

Designed Interfaces in Polymer Nanocomposites: A Fundamental Viewpoint

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Abstract

Using nanocomposites in design-critical applications requires an understanding of their structure–property–function relationships. Despite many reports of highly favorable properties, the behavior of polymer nanocomposites is not generally predictable. The ability to tailor the filler/matrix interaction and an understanding of the impact of the interface on macroscopic properties are key to designing their properties. Tailoring can be achieved by grafting short molecules or polymer chains from the surface with precise control over their chain length (1–1000 mers), graft density (0.01–1 chains/nm²), and chemical architecture. The challenge is understanding the impact of the modified surfaces on the properties of the interfacial polymer, which can be more than 50% of the volume of the polymer matrix and, hence, can exert significant control over the macroscopic behavior of the nanocomposite. This article highlights the fundamental technical challenges that need to be overcome before spherical nanoparticle or nanotube composites can be designed. In particular, we discuss results from the recent literature that have significantly advanced our ability to predict and control nanocomposite properties through the use of designed interfaces.

Introduction

Nanoscale fillers blended with polymers (“nanocomposites”) offer the real possibility of creating materials with properties that are not realizable with traditional, micron-scale fillers. These unusual properties arise because of three attributes of nanofillers. First, they can have properties distinct from micron-scale fillers. For example, carbon nanotubes are as stiff as graphite fibers, but are almost an order of magnitude stronger.¹ Second, nanoscale fillers play the role of small mechanical, optical, and electrical defects. These provide an opportunity for multifunctionality (e.g., scratch-resistant, transparent polymers²). Third, they create a

large volume of interfacial polymer with properties different from the bulk, providing an opportunity for tailoring properties.

It is imperative to have a fundamental understanding of each of these aspects to understand structure–property–function relationships in these materials and to design composites with specific properties. In this review, focus is placed on the third aspect, and the role of the interface in modifying the thermomechanical properties of the composite is critically examined. Because this area of research is extremely broad, the discussion is further focused on the case of curved nanofillers (spherical and cylindrical); these systems are of particular

interest because they provide a contrast to the case of composites with micron-scale spherical or cylindrical fillers, which have been studied for nearly half a century.

In traditional composites, the interface is critically important for controlling properties and has been the focus of significant research.³ The interface is defined in the literature as the region in the vicinity of the particle surface where polymer properties are altered as compared with the bulk.⁴ The size scale of the interface depends on the particular property measured: chain dimensions can be perturbed in the immediate vicinity of the surface (typically on the order of the size of the molecule, 10 nm),^{5–7} but the chain center of mass diffusivity can be perturbed even 100 nm from the surface.^{8,9} Whereas the interface is present in all composites, the difference between nanocomposites and traditional composites is the volume fraction of polymer that is affected in the two cases.

Figure 1 in the introduction by Winey and Vaia in this issue highlights this point. This figure implies conservatively that the interfacial volume occupies 5% of the composite for spherical fillers of 10-nm radius (thus, $\delta \approx 1$) at a loading of 1 vol %. In contrast, the interface volume at these loadings is negligible in a traditional composite.

Figure 1 in this article shows this effect pictorially.¹⁰ Given the large fraction of polymer in the interface, the fundamental challenge to designing the properties of polymer nanocomposites is to understand the role of filler chemical modification as a vehicle for controlling interfacial polymer structure (and properties) with the goal of optimizing properties all the way from the nanoscale to the macroscopic level. At this point, this understanding is only qualitative and limits the ability to design composites with specific properties. For the purposes of this review, these fundamental challenges are distilled into two sets of questions:

1. Local Interfacial Properties: What is the effect of highly curved surfaces on the structure and dynamics of polymer chains? What is the size of the interface region? How do enthalpic interactions and entropic interactions control filler/matrix wettability and the resulting structure, dynamics, and properties of the polymer chains?
2. Consequences for Macroscopic Properties: How does the interface affect macroscopic properties such as the miscibility of polymers and particles (i.e., particle dispersion in the matrix)? Additionally, how does this dispersion quantitatively affect macroscopic properties, such as mechanical response and dielectric behavior? Can these macroscopic properties be predicted based on nanoscale information alone?

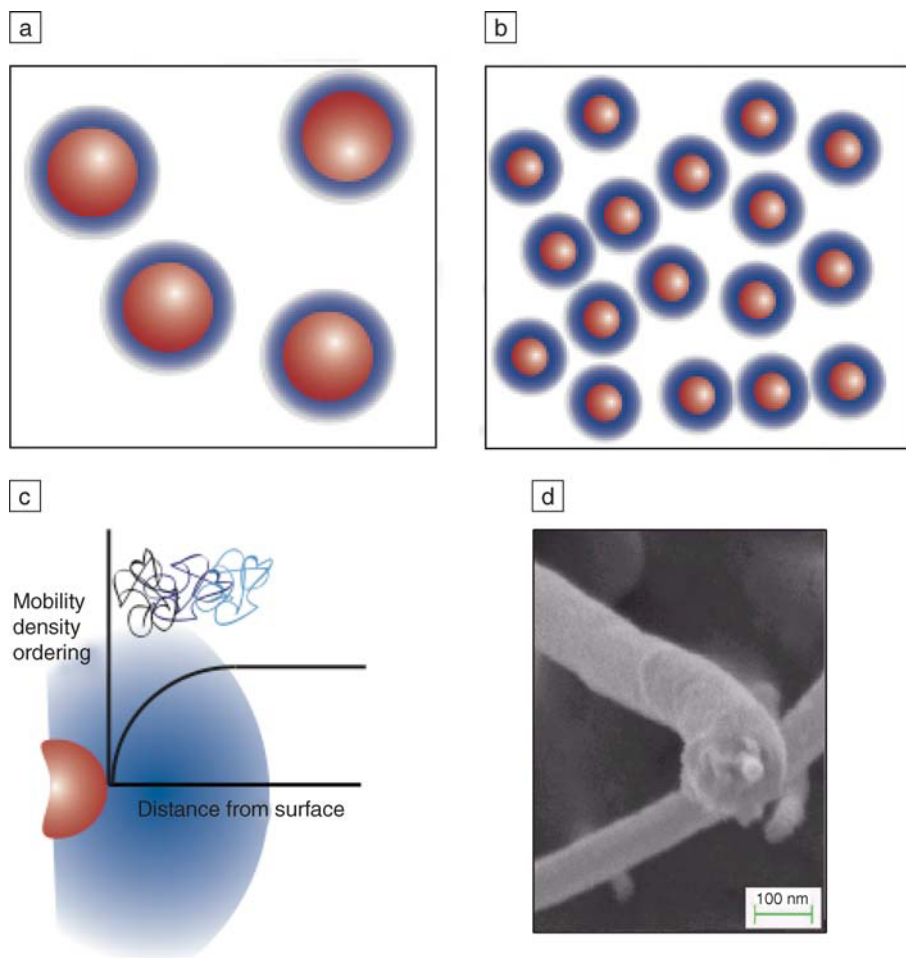


Figure 1. (a), (b) Schematic illustrations showing the difference in the volume of interfacial polymer (shown in blue) for nanocomposites compared with micron-scale composites. The area of red is about the same in the two images. (c) Schematic illustrations showing that the properties of the polymer change as a function of distance from the particle surface. (d) Scanning electron micrograph of a nanotube/polycarbonate fracture surface, showing the interface zone on the nanotube.¹⁰

With the questions defined, it is apparent that there is a need for systematic modeling and experimental studies that probe the effect of radius of curvature, and surface molecule chemistry, density, and length on the structure and dynamics of matrix polymer chains in the vicinity of a surface. For example, to predict particle dispersion requires “miscibility” maps similar to those derived for flat surfaces¹¹ (e.g., for melt intercalation into clays¹²). This dispersion will determine key quantities such as the structure and dynamics of the composite and thus enable us to relate nanoscale properties (e.g., wetting behavior, glass-transition temperature, or dielectric relaxation) to macroscale properties. When this knowledge is quantitatively integrated from the molecular scale to the macroscale, the design process to create nanocomposites with specific properties is enabled.

While recognizing that both sets of questions and their interplay are critical to the understanding of the role of the interface on the properties of the resulting nanocomposite, this article will address primarily question set 1, which has been the focus of considerable experimental and theoretical research in the last few years. The understanding of the relationship of interfacial properties with the macroscale properties of the nanocomposite (question set 2), which is critical to the applications of these materials in an engineering context, however, is at a nascent stage, and is hence only briefly discussed in this article. The article begins by identifying key components from the traditional composites and thin-film literature that apply to nanocomposite design. The article then selectively describes the toolbox of modification methods available for tailoring the interface. Finally, by considering

separately the enthalpic and entropic effects at the interface, the challenges to the technical community are identified.

