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Nanocomposites with Polymer Grafted Nanoparticles

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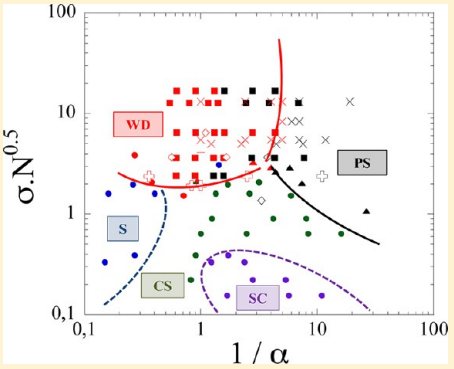
ABSTRACT: A recurring challenge in the field of nanocomposites is to control the spatial distribution of nanoparticles (NPs) in a polymer matrix. This issue is of critical importance since it is now well-established that a specific NP dispersion state is necessary to optimize a desired property of polymer nanocomposites (PNCs). This Perspective focuses on one particular approach to controlling NP spatial dispersion, and hence the properties of polymer-based nanocomposites: the use of polymer-grafted NPs. Novel developments over the past decade in synthesis techniques allow us to controllably functionalize NPs with polymer chains. This has ignited considerable interest in this field, leading to significant advances in creating nanocomposites with tunable physical properties. We begin by briefly outlining the various synthetic strategies for functionalizing NPs and then discuss various methods for controllably dispersing them in a polymer matrix. The consequences of having states with controlled NP dispersion on nanocomposite properties, primarily the mechanical and optical properties, will then be discussed. In every section of this Perspective, we have an explicit discussion of unresolved issues and critical questions which need to be addressed for continuing progress, especially as it relates to current and potential applications of this class of materials.



1. INTRODUCTION AND CONTEXT

It is now accepted that the addition of nanoparticles (NP), i.e., nanospheres, tubes, or sheets, to a polymer melt can result in materials with significantly improved thermomechanical, optical, and electrical properties.[1−14] While this guiding principle is well established, it is also clear that a specific NP dispersion state is necessary to optimize a desired property of these hybrids. Importantly, the issues that determine NP spatial dispersion and organization, and how they affect the macroscale properties of the hybrid, remain largely unresolved even from an empirical perspective. These remain as the ultimate barrier to the more ubiquitous application of these materials.

There have been multiple strategies to control the NPs dispersion in a polymer matrix. We focus here on one strategy—suspending NPs grafted with polymer chains in a polymer matrix (Figure 1). A considerable amount of work on larger, micrometer-sized colloidal particles shows that particles with high grafting density of chains, σ,[15] are miscible with matrix chains of the same architecture, so long as the free (matrix) chains have lower molecular weight than the brush. (In the following, P and N denote the degrees of polymerization of the matrix and the grafted chains, respectively.) Since both the matrix and the brush have the same chemical structure, the immiscibility for longer matrix chains is entropic in origin and attributable to the concept of "brush autophobicity".[9,16−20] Extension of these ideas to NPs suggests that we can control NP−polymer matrix miscibility (and hence spatial dispersion)[15,21−39] by changing matrix chain length, P,

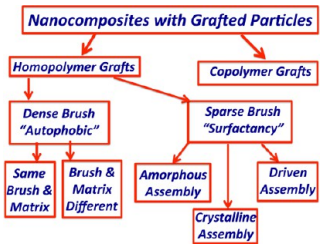


Figure 1. Broad area covered by review. Discussion is primarily on the left side of this diagram, in the case of "homopolymer" brushes.

with the only difference being that the absolute ratio of matrix to graft chain length P/N ($\equiv\alpha$) where this crossover occurs may be NP size dependent ("Dense Brush" regime in Figure 1). The underpinnings of these experiments were established by simulations,[37,40−42] which point to the essence of this brush-driven miscibility. While much of the experimental work has focused on the case where the matrix and the graft have the same structure, the use of matrix polymers with a different chemical structure than the brush remains unexplored at this time.

This idea of achieving a good, uniform NP dispersion state has been the focus of considerable research, especially because

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of its favorable impact on optical and some mechanical behavior of the resulting composites.[43,44] Even more interesting are emerging ideas which focus on controlling the NP spatial distribution, i.e., the creation of alternative structures like sheets, vesicles, percolating clusters, etc., with the goal of improving a range of other properties, e.g., thermal conduction, selective permeation of gases.[45−50] It has now become well-established that these "new" self-assembled structures form when NPs with much lower grafting densities are used, especially when the grafted polymer chains energetically "dislike" the particles ("Sparse Brush" regime in Figure 1). In these cases, the grafted NPs act like microphase-separated block copolymers and assemble into a range of morphologies.[19,46,48,51−57] The structures formed by this mechanism, the factors that govern their formation, and the effects of the resulting spatial NP dispersion on properties are the central focii of this Perspective. It is important to emphasize that, while the field of nanocomposites has been the focus of several reviews, this paper emphasizes one subfield. Thus, it is not comprehensive, and the interested reader should refer to several review papers on this rapidly evolving discipline.[1−3,12,31,46,58−91] We organize our review around some unresolved questions:

(i) *Controlling NP Dispersion*: Are there general strategies to control the particle dispersion and their three-dimensional arrangement by varying the grafting density σ, grafted chain length N and matrix chain length P? What relative roles do thermodynamics and dynamics play? Are these effects size dependent, and if so, are NPs unique in this structure formation?

(ii) *NP Dispersion and Its Role on Properties*: What role does particle dispersion and particle organization play in specific property enhancements ? Can we *a priori* predict the particle dispersion and organization state that can optimize one (or more) property of the resulting nanocomposite? While NP dispersion is believed to critically affect properties, it is not apparent that a single state of particle dispersion or organization should optimize any given or all macroscale properties. To bolster this argument, we point to Torquato's work[92−94] on macroscale composites. Let us consider a case where one "phase", say A, of a binary composite is mechanically reinforcing and electrically nonconducting, while the other, B phase, is not reinforcing but conducting. If one only needed to optimize conductivity, then a percolating B phase would be sufficient. In contrast, simultaneously optimizing both the electrical and mechanical properties of the composite requires that the two "phases" are connected in a triply periodic fashion; i.e., both are simultaneously percolating. This immediately suggests that optimizing one versus two properties of a composite can require very different morphologies.

A final aspect we touch on here are the roles played by NP size and shape; these are issues that have not been explored by us in detail to date, and so we leave them as open questions, outside the focus of this Perspective. Instead, here we discuss spherical nanoparticles and do not consider other NP geometries such as platelets (clays and graphene), nanotubes (carbon based and others), and nanorods. While these other anisotropic NP shapes can achieve mechanical and electrical percolation at even lower loadings than spherical NPs, we would like to first understand the spherical NP case, which we believe should serve as a canonical example of behavior. The behavior of other shapes, which is already being researched in other groups, can thus be considered on this basis. A challenging future direction is making anisotropic silica or latex particles and grafting them with polymer chains. In the same vein, the role of particle size has also been a topic of continuing discussion for the past 50 years, but this is a topic that has not received as much attention as particle shape. While we shall not spend time on this topic, we note that, in the limit of large sizes, the increase in specific nanoparticle surface area with decreasing diameter improves properties. Previous workers have conjectured that this effect is counteracted by a reduction in the thickness of the adsorbed "bound" polymer layer with decreasing size, leading to decreased interparticle "coupling". It is then speculated that a balance of these factors leads to a particle size, in the nanoscale (∼100 nm), with optimum properties.[95−100]

2. SYNTHESIS AND CHARACTERIZATION OF NANOPARTICLES

2.1. Synthesis. There are primarily two synthetic methods to create grafted nanoparticles: "grafting-to" and "grafting-from". In the grafting-to method, a preformed and end-functionalized polymer is attached to the surface. Although the grafting-to method has the advantage of a simple and modular approach, there are drawbacks. Steric repulsion between polymer chains already attached and a chain diffusing to the surface limits the available graft density.[101] In the grafting-from method, the surface is functionalized with an initiator or chain transfer agent and the polymer is grown from the surface. The diffusion of a relatively small monomer to the surface does not suffer from the same steric repulsion as a diffusing polymer chain. Controlled radical polymerizations (CRP) offer an attractive method for the functionalization of the interface between the nanoparticles and polymer matrix, allowing for the control over multiple molecular variables including chain composition, molecular weight, architecture, and polydispersity as well as end- and side-group functionality.

Over the past several years, a variety of methods have been developed, using controlled radical polymerization techniques, to graft polymer chains to nanoparticle surfaces.[9,102,103] The main CRP methods for growing polymer chains are atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), and reversible-addition−fragmentation chain transfer polymerization (RAFT).

The first reported use of ATRP for the modification of surfaces was in 1997 by Huang and Wirth.[104] These authors were able to successfully graft poly(acrylamide) brushes from benzyl chloride-functionalized silica particles. While the application was analytical in nature, the results sparked ATRP to become extensively used for the creation of polymer brushes. Matyjaszewski et al. have made significant contributions to the expansion and refinement of ATRP in solution and on surfaces.[105−107] Russell and Hawker reported the earliest work with NMP on surfaces using silicon substrates.[108] Although these techniques have been used for a variety of monomer and substrate combinations, the versatility of monomer choice, lack of catalyst, and mild reaction conditions of RAFT have allowed for its rapid use in the past decade. Its first reported use for graft polymerization was in 2001,[109] and since then it has been used for the modification of various surfaces using multiple approaches.[110]

Through the use of new RAFT agents and coupling agents, we can now control the graft density from 0.01 to ∼0.7 chains/nm^2 and grow brushes of molecular weights up to 150 kg/mol with a dispersity index below 1.15. The general steps to prepare grafted NPs involve: (i) the initial step to functionalize the

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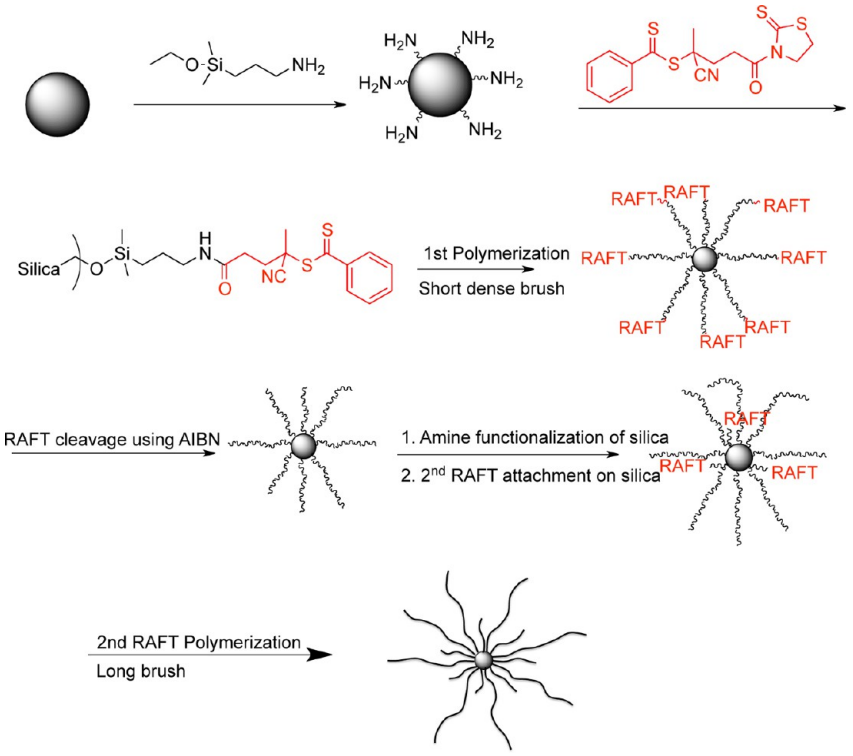
Scheme 1. Synthesis of Bimodal Brush Particles Using Sequential RAFT Polymerization



inorganic surface with an organic functionality, (ii) conversion of organic functionality into a RAFT agent, and (iii) subsequent polymerization of the desired monomer using the control of the designed RAFT agent.[102] We do not discuss this issue further but refer the interested reader to published work in this field. Instead, here we focus on two new synthetic protocols for creating bimodal grafted NPs and NPs grafted with block copolymers, which may have significant impact on emerging applications.

NPs with Bimodal Brushes. Our previous work suggests that NP assembly in the sparse brush regime is a competition between core−core attractions and the accompanying entropic repulsion caused by brush distortion.[46,111] Also, work by Matsen et al. suggests that a bimodal brush could overcome autophobic dewetting between the polymer grafted chains and the chains of the matrix.[112] A bimodal brush is defined as a homopolymer brush with two distinct lengths of chains attached to the surface. When these chains are also chemically distinct, it is deemed a mixed bimodal brush. Few methods have been described in literature for the synthesis of bimodal brush grafted surfaces. Minko and Stamm have used both grafting-from and grafting-to approaches to prepare bimodal brushes on flat surfaces.[113,114] Recently, Minko et al. have used consecutive activator generated electron transfer (AGET) ATRP polymerizations to produce a mixed polymer brush from the same layer of attached 3-aminotriethoxysilane.[115] This alternative approach uses a triethoxysilane which can condense with each other producing a multilayer and limiting available graft density. Also, by using the residual aminosilane remaining after the first polymerization, ultimate control over both graft densities is minimized. Dyer et al. have used a combination of photochemical initiation through a mask for the first brush with the second brush formed from azo initiators that were previously covered by the mask.[116] Although techniques such as these create the desired binary brush, they lack control over some of the molecular variables such as graft density. Consecutive CRP techniques were used by Zhao et al. to create mixed brushes while allowing for control of molecular weights.[117] Through use of a Y-shaped initiator, consecutive ATRP and NMP reactions were completed followed by hydrolysis to produce responsive poly(acrylic acid)/polystyrene mixed bimodal brushes. While overall graft density can be controlled with this method, the graft density of each chemically distinct chain cannot be controlled separately and independently. More recently, Ye et al. have performed a two-step approach with reverse ATRP, where the polymerization is initiated from azo initiators anchored on the surface of silicon wafers to produce mixed bimodal brushes.[118] All of the previously mentioned methods for bimodal brush production, however, have been performed on either silicon wafers or 150 nm silica particles. Silica nanoparticles (diameter <100 nm), which are used pervasively in polymer nanocomposites, have only recently been functionalized by bimodal brushes.[119] The investigation into their effects when incorporated into nanocomposites has only recently been reported.[120]

As a new strategy to alter inter-NP attractions, we have synthesized bimodal brushes on silica nanoparticles (Scheme 1). Thus, both the entropic and enthalpic driving forces for NP organization can be varied in a controlled manner. Synthesizing such particles is a challenge and is achieved based on consecutive RAFT polymerizations.[102,119] In the first step, a dithioester capable of polymerizing a variety of monomers, including styrenics and methacrylates, is reacted with amino-functionalized silica particles by direct condensation of the mercaptothiazoline-activated RAFT agent with surface amino groups. The RAFT agent grafting density is easily varied (0.1−0.7 chains/nm^2) by controlling the amount of 3-amino-propyldimethylethoxysilane used to initially functionalize silica.

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RAFT polymerization is then conducted from the particle surface to synthesize the first polymer brush. Before the second RAFT agent attachment, the first RAFT agent anchored at the polymer chain end is cleaved by reacting the particles with excess AIBN (10:1) in dilute THF solution. By keeping an intermediate grafting density around 0.5 chains/nm^2 (maximum achievable is ~0.7 chains/nm^2), some silica surface is available for further modification. The second RAFT agent is attached using identical attachment chemistry as for the first brush, thereby yielding bimodal/mixed brush anchored NPs.

Physically, the denser, shorter brush allows one to systematically introduce roughness to the soft corona layer. This method allows for the control of the previously mentioned molecular variables for both chain populations, separately and independently, allowing for the production of bimodal/mixed polymer brushes. Similarly, by creating protonated/deuterated combinations of the short and long chains, we can enhance the contrast in the system for their study by neutron scattering.

NPs with Grafted Block Copolymers. We can also grow block copolymers, which can provide a range of different morphologies and thus different properties.[121] Control over these chain parameters has been demonstrated for styrenic, acrylate, and methacrylate type monomers. In addition, we have shown through click chemistry that we can add other functionality such as conductivity to the polymer brushes.[122] While it is commonly believed that click chemistry is not useful due to the relatively low graft densities that can be achieved, we emphasize that much of the interesting physics, i.e., where the NP acts akin to a block copolymer or a surfactant, only occurs in this weakly grafted limit.[123] Hence, we believe that both of these synthesis strategies have value in this context.

Looking Ahead. (1) The attachment of homopolymer chains where the chemistry of the chains are the same as the matrix is relatively well developed and thus has focused much work on controlling entropic effects in PNCs. New attachment strategies will need to be developed to expand current and future work from silica or other similar metal oxides to many other substrates. (2) Placing chains on NPs with spatial resolution; i.e., the development of functionalized Janus particles, is a challenging synthetic target. More work is clearly needed to further develop the methods and techniques to accurately control the molecular variables of two different populations of chains independently and characterize them accurately. (3) The development of bimodal mixed brushes is particularly exciting since it allows independent control of entropic and enthalpic effects by the two distinct populations of chains. Having this ability will permit us to further probe enthalpic effects in the interface region and presents many opportunities to mix diverse interactions (e.g., hydrophobic/hydrophilic) while controlling the dispersion state. We believe this opens up possibilities to create entirely new interfaces between nanoparticles and the matrix and thus new properties and combinations of multifunctional properties in PNCs.

2.2. Characterization of Grafting Uniformity. We now return to the canonical case of NPs grafted with homopolymers. The grafted NPs created in this manner will, on average, have a certain number of chains per particle each with a certain length. While the chain length distribution can be characterized after the dissolution of the particle cores, and subsequent characterization (say by GPC), the more important unknowns are the distribution of the number of chains per particle and the spatial distribution of the graft points on the particle surface (which is assumed to be random). While there has been little focus on the second aspect, considerable progress has been made in characterizing the particle-to-particle variations in the number of grafted chains. In pioneering and creative work, Bockstaller and co-workers[124,125] have used MALDI-TOF in conjunction with a population balance model to derive the distribution of grafted polymers per particle (Figure 2). The results clearly show that the width of this distribution is finite and that it does not follow a Poisson distribution.

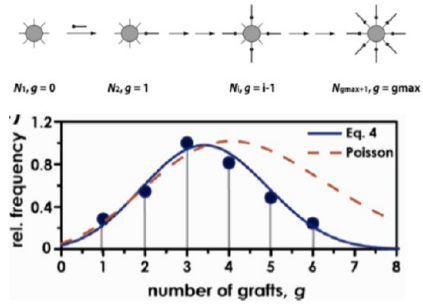

Figure 2. (top) Schematic representation of the surface functionalization reaction. The total number of reactive sites per particle is g_{max}. The coupling of functional ligands is assumed to proceed by a sequence of irreversible coupling reactions with equal and constant rate. (bottom) Distribution of the number of grafting sites per particle. The dotted line is a Poisson distribution, while the solid line is derived from a population balance model. Adapted from ref 124.

More recently, theoretical work has emerged from the group of Vaia,[126] who has studied the grafting density distribution of end-functionalized chains on particles of finite size. Their theoretical work concludes that it becomes progressively harder to obtain monodisperse grafting as one decreases particle radius; that is, the particle-to-particle variations in grafting density become larger as we deal with progressively smaller particles. These results imply that significant polydispersity effects exist in many of the experiments, and theoretical works suggest that this might play a central role in determining the physics, especially the self-assembly of these grafted nanoparticles.[127] The experimental validation of these interesting conclusions are pending.

Looking Ahead. While the information on particle-to-particle variations in grafting density is important, information on the spatial distribution of grafting sites on a single particle is missing. The development of techniques to characterize this quantity are critically important, especially because of the relatively small number of grafts that are typically involved in the systems of our interest. Intuitively, we expect that fluctuation effects may dominate here and thus lead to new emergent behavior. More theoretical understanding and experimental characterization of these ideas are necessary to better characterize and control these grafted chain structures.

2.3. Characterization of the Brush Structure.[128,129] We also need to characterize the brush's dimensions, especially in the presence of the matrix polymer. To date, most of the work in this area has focused on the spatial size of the brush under good solvent conditions,[130−133] primarily using dynamic light scattering, complemented by theory and simulations.[134−143] These results establish that, in good solvent, most spherical brushes, even at relatively high graft densities, have a size whose chain length scaling is consistent with the dimensions assumed by a free chain in the same solvent (i.e., ~$N^{3/5}$) rather than the planar brush result (i.e., ~N). That is, the chains are not highly

extended, versus what has been found repeatedly for the case of planar brushes where large extensions are the norm. This result is a direct manifestation of the fact that the space available to the chains increases with the distance from the center of a particle: in fact, the effective grafting density decreases with the square of the distance from the particle center.[144,145] Hence, regardless of grafting density, long enough chains experience very little crowding at sufficient distances from the grafting surface.[146] In this context it is important to emphasize that stretching is expected, following extensive work on star polymers, to scale as $f^{0.2}$, where f is the number of chains attached to the star core.[144] Given that a very large number of (~1000) chains can be attached, we expect that very high graft densities might yield different results.

Recent work has probed the dimensions of brush chains in a polymeric solvent using small-angle neutron scattering (SANS) and selective labeling (see Figure 3).[148,149] These results

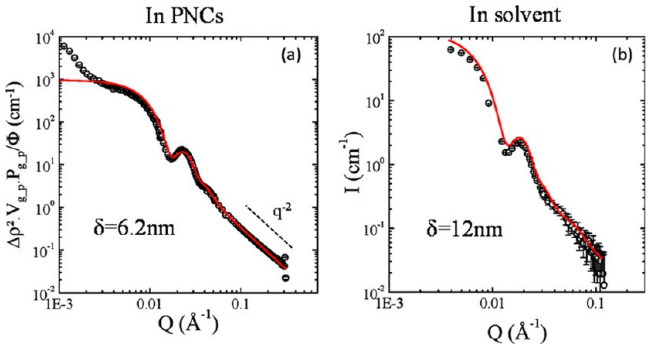

Figure 3. Grafted chain thickness δ in (a) PNCs and in (b) solvent as determined by small-angle neutron scattering (SANS). Using an appropriate contrast variation, one can match the silica scattering to the matrix polymer and thus only measure the signal of the grafted corona. The continuous lines are the best fits using a Gaussian chain model (a) and a "core/shell" model (b). Adapted from ref 147.

illustrate that brush dimensions decrease dramatically when one goes from a small molecule solvent (δ = 12 nm) to a polymer matrix (δ = 6.2 nm).[147] However, there is no detailed study of the change in brush size when one goes from a wet to a dry brush in PNCs, an effect which is thought to be caused by variations in the matrix molecular weight (see ref 150 for interesting results on a related system).

Looking Ahead. Several issues remain unresolved at this time: (1) Intuition would suggest that the brush size should decrease when it undergoes its autophobic, dewetting transition with increasing matrix molecular weight. However, experimental results do not provide conclusive proof for this conjecture. So far, one work measured the decrease of the brush size in going from solution to films (see Figure 3), only in the miscible regime (see below).[147] The authors also concluded that no matrix chains are present in the grafted shell. How then can we explain the good dispersion? Thus, the experimental verification of the autophobic dewetting transition, which is postulated to play a central role in the miscibility of densely grafted NP with polymer matrices, is an open question. (2) For high graft densities and short chain lengths, theory predicts that the brush size should scale as N.[144,151] Instead, experiments always show an $N^{0.8}$ dependence.[152] Similarly, the grafting density dependence of the brush height predicted by theory is not observed. Are these important differences, and do they reflect on a lack of understanding of this physical situation? A more exhaustive set of data to resolve this discrepancy is necessary. (3) Theory also predicts that polydispersity effects should have a large role in determining the crowding effects due to large grafting density near the surface.[127] Experimental validation of these ideas might be critical to understanding practically relevant situations where such grafted nanoparticles might find use.

3. ASSEMBLY

3.1. Quiescent Assembly. Figure 4 plots all of the available data for NP morphologies found in bulk, three-

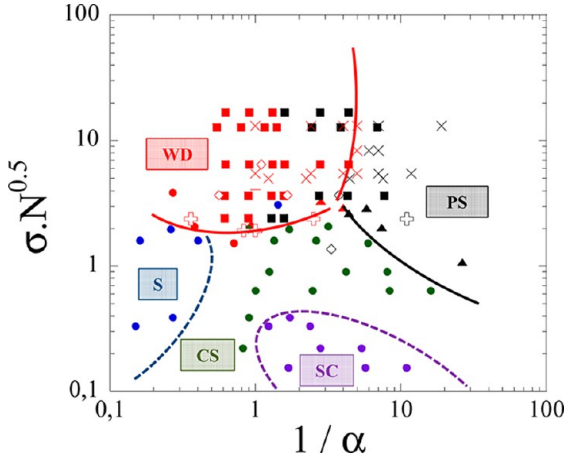

Figure 4. A composite morphology diagram created from all of the available data in the literature: $\sigma\sqrt{N}$ as a function of $1/\alpha$ with $\alpha = N/P$. The points, adapted from the literature, are color coded so that a red point corresponds to well dispersed particles (WD); black to phase separated samples (PS); blue to strings (S); green to connected sheets (CS) and purple to small clusters (SC). The color-coded lines represent a first-order cut at classifying the data into well defined regions in the plot where different morphologies occur. This classification is not perfect – for example, there are black squares in a red region. (□) is for 18 nm PS-*g*-SiO_2 NP from ref 29, (×) for 10 nm PEO-*g*-SiO_2 NP from ref 44, (♦) for 17 nm PS-*g*-SiO_2 NP from ref 160, (●) for 14 nm PS-*g*-SiO_2 NP from ref 46, (△) for 28 nm PS-*g*-SiO_2 NP from ref 154, (—) for 12 nm PBA-*g*-SiO_2 NP from ref 207, and (+) for 8 nm PS-*g*-γ-Fe_2O_3 NP from ref 220.

dimensional systems comprised of grafted NPs (silica or magnetic NPs). Note that all of the particles tested are of similar size (diameter between 7 and 18 nm), except for the results of Chevigny et al. that employed larger, 27 nm diameter particles. Further, while some experiments used polystyrene (PS) for both grafts and matrix, others used poly(ethylene oxide) (PEO) or poly(butyl acrylate) (PBA). Regardless of these differences, it appears that the behavior of these systems appear to show "universal" trends for these relatively low NP loadings (typically ≈5 vol %). In Figure 4, we plot $\sigma\sqrt{N}$ on the y-axis following Archer[44] because this reflects the extent of crowding of the brush—while this metric is derived from brushes on flat surfaces, we continue to use this form here since we do not have any different theoretical guidance.

First, we consider the limit where the grafting densities are high ($\sigma\sqrt{N}$) > 2. This should correspond to the regime of steric stabilization, where the core, which is shielded, should play a minimal role, and hence the behavior should be determined by brush physics. Here, only the two limits of phase separation (PS) or good dispersion (WD) seem to be achieved, with the crossover occurring for $1/\alpha \sim 4-5$.[25,27,29,44,146,153,154] Exceptions to these statements are recent findings that densely

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grafted particles apparently crystallize when present in large concentrations (see below).[151,155−157] A theoretical understanding of the role of NP size on the crossover to dense brush behavior is an open question at this time.[158,159]

The more interesting regime is for lower grafting densities, where a range of structures, which apparently represent a balance between core−core attractions and brush physics, occur (Figure 5).[3,19,25,77,90,161] Note that the structures that form,

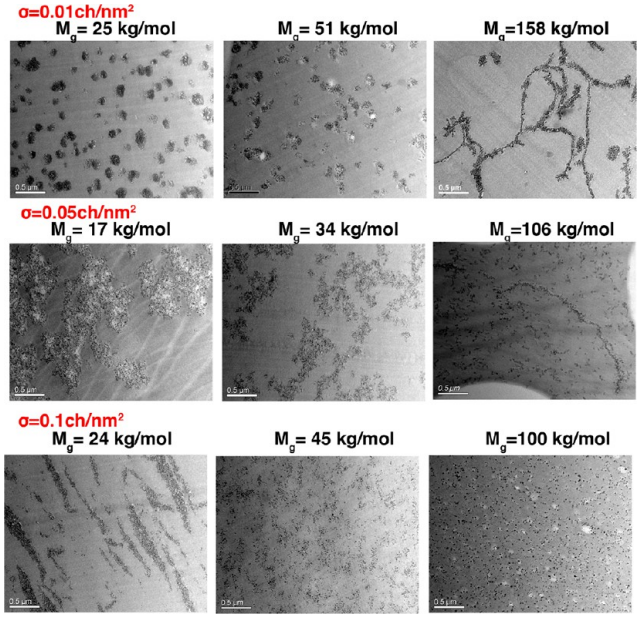

Figure 5. TEM determined temporal structuring. In all cases 5 mass % silica grafted with a variety of graft molecular weights, M_g, of a polystyrene brush with varying grafting densities, σ, is mixed with polystyrene matrices of M = 142 kg/mol and annealed at 150 °C for 5 days. The scale bars are 0.5 μm. Adapted from reference 46.

namely strings and sheets and in some case small spherical aggregates, represent a small subset of the known structures that are formed by surfactants. Why other structures do not form is unknown at this time. A similar result has been found when thin films of these nanocomposites are also considered.[56,162] The nanoparticles in this case "bloom" to the air surface of the film and then assemble into a range of superstructures, which are the 2-dimensional analog of the bulk structures. Finally, we point to recent experiments on the behavior of nanocubes (~80 nm diameter) grafted with short chains (either P2VP/PEO) and placed in a thin film of polystyrene.[163] Again, these NPs assemble readily into strings, but because these are cubes, they can assemble face-to-face or edge-to-edge. The surprising conclusion is that spherical NPs nominally isotropically grafted with polymer chains can assemble into anisotropic superstructures. Another point to emphasize is that there is a threshold grafting density, $(\sigma\sqrt{N}) < 2$, below which good dispersion can apparently never be attained.[15]

Theory and simulation, primarily on coarse-grained models,[42,46,54,81,163−167] show that the assembly behavior is driven by the microphase separation between the immiscible, inorganic particle core and the organic grafted chains—a process analogous to the self-assembly of block copolymers (or amphiphiles).[168] Note that, as expected, we do find the extremes of phase separation and well-dispersed particles in the two limits of no grafting and dense grafting but that the intermediate structures occur at intermediate grafting densities. To gain a better understanding of these results, an analytical theory which has the following two essential ingredients was developed. It was assumed that there is an extremely short-ranged ("point") interparticle attraction. This is counteracted by the entropy of distorting the polymer brush chains when two particles approach each other. The minimization of the resulting free energy yields a "morphology" diagram which is similar to the simulations. These results are also consistent with recent simulations for fullerenes with multiple PEO grafts which are uniformly distributed on the particle surface. These are found to assemble into stringlike and branched polymers.[81,169−173] More recent simulations[141−143,174] have begun to focus on systems closer to the experiments and are beginning to provide a more thorough understanding. Jayaraman and Schweizer generalized polymer reference interaction site model (PRISM) theory to polymer grafted NPs and elucidated the structure, assembly, and phase separation behavior.[175,176] They also predicted the corresponding behavior when these NPs were placed in a homopolymer matrix.[177−182] These workers recently found that polydispersity effects on brush structure can play a profound role in the self-assembly and phase behavior of these structures. This remains an unexplored, open experimental question.

An aspect we focus on here is that some of these structures such as sheets appear to be kinetically controlled. Figure 6 from

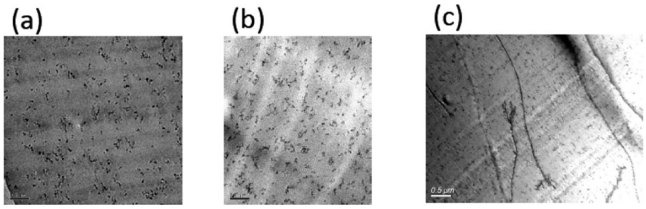

Figure 6. Time evolution of the bulk structures formed by 14 nm diameter silica NP grafted with PS chains (106K, 0.05 chains/nm^2) in a PS matrix (231K): (a) as cast, (b) annealed for 3 days, and (c) annealed for 5 days at 150 °C. The samples were annealed for up to 28 days, and the structures continue to grow.

our work for the bulk systems clearly shows that the sheets that form grow with time but that the growth is only along the lateral dimensions of the sheets. More significantly, it is apparent that there are no structures that are formed in the as-cast state, and thus structure formation is really a drive by the system to approach its equilibrium state. Another point to note here is that the time scale over which the sheets grow is on the order of several days to a month. To understand this long time scale, we point to our recent X-ray photon correlation spectroscopy measurements, which are sensitive to the collective dynamics of the silica NP cores.[51] Our results show that the primary mode of relaxation appears to be the "ballistic" motion of the NPs (~10 s) but that this time scale increases by 1−2 orders of magnitude as the sample is annealed over a time scale of 5 days, over which these experiments are conducted. By comparing to several literature reports, it is apparent that our grafted NP systems are behaving akin to gels, which appear to have solidlike behavior at short times but liquidlike behavior in the limit of infinite relaxation times. While the mechanical response of these samples (discussed below) are consistent with this solidlike behavior (by the manifestation of a low-frequency plateau in the storage modulus, G'), at this time we

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do not have a good molecular understanding of the origins of this behavior. Does it arise because of the relatively strong attractions between the silica cores, which makes them behave akin to a colloidal gel in this limit of sparsely grafted NPs? Or is it an exponential increase in the relaxation time of the system as seen in the case of star polymers?

In a different vein, a continuing challenge is to measure the dynamics of the grafted chains in bulk PNCs especially as the NP dispersion state is altered.[146,183,184] Inelastic and quasi-elastic neutron scattering are promising techniques to investigate the local dynamics of the grafted chains by probing the local motions of hydrogen in the samples.[183−186] Using appropriate hydrogenated/deuterated labeling allows us to monitor the dynamics (via the mean-square displacement $\langle u^2 \rangle$ in a quasi-elastic neutron scattering (QENS) experiment) with changes in graft length and matrix length. Figure 7 shows the

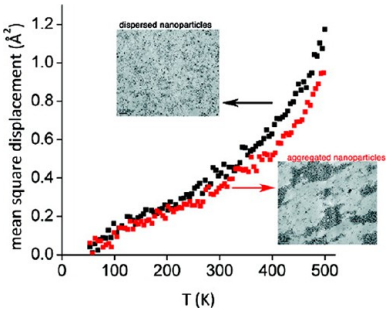

Figure 7. Mean-square displacement $\langle u^2 \rangle$ obtained by QENS for well-dispersed (black symbol) and aggregated (red symbol) NP states. Reproduced from ref 184.

mean-square displacement $\langle u^2 \rangle$ of grafted chains in well-dispersed and aggregated dispersion states for PMMA-*g*-SiO_2/PMMA PNCs. The segmental mobility of grafted chains slightly decreases with NP aggregation. The relationship between the autophobic dewetting, changes in local dynamics, and potentially any changes in macroscale dynamics (as characterized, for example, by the glass transition temperature, T_g) remains unresolved. These measurements are expected to be central to our understanding of the dynamic response of these materials and how they impact their time-dependent properties such as mechanical and electrical behavior (i.e., storage and loss moduli).

Looking Ahead. There are several questions that need to be understood further: (1) Why do spherical particles that are isotropically grafted assemble into anisotropic structures such as sheets and strings? (2) Which of these structures are equilibrium, and which of these are kinetically evolving? Why are the kinetics of this growth so slow, and what sets the time scales for this structural evolution? Why do these systems behave akin to soft glasses? Can we tune a single system parameter that can turn this "glasslike" behavior on and off? (3) Theories need to be developed to understand the crossover to dense brush behavior and the molecular weight of the matrix for the autophobically dewet regime. While there is some theoretical work in this area, especially on the role of particle curvature,[19,158] a model for the autophobic dewetting that is critically validated against experiments is necessary. (4) We point to some interesting new results on the behavior of NPs grafted with bimodal brushes (comprised of a dense covering of short chains and a low density of long chains) which do not show assembly, but rather appear to yield well-dispersed NPs over a much broader range of parameter space than their monodisperse analogues (see Figure 12).[120] The use of polydispersity, which is really in its infancy, might allow us to leverage the essential nature of polymeric systems as an additional handle in controlling assembly behavior.

3.2. Crystalline Assemblies. In contrast to NPs with low grafting density, where the particles typically form amorphous assemblies, pure phases of NPs with higher grafting densities assemble into ordered, nearly crystalline cubic structures (Figure 8). This phenomenon has parallels in the behavior of

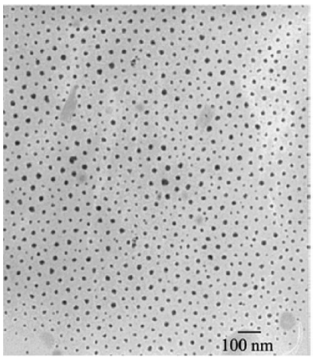

Figure 8. TEM micrograph of 14 nm silica nanoparticles grafted with a 80K poly(*n*-butyl acrylate). The sample was drop-cast on a TEM grid and then imaged. Adapted from ref 155.

highly functionalized star polymers.[155,187] As with our previous discussion, the conformations of the chains are consistent with the mean-field predictions of Daoud and Cotton[144] and indicate that the chains, when long enough, adopt ideal conformations because of space filling.[145] Further, these hybrid NPs with high grafting density behave as soft spheres, with a repulsive potential extracted from equilibrium modulus that scales as $\sim r^{-12}$.

The dilution of such grafted NPs with homopolymers up to a NP loading of 25 vol % (so that the mean interparticle spacing is up to several times the brush size) does not alter the occurrence of an ordered structure; below this concentration the particles have liquidlike ordering as has been discussed above. Further, blending the particles with matched molecular weight homopolymers leads to chain size scaling that is consistent with good solvent conditions, suggesting that these materials do not undergo the autophobic dewetting phenomenon under these conditions.

Looking Ahead. The ability to create materials with different crystal structures, which parallels work done recently on DNA grafted colloids,[188] may require the use of binary mixtures of NPs, either of different size or with ligands which permit for specific bonding between different NPs alone. Such work has not been performed to date but could lead to a class of materials analogous to the DNA grafted colloids, but with the advantage that they could operate out to much higher temperatures than the biomolecular analog which typically functions at temperatures below ~50 °C. What groups can be attached so that we can obtain reversible "cross-links" between two NPs? Are they reversible, and hence are the structures reformable?

In a different vein it is known that, often, vitrification of hard spheres and stars masks the crystalline transition. However, after a long time Bragg peaks develop.[189] The interesting thing for hairy NPs is that this, as well as any other motion (say alpha

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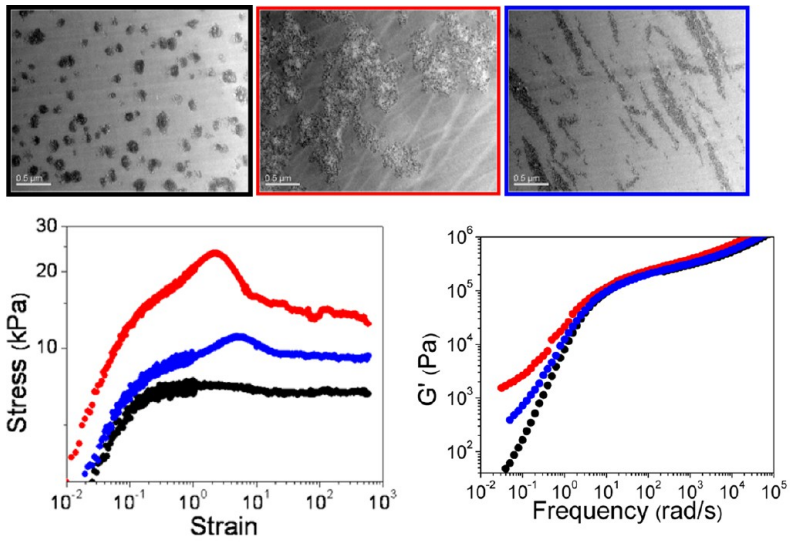

Figure 9. (A) TEM images showing nanoparticle dispersion states. All three samples have a 142 kg/mol matrix. Left: agglomerated, 25 kg/mol graft, 0.01 chains/nm^2 (black). Center: a particle network, 17 kg/mol graft, 0.05 chains/nm^2 (red). Right: sheets of particles, 24 kg/mol graft, 0.1 chains/nm^2 (blue). (B) Steady shear data at 180 °C at a shear rate of 0.2/s. (C) Storage modulus data for the same three nanocomposites, also taken at 180 °C. Reproduced from ref 57.

relaxation), is controlled/facilitated by the fluctuations of the hairs. Hence, these hairy NPs can play a role in understanding the generic and fundamental interplay of glass transition and crystallization.

3.3. Driven Assembly. The use of external fields, e.g., flow, electric, and magnetic, to orient NPs and NP assemblies has the potential to lead to highly improved and often tailorable anisotropic mechanical properties in such nanocomposites.[190] In the case of anisotropic fillers, processing using external fields (such as large-amplitude oscillatory shear flow) significantly impacts the structure and properties. From a different angle, it is now established in the colloid community that the application of shear flow to spherical particles dispersed in a shear thinning fluid can lead to their orientation in the flow direction.[191,192] Under special circumstances, the colloids can even crystallize in this planar geometry.

As discussed above, PNCs can be considered to be soft colloidal dispersions, the rheology of which has been studied in great detail recently. In the case of soft colloidal dispersions it has been conjectured that structural disorder creates energy barriers that cannot be overcome by Brownian forces alone. Upon application of a stress, the energy landscape is changed and the system takes on a new metastable structure. This analogy to glass formation has allowed for the interpretation of the viscoelasticity of these dispersions in terms of physical aging.[193]

So how do NP superstructures assemble and rearrange under the action of external forces such as flow? There has been some theoretical work in this, especially in the case of ungrafted nanoparticles, but the experimental observation of these effects remain unexplored.[194] Our conclusions are that there are two regimes of flow behavior, which are differentiated simply by examining the start-up of steady shear behavior. Certain classes of composites, comprised of either well-dispersed particles or spherical particle agglomerates, show no features in the start-up of steady shear—that is, the measured shear stress is independent of the applied strain. These systems, in contrast to the colloidal systems discussed above, show no change of particle structuring on the application of flow. The second class of behavior is found for all systems that have anisotropic NP assemblies. In this case, the stress as a function of time goes through an overshoot. Before the overshoot, TEM results show that anisotropic NP assemblies are flow aligned into planes. However, no domain growth occurs. For times beyond the stress maximum, the NP structures coarsen as has been anticipated by the soft glass community.[193] The surprising findings here are that spherical assemblies are not affected by flow and that anisotropic assemblies are flow-aligned but do not grow. Our current understanding here is that since the Peclet number, $Pe = ((\dot{\gamma}R)R)/(kT/6\pi R\eta) = (6\pi\dot{\gamma}\eta R^3)/(kT)$ is of order 1, with $\dot{\gamma}$ the shear rate and η the viscosity, for these NPs, flow cannot overcome diffusion and order these particles. In these situations the physics appear to be dominated by interparticle attractions, which are strong enough to cause these materials to behave akin to soft glasses.

Looking Ahead. (1) Our first work appears to suggest that shear flow is only useful in aligning anisotropic NP assemblies. What is the critical NP size above which flow is able to orient individual NPs into the flow direction? It is important here to emphasize that the Peclet number has a cubic dependence on particle size, and thus, even an order of magnitude increase in particle size could be enough in this context. (2) We also need to consider other external fields such as electric and magnetic (with magnetic NPs) to see whether these variables can be used more effectively to orient and assemble NPs along desired directions.[195,196]

4. PROPERTIES

The most important desired outcome of assembling NPs into different structures is to locate the optimal particle dispersion state for a particular property of the polymer nanocomposite. Most of our work to date has been focused on the mechanical, optical, and electrical properties of the nanocomposite,

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although other properties are being considered. We discuss developments in these areas here.

4.1. Mechanical Properties. Perhaps the most well-investigated PNCs property is their mechanical behavior, in both the liquid and solid states. Emerging evidence shows that the optimal NP dispersion state for grafted particles is very different from their ungrafted analogs in the melt state.[51,57,154,197,198] Further, in the case of grafted particles, the optimal dispersion state in the melt and the glass state are very different.[199] These results point to the complexity and the richness of the problem at hand.

Liquid State Behavior. In the liquid state, it is well established that mechanical reinforcement occurs with a "percolating" NP structure,[12,13,76,198,200−203] i.e., when NPs can form a network spanning the system. Note that the percolating structure is also pertinent for electrical and conductive applications. Two network scenarios have been proposed: (i) "particle-only": NPs form a direct pathway for the propagation of the stress, as for example in the case of fumed silica in elastomers; (ii) a hybrid "particle-polymer" scenario involving a percolated NP structure, mediated by polymer. The nature of this "mediating" polymer has been conjectured to be grafted chain,[46,52,106] glassy bridges,[204] or polymer chain bridges between NPs.[205,206]

In this context, in nanocomposites with grafted NPs, the possibility of having a polymer-mediated network connectivity offers promising advantages like (i) the precise control of interparticle distances and interactions and (ii) the possibility of getting percolated structures at very low NP concentrations.[46] In the well-dispersed regime, for example, one can reach the percolation threshold "earlier" in concentration compared to the ungrafted NPs, simply because the grafted chains make the particle look larger.[207] Other issues, such as a nonrandom distribution of NPs, can help, under certain circumstances, to even further reduce the percolation concentration.

The evidence for the role of a percolated NP network in the nanocomposites' mechanical behavior is reflected in several rheological measurements: (i) a low-frequency plateau in G' in small-amplitude oscillatory shear (SAOS) experiments; (ii) an overshoot in stress−strain curves in a start-up of steady shear experiment; (iii) uniaxial stretching experiments with a divergence in Young modulus at percolation.[197]

To illustrate this percolation behavior in mechanical properties, we point to linear oscillatory shear and "start-up" of steady shear experiments for a range of nanocomposites with 5 wt % grafted NPs (Figure 9).[51,57] The samples where the NPs form structures show an increase in G' at low frequencies and a stress overshoot in each case. The magnitude of this overshoot varies according to the NPs morphology, and as Figure 9 shows, we get the largest overshoot for samples where the NP clusters appear to span the TEM images. This is also correlated with the appearance of a low-frequency stress plateau in the G' plots, the ultimate manifestation of mechanical reinforcement.

Let us now describe the mechanical behavior in the other regions of the phase diagram (Figure 10). In contrast to the previous results illustrating reinforcement, the sample with well-dispersed NPs shows no overshoot or mechanical reinforcement. Our past work suggests that samples with this state of NP dispersion will also show solidlike behavior, but at higher particle concentration (~15 wt % silica), i.e., when the grafted objects start to overlap, which is consistent with several earlier works.[51,207] In the region where the NPs form spherical aggregates, SAOS showed a slight increase (not a plateau) of G'

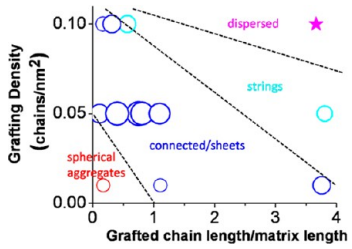

Figure 10. In a "morphology" diagram we plot symbols whose size scale with the degree of reinforcement as characterized by the ratio (stress overshoot maximum value)/(plateau value). Other measures give qualitatively similar results. Only the well-dispersed sample yielded no stress maximum. Reproduced from ref 57.

at low frequencies,[52,106] which can be attributed to the relaxation of the aggregates (as they are not connected to each other) as already observed for individually grafted NPs at low concentration.[207] McEwan et al.[27,208] combined SAXS (to extract structure) and rheology to quantify the interactions between the NPs. They pointed out that decreasing the matrix molecular weight M_w increases G'. They explained this result by the stretching of the grafted brushes leading to larger repulsion between the NPs.

To critically resolve the role of the polymer matrix in the mechanical reinforcement, it is important to consider samples across the whole morphology diagram. A difficulty here is that the matrix polymer molecular weight has to be varied to achieve the desired broad range of the ratio of the graft length to matrix length. Since there is a strong dependence of the absolute values of the modulus on the matrix molecular weight, we need a measure of mechanical reinforcement that normalizes out this variable. We found that the stress value at the peak of the overshoot scaled by the stress plateau value at large strain (long time) is particularly appropriate. This analysis shows that, as expected, the largest reinforcement occurs in the regions corresponding to networks of particles (connected/sheets, Figure 10). Perhaps more interesting is the trend seen for various percolated samples, all with similar morphologies, but with widely varying graft densities—apparently, the reinforcement goes through a maximum at an intermediate graft density (0.05 chains/nm^2). This result offers a crucial insight—apparently, the grafted chains play a central role in reinforcement. Were a particle-only scenario operative, then we should have maximum reinforcement in the limit of very low grafting densities, where the particle cores could contact other cores.

Thus, in summary, liquid-state reinforcement occurs when the particles percolate across the system, a state that is most easily achieved when the NPs are agglomerated into anisotropic objects such as connected sheets. It appears that the reinforcement is augmented by the interaction between the brushes grafted on the NPs, and the matrix polymer plays basically no role in this context.

Solid-State Behavior. The NP dispersion state that optimizes the solid-state mechanical properties was also investigated by using a novel bubble inflation technique.[199] We are concerned about whether the same material design criteria apply to both optimizing melt-processing properties and the end-use mechanical properties of the glassy nanocomposite. It is thought that the addition of spherical NPs cannot simultaneously improve the elastic modulus, the yield stress, and the ductility of an amorphous glassy polymer matrix. In contrast to this conventional wisdom, we have shown that

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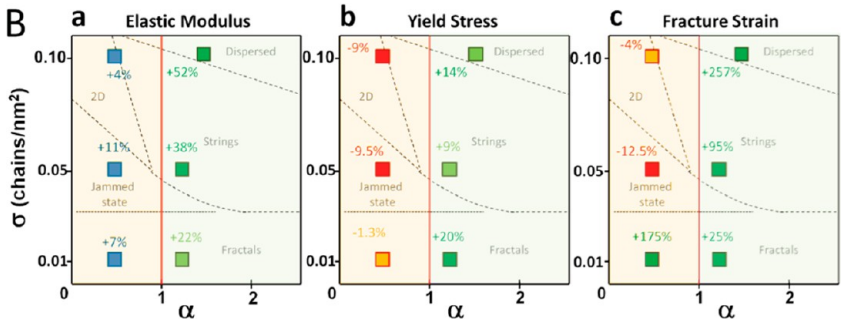

Figure 11. Reinforcement percentage of the (a) elastic modulus, (b) yield stress, and (c) failure strain relative to the pure polymer depending on grafting density σ and grafted/matrix chain lengths ratio α. The loading of the silica core was 5 mass % in all the samples, and the morphologies of NP in these thin films are those reported in ref 56. Reproduced from ref 199.

ductility can be substantially increased, while maintaining gains in the elastic modulus and yield stress, in glassy nanocomposite films composed of spherical polystyrene grafted silica NPs in a PS matrix. Figure 11, which is a summary of our mechanical measurements, is plotted on the same thin-film morphology diagram presented in ref 56. The % signs denote increases of a particular property relative to the polystyrene matrix polymer. In contrast to conventional expectations, we find that we can simultaneously improve the elastic modulus, the yield stress, and the fracture strain (or toughness) of the polymer by the addition of NPs. The keys to these improvements are (i) uniform NP spatial dispersion and (ii) strong interfacial binding between NPs and the matrix, by making the grafted chains sufficiently long relative to the matrix. Strikingly, the optimal conditions for the mechanical reinforcement of the same nanocomposite material in the melt state is completely different, requiring the presence of spatially extended NP clusters. Apparently, NP spatial dispersions that optimize material properties are crucially sensitive to the state (melt vs glass) of the polymeric material.

Looking Ahead. (1) The results presented above show that changing the state of the polymer from a melt to a glass qualitatively alters the NP dispersion state that optimizes properties. Does this transition happen abruptly or does the NP dispersion state change continuously as one cools a PNC from above its glass transition temperature to well below T_g? Studies of mechanical property measurements as a function of temperature, particularly focusing on the vicinity of the glass transition, would thus be of tremendous value. (2) We note that our solid-state mechanical properties were on thin films of nanocomposites. What role does film thickness play, and do these results correspond to macroscale samples of practical interest? There is no technical barrier to answering this question except for the need to produce macroscopic amounts of grafted NPs. (3) In the same vein, there is a singular need for theory/simulations to have a predictive ability for the role of NP dispersion state and the polymer matrix relaxations on mechanical properties. Such a model is critical to the development of practically useful materials and remains an outstanding challenge at this time. (4) For liquid-state reinforcement is it possible, like for the percolation effect, to extract general trends between reinforcement level and the morphology of the aggregates (size, fractal dimension)? Are there ways to quantify these ideas?

4.2. Optical Properties. Another important application of nanocomposites is in the context of the optical behavior.[209−211] Several questions are of interest: (i) Can we raise the refractive index of a polymer without raising scattering?[43,209,211,212] (ii) Can the NPs be used to create plasmonic junctions useful for subwavelength focusing, surface-enhanced Raman spectroscopy, and electromagnetic transparency?[163,213] (iii) Can the NPs be used as a means of improving the dielectric properties of the material, namely improve the dielectric storage without increasing dielectric loss, so as to create better capacitor materials?

There has been considerable interest in dispersing high-refractive index NPs into transparent polymer matrices, with the goal of increasing the polymer's dielectric constant. Equally important here is that scattering needs to be minimized, a requirement that is met by ensuring that the NPs are uniformly (or randomly) dispersed. Schadler and her group have focused on dispersing NPs into epoxy matrices, and recent work clearly shows that grafts which are bimodal in length provide the most effective means of achieving the good dispersion states necessary.[120] Figure 12 shows the comparative results of dispersing 5 wt % TiO_2, the classical filler used to "whiten" polymers, in silicones to create transparent high refractive index nanocomposites.

These workers also modeled this good dispersion through a mean-field model designed to predict NP assembly in polymer matrices.[214] The essential picture that emerges is that the

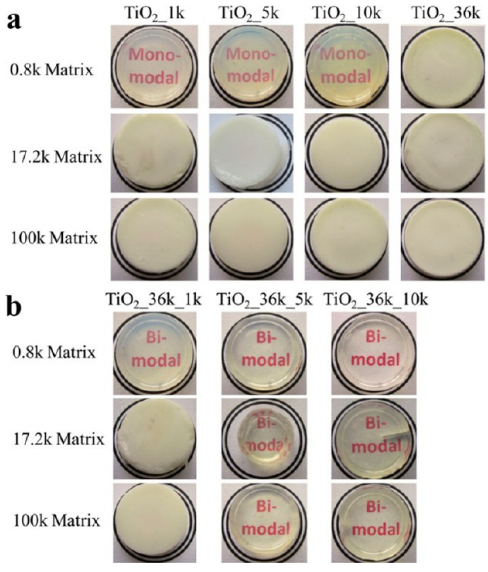

Figure 12. Visualization of nanocomposites formed by TiO_2 grafted with PDMS in a PDMS matrix. Reproduced from ref 120.

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presence of the short brush shields core−core attractions. As suggested previously, the self-assembly of grafted NPs represents a competition between core−core attractions and brush-induced repulsions. Reducing the core−core attractions thus reduces the driving force for phase separation—thus, brush-induced steric stabilization is made easier, resulting in a much broader range of parameter space over which good, random, particle dispersion is achieved. The resulting materials have refractive indices that follow a rule of mixtures, and effectively no optical scattering as can be visually observed.

In contrast to the work on building optically clear materials, materials with improved plasmonic properties require a small gap between NPs with high curvature; both of these criteria are required to enhance the local electric field. This, in general, requires the placement of nanoparticles close to each other, but in a highly controlled manner. Recent independent work by Tao et al.[163] and Vlassopoulos and co-workers[213] have achieved the self-assembly of polymer grafted silver NPs into superstructures to achieve these goals. Tao et al. for example use short chain grafted silver nanocubes and show through the use of experiments and simulations that they order into strings, with the relative orientation between the cubes being face-to-face, edge-to-face, or edge-to-edge depending on the grafting density and the relative molecular weights of the grafts and the matrix. They also showed that the plasmonic response of these materials could be substantially affected, thus providing a direct pathway between NP morphology and optical properties.[163]

Looking Ahead. We see considerable interest in the use of polymer grafted nanoparticles in improving the dielectric properties of polymers, with direct impact on the creation of improved polymer-based dielectrics. To date, there has been considerable work on bare nanoparticles (both spheres and rods) with mixed results. The ability to control the nanoparticle dispersion might offer new insights into this difficult but technically crucial application.

5. FUTURE DIRECTIONS

5.1. Relationship between Dynamics and T_g. There has been an ongoing discussion about using the glass transition temperature of a nanocomposite (i.e., of the polymer phase) as a proxy for the mechanical reinforcement afforded in PNCs.[183,215,216] While there is a good correlation in some cases between the state of particle−matrix miscibility (and hence mechanