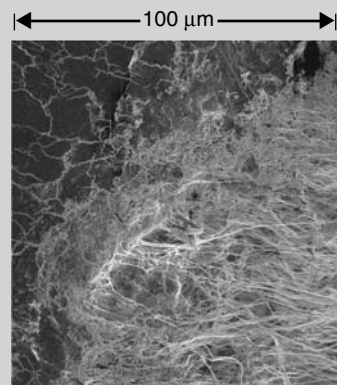
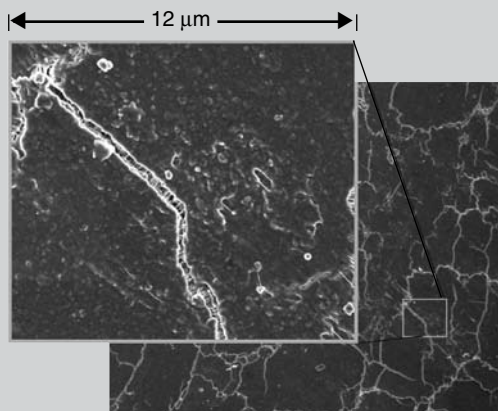
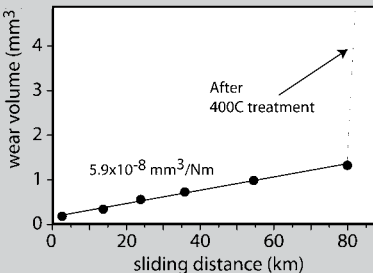
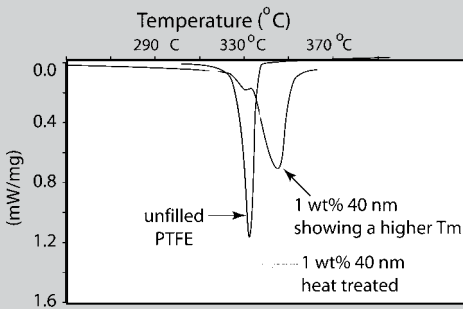


Figure 9. (a) Differential-scanning calorimetry results for unfilled, nanofilled, and nanofilled and heat treated PTFE. The peaks show the melting behavior and indicate that the nanofilled PTFE has a significantly higher melting point; (b) a plot of the wear loss as a function of sliding distance for 1 wt.% nanofilled PTFE showing a low wear rate before heat treatment and a high wear rate after heat treatment of the same sample; (c) a scanning electron microscopy image of the wear surface in PTFE showing periodic failure in the film with a higher resolution scanning-electron microscopy image of the wear surface showing the fibrils that span the cracks in the wear surface; (d) a lower resolution scanning-electron image showing that in some cases, the fibrils can span large cracks.

shown in the phase diagram for PTFE (Figure 8b),<sup>74</sup> there are three crystalline phases that are relatively stable around room temperature at atmospheric pressure. This is important because, as shown in Figure 8c, phases I and IV have a higher  $J_{1C}$  fracture toughness than phase II.<sup>75</sup> Since the crystalline phase and the morphology affect the deformation behavior of PTFE, it might be expected that they would also affect the tribological behavior. Therefore, one hypothesis for the role of nanofillers in PTFE is that they stabilize phase I. Phase I is a tougher phase and fibrillates more easily, which provides an opportunity for a well-adhered thin transfer film to form.

To test the hypothesis that nanofillers stabilize phase I, the melting behavior of unfilled PTFE and nanofilled PTFE (Figure 9a) was monitored using differential scanning calorimetry. The peaks in the plots are showing melting and indicate that the nanofilled PTFE has a higher melting temperature than the unfilled PTFE. A higher melting point is indicative of thicker lamellae. In addition, x-ray diffraction (XRD) of these same materials showed that the nanofilled PTFE had a higher fraction of phase I at room temperature. It was also noted that after treatment at 400°C, the melting behavior and the phases present (as shown by XRD) of the nanofilled PTFE more closely matched that of unfilled PTFE. If the hypothesis is correct, then after heat treatment, when phase I is no longer preferred, the wear rate should increase significantly. Figure 9b shows a nanocomposite that was tested for several kilometers and then placed in an oven at 400°C and cooled slowly. This same sample was placed back on the tribology testing rig, and the wear rate did indeed increase (by 2 orders of magnitude). In addition, Figure 9c and d shows scanning electron micrographs of the wear surface of PTFE showing a periodic cracking on the wear surface. A close look at the surface reveals fibrillation bridging the cracks. This prevents the formation of wear debris. Unfilled PTFE does not show this periodic cracking and instead shows significantly more wear debris. Therefore, it seems clear that the role of the nanofillers is to stabilize phase I increasing the ease of fibrillation. This provides an opportunity for a

well adhered transfer film to form and also leads to crack bridging on the wear surface and inhibits wear debris formation.

In summary, less than one volume percent of nanofiller with the correct interaction with the PTFE can improve the wear resistance by 4 orders of magnitude compared to unfilled PTFE and 2 orders of magnitude lower than micrometer filled PTFE while maintaining a low sliding friction coefficient. The authors hypothesize that one major reason for this dramatic improvement in wear rate is that even 1 wt.% of nanofiller stabilizes a tougher PTFE phase (phase I) not normally present at room temperature.

## CONCLUSIONS

This paper highlights the impact of the large interfacial area of nanoscale spherical and tubular fillers on the behavior of polymer nanocomposites. A discussion of the structure and properties of the interface indicate that quantitative knowledge is growing, but needs further focus. In addition, this lack of quantitative understanding significantly impacts the ability to model the behavior of polymer nanocomposites and hybrid approaches that include molecular scale and continuum level models will be critical in developing efficient design capability.

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