Building from Traditional Composites

Fortunately, there is a large body of literature in the field of traditional composites that provides an excellent starting point for understanding the behavior of polymer nanocomposites.^{13,14} In addition, there are many models that provide accurate predictions of composite properties, for example, modulus and thermal conductivity.^{15–17} At the micromechanical level, it is understood that aspect ratio, geometry, and interfacial shear stress are relevant parameters.¹⁸ From this, it is expected (and observed) that nanoscale clays and high-aspect-ratio nanotubes should have the highest reinforcing capability.^{19,20} These models also predict that percolation should not depend on filler size, but that higher-aspect-ratio fillers will be more efficient for altering transport properties across a composite. It is also well understood from traditional composites that controlled dispersion and alignment of fillers is critical for well-controlled properties.

Traditional composites exploit the unique role played by the interface. There are many methods for compatibilizing fillers with the matrix, and significant research has been done to understand the chemistry of filler surfaces and, hence, to tailor interactions with the matrix.²¹ For example, work by McCullough’s group²² and Dibeneditto²³ bring rigor to understanding how the compatibility between the polymer matrix and fiber reinforcement is controlled by both enthalpic and entropic interactions between the two components. A review by Sottos and McCullough²⁴ makes a point that is still relevant today: “In order to develop and evaluate such models (that include the interphase) . . . the properties of the interphase must be accurately known.” This is a significant issue in traditional composites, but it is even more crucial in polymer nanocomposites, where the interface represents a much larger volume fraction.

What Do Thin Films Teach Us?

Given the dominant role played by the interface, crucial guidance can also be drawn from the thin-film literature. One of the properties that is sensitive to polymer structure and mobility is the glass-transition temperature. Thus, it is often used as a metric to monitor thin-film behavior. Comprehensive work on polystyrene and poly(methyl methacrylate) thin films has shown that the glass-transition temperature T_g increases if the film interacts favorably with the substrate.^{25–28} In limited cases, it has

been shown that increases in T_g reflect a reduction in the mobility of the interfacial polymer chains. On the other hand, in freestanding ultrathin films, T_g decreases (Figure 2, open circles).^{29,30} Because of the small radius of curvature of the particles and the highly polydisperse particle spacing in typical situations, the application of the thin-film work is not straightforward. Recent work³¹ by our group suggests that a quantitative correlation can be drawn between the thickness of thin films and the interparticle spacing in nanocomposites (Figure 2, solid circles) and that the interfacial width in the two cases is similar.^{32,33} In addition, the glass-transition temperature of a polymer nanocomposite can be raised or lowered with the addition of nanoparticles with attractive or repulsive interaction with the matrix.^{34,35} The mechanism causing these changes in T_g , however, is currently under discussion.³⁶ Thus, from thin films, it is known that the effect of a surface can impact the polymer structure and properties more than a radius of gyration away and that the chemical interaction at the surface is a critical parameter that affects whether the T_g increases or decreases.³⁷ This is important, because we shall assert that T_g can then be used in

bulk nanocomposite systems as a measure of the particle/polymer interaction.³¹

Toolbox for Interfacial Modification

To design and tailor the interfaces for specific properties and applications, a "toolbox" of methods for interface modification is necessary. This toolbox should enable the control of molecule length, graft density, and chemical composition. The attachment of short molecules to the surface provides an opportunity for tailoring the energetics of the polymer-surface interaction. Silane coupling agents (i.e., silicon-containing molecules covalently attached to the particle surface) are frequently used to functionalize the surfaces of silicon, aluminum, zirconium, tin, titanium, and nickel oxides. Less stable bonds can be formed with other oxides.³⁸ They may also contain reactive groups that can copolymerize with the matrix monomers: these are commonly used in thermoset polymers to covalently incorporate fillers into the matrix.

An alternative approach that has gained considerable popularity recently is the covalent attachment of polymers to the filler surface.³⁹ There are generally two

approaches to prepare polymer-grafted nanoparticles: grafting-to and grafting-from methods. Grafting-to methods, in which polymers bearing functional end groups are attached to the appropriate surface, are restricted to low grafting densities because of the steric hindrance imposed by the already grafted chains. In the grafting-from approach, the initiating sites are attached to the substrate surface.^{40,41} Polymerization is then conducted from the particle surface to prepare polymer-grafted nanoparticles. Higher graft densities and molecular weights can be achieved. Recently, advances in controlled radical polymerization techniques (e.g., nitroxide-mediated polymerization, atom-transfer radical polymerization, and reversible addition-fragmentation chain-transfer polymerization) have greatly facilitated the controlled synthesis of these polymers and, thus, our ability to design these interfaces.⁴²⁻⁴⁷

Collectively, these methods (and others not mentioned) are exciting because a toolbox of methods is available that enables researchers to design interfaces with several levels of control over chemistry, chain length, chain density, and layer thickness. In some cases, short molecule modification will be ideal, in others a heterogeneous surface, whereas for a third, high graft densities with a homogeneous layer thickness may be desired. The challenge remains, however, to understand which interface structures are optimal for achieving specific composite properties.

Characterization of Nanocomposites Formed from Functionalized Nanoparticles

The premise of this article is that to understand the structure-property-function relationships in nanocomposites, a fundamental understanding of the effect of the large surface area of nanofillers on the interfacial polymer structure and properties must be developed. It appears well accepted in the literature that the dispersion of the particles in a polymer matrix can be greatly facilitated by creating particle surfaces that are wet by the polymer. In addition, one fundamental property that is sensitive to the wetting properties of the interface and can be measured with relatively minor mechanical and electrical perturbations is the glass-transition temperature. This section, therefore, focuses on this property, where it is used as a measure of the filler/matrix interaction with the implicit understanding that the filler/matrix interaction is also known to affect the mechanical, optical, electrical, and thermal properties of bulk nanocomposites as well as dispersion.^{2,46,47} It is the degree to which

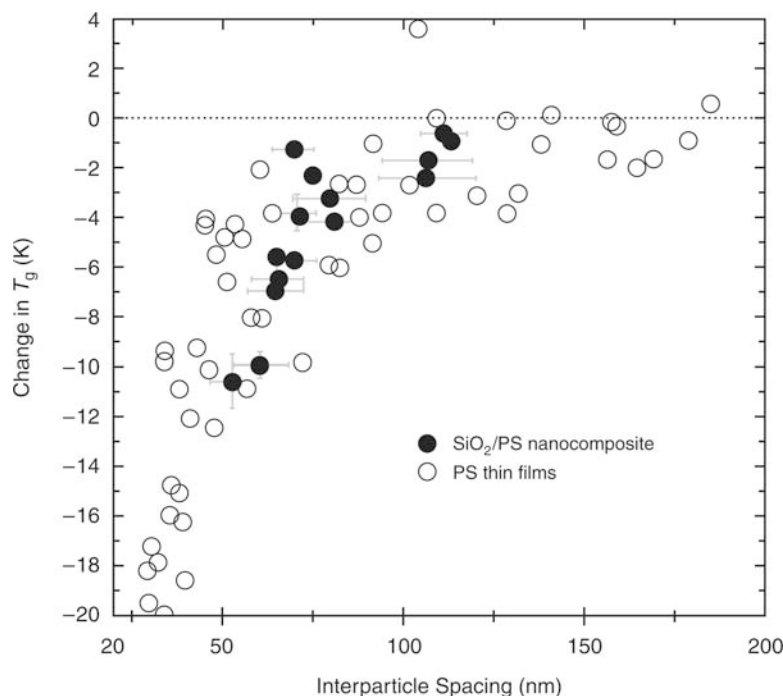


Figure 2. Comparison between the glass-transition response of polystyrene nanocomposites and polystyrene thin films as a function of interparticle spacing, which represents the film thickness for thin films and an average interparticle spacing in the nanocomposites. The x-error bars represent a 95% confidence level. Data from literature on freestanding ultrathin films²⁹ and supported films³⁰ are shown as open circles. (Taken from Reference 31.)

each of these properties is affected by the interface that is not known quantitatively.

Enthalpic Control of Interfacial Properties

Consider first the role of short molecules on the filler/polymer interaction. In this case, entropic effects play a small role, and energetic interactions control the interfacial behavior. It is well known that the nanoparticle surface can be modified with silane coupling agents so as to affect many properties, including the glass-transition temperature. The hypothesis from the literature is that if the surface is attractive to the polymer, then T_g will increase. If it is neutral, T_g will not change, and if it is repulsive, or nonwetting, T_g will decrease.^{23,48}

The adsorption energy of a polymer segment is the difference between the energy of interaction of a polymer segment with the surface (ϵ_{ps}) and the interaction of the same segment when it is interacting with another polymer segment (ϵ_{pp}), that is, $\epsilon_{ps} - \epsilon_{pp}$. If the interactions are modeled as being purely dispersive in character, then the solubility parameter of the surface and the polymer can describe the energetic interactions in the system.⁴⁹ In this situation, the adsorption energy of a segment to the surface is $\propto -\delta_p \times [\delta_s - \delta_p]$, where δ denotes the solubility parameter of the surface and the polymer, respectively, for subscripts p and s, and the negative sign after the proportionality sign is because the energy of interactions are generally negative while the solubility parameters are positive.

Thus, polymers will wet the surface if $\delta_s \geq \delta_p$, and the miscibility of the polymer and the particle, and hence the T_g shift, should scale with the difference in the solubility parameters. Additionally, the surface area of the particles can be used to normalize across particles of different size and volume fractions. Although these ideas were presented for micron-scale composites, they were only tested in limited cases and for positive interactions.²³

To test this simple set of ideas on nanocomposites with a range of interactions, Figure 3 shows data from the literature for the changes in T_g in nanocomposites.^{50,51} Cohesive energy density values were obtained from the literature⁵² and in some cases were estimated based on similar materials or using group theory.⁵³ Figure 3 shows that these ideas work rather well for the range of systems examined here. Significantly more systems must be tested to establish the general power of this approach, which is analogous to the highly successful regular solution theory for bulk miscibility. It is important to note that there are significant limitations to this

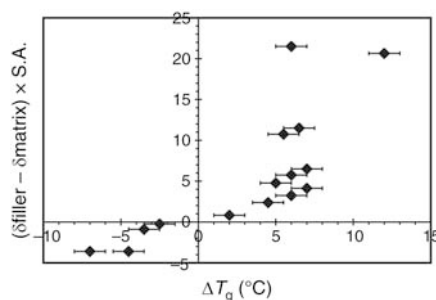


Figure 3. Plot showing the effect of the difference in the solubility parameters multiplied by the surface area as a function of glass-transition temperature. The glass-transition data include melt-processed ZnO/polystyrene⁵⁰ and calcium carbonate/poly(methyl methacrylate) composites⁵¹ with several surface modifications as well as data generated by our group on solution-processed silica/polystyrene nanocomposites using both as-received and fluorinated 15-nm silica.⁶⁴

approach, including the error caused by specific interactions and estimation of surface area based on particle size. Nevertheless, it is encouraging to see the correlative ability of these ideas in understanding the behavior of T_g .

Entropic Control of Interfacial Properties

Wettability can also be controlled by entropy. Consider cases, therefore, where enthalpic interactions are minimized, such as when nanofillers with long-grafted polymer chains are placed in matrices of the same chemistry. This problem is essentially that of the wetting properties of curved brushes, especially when the particle sizes are in the nanoscale. Until a decade ago, most theoretical efforts in this area modeled flat surfaces and then accounted for the particle curvature at the level of the Derjaguin approximation. Although this approach should work for micron-scale particles, it is likely to be incorrect for spherical nanoparticles. More recent theories have recognized this fact and have explicitly accounted for the role of curvature in both theory^{11,54} and simulations.⁵⁵ For chains grown from curved surfaces, the effective crowding decreases with increasing distance from the surface, because the volume available to the polymer segments increases with the square of the distance from the particle center. Thus, even though chains may be strongly extended at the particle surface, they may locally assume Gaussian conformations some distance away.⁵⁶

Whereas this diminished crowding issue is well appreciated when curved brushes are placed in a small molecule solvent, the

corresponding behavior in the presence of polymeric solvents is not clear. For flat surfaces and a given graft chain length, N_G , there exists a critical matrix length, N_{matrix} , beyond which free melt chains will not wet the brush. This autophobic dewetting effect is purely entropic in origin when the grafted and matrix chains are chemically identical and represents a balance of two competing tendencies. Wetting is favored because the system gains translational entropy by mixing brush chains with the matrix. This is balanced by the loss of entropy of the melt chains when they are placed in the geometrically crowded environment of the stretched brush. Theory and some experiments show¹¹ that this transition occurs when $N_{matrix} \approx N_G$ for the case of flat brushes.

Self-consistent mean-field calculations⁵⁷ for the wetting behavior of polymer melts on spherical surfaces with grafted polymer chains were used to explore the consequences of particle curvature.⁵⁸ The roles of brush molecular weight, brush density, and the particle radius of curvature were systematically explored while examining long-enough matrix chains to remain in the limit of infinite matrix molecular weight. Although the system has no net "excess" enthalpic interactions between the grafted polymer and the matrix homopolymer, there is an effective mean-field interaction (χ_{eff}) that arises because of the entropic penalty associated with the interface formed between the brush and the matrix chains. The effective mean-field interaction is estimated following the ideas of Helfand,⁵⁹ and the results show that for a fixed grafted chain length and grafting density, the interaction parameter becomes smaller with decreasing particle radius. Further, it scales with N_G as $\chi_{eff} \sim N_G^{-1.1}$ (Figure 4). Flory's theory for bulk miscibility⁶⁰ suggests that the grafted chains and matrix chains will mix if $N_{matrix} \leq N_G^{+1.1}$. This result is very similar in functional form to that derived for planar brushes,⁵ except that the prefactors ignored in this scaling analysis are strongly dependent on particle radius.⁶¹ This theoretical result suggests that longer grafted chains (i.e., higher N_G) indeed will be more wettable. Furthermore, miscibility is enhanced for smaller particles—a significant result, as it is hard to mix polymers with small bare nanoparticles.⁶² Thus, these theoretical results confirm the hypothesis that the use of brushes should enable the facile tuning of the interfacial properties of these nanoparticles, presumably facilitating the creation of nanocomposites with any desired structure and properties.

Recent preliminary experiments lend credibility to the assertion that the wetting

behavior of the particles can be controlled by the use of grafted polymer chains.⁶² Dense polystyrene chains were grown on silica particles with a nominal diameter of 14 nm using reversible addition-fragmentation, chain-transfer (RAFT) polymerization.^{46,47} This method enables simultaneous control of both σ (0.05–0.8 chains/nm²) and N_G (to molecular weights of more than 100,000 g/mol) of the grafted polymer without sacrificing the polydispersity index (PDI, <1.2) of the resulting chains. Figure 5 shows the effect of changing N_{matrix} with $\sigma \approx 0.27$ chains/nm².⁶³ For N_{matrix}/N_G ratios of >1, the polystyrene matrix dewetted the particles and the glass-transition temperature of the matrix was reduced. For ratios <1, partial wetting and an increase in T_g were observed. This suggests that the controlling variable is N_{matrix}/N_G for the case of a fixed σ . Figure 5b shows a study⁶⁴ in which the N_{matrix}/N_G ratio was held constant

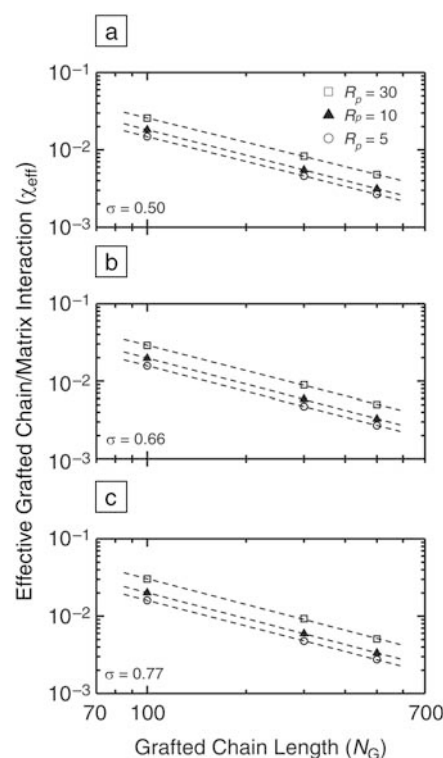


Figure 4. Plot of the effective interaction parameter, χ_{eff} , for a matrix of effectively infinite molecular weight as a function of graft chain length. The three plots correspond to three different grafting densities, (a) $\sigma = 0.50$, (b) $\sigma = 0.66$, and (c) $\sigma = 0.77$, where in each plot the three lines correspond to three different particle diameters. These diameters are in units of lattice units, where each site is ~ 1 nm. The dashed lines show that $\chi_{\text{eff}} \sim N_G^{-1.1}$.⁵⁷

and the σ was changed. The plot is the change in glass-transition temperature as a function of σN_G . It is encouraging to see that the data appear to follow an apparently universal law across this limited range. Although these are interesting results, it is not clear from theory what the scaling laws should be, and this is only a hint of the work that must be done to achieve understanding.

Relationship between Local Interface Behavior and Macroscopic Properties

So far, the focus has been on the first set of questions posed in the introduction. Reflecting on the second set of questions requires that two issues be understood: first, how do the nanoscale interactions at the particle/polymer interface affect the dispersion of the particles? This is particularly important, because it has been suggested that the mechanical (and presumably

other macroscopic) properties of the resulting composites are sensitively determined by dispersion.⁶⁵ It has been recently appreciated across a wide range of systems (mainly micelles, star polymers, and more recently, particles with grafted brushes) that particle dispersion in polymer matrices is facilitated when the molecular weight of the polymer matrix is smaller than the brush chains.^{66–68} However, it is unclear at this time if this result represents the equilibrium state of the system, or rather reflects the role of processing. This is highlighted in particular by the work of Bansal et al.,⁶³ who found that particles dispersed into matrices even when the matrix chains were much longer than the brush (i.e., even when the matrix did not wet the brush). Whereas this has become a topic of considerable interest in the community, with several unanswered issues, it is perhaps equally important that the relationship between the particle dispersion and macroscopic properties is not quantitatively understood at this time. Understanding this relationship, which is the second unanswered question, requires the development of multiscale models/experiments that can bridge across these scales. The use of micromechanical models can be helpful in predicting mechanical properties,⁶⁹ however, to design composites from the molecular scale to the macroscale, the role of the particle surface on interface region properties must be included not only for macroscopic property prediction^{70,71} but to predict dispersion,⁷² phase segregation,⁷³ and polymer crystalline structure.⁷⁴ Such multiscale tools are extremely challenging to develop^{75,76} and require not only modeling/experiments at all scales, but bridging across these scales. These next few years will be exciting as this field continues to emerge and we begin quantitative design of nanocomposites.

Summary and Conclusions

Our results unequivocally point to the critical role played by the polymer-particle interface in controlling the local polymer structure in polymer nanocomposites. This article demonstrates that both in the cases where energetic interactions dominate and for particles with long-chain brushes (where entropic factors are crucial), the thin-film literature and traditional-composites literature can provide significant insight. While this work has provided a brief overview of current developments in this field, it is important to stress that much more experimental information is required to gain a thorough fundamental understanding. More effort must be expended in understanding how these nanoscale interactions affect the macroscopic properties of

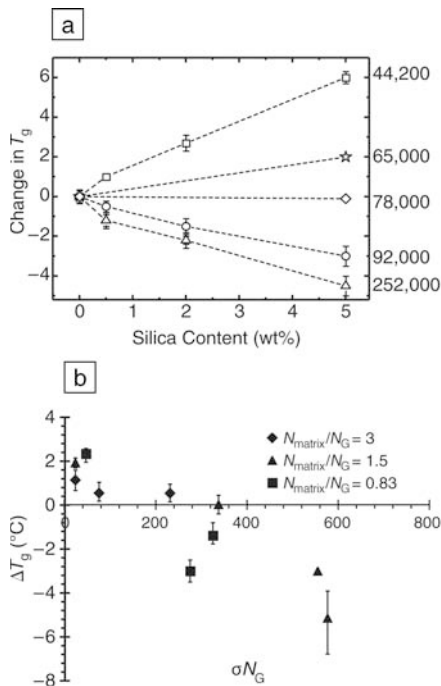


Figure 5. Plots of (a) the change in glass-transition temperature (ΔT_g) as a function of SiO₂ concentration for silica nanoparticles with 110,000 g/mol polystyrene on the surface, graft density of 0.27 chains per nm², and matrix of various molecular weights (in g/mol), shown at the right in the Figure. Dashed lines are a guide for the eye.⁶³ (b) The change in glass-transition temperature T_g for polystyrene-grafted silica/polystyrene nanocomposites as a function of the graft density σ , multiplied by the chain length of the grafted chain N_G .⁶⁴

nanocomposites, a nascent area of research that is expected to be crucial in designing materials for use in any desired application.

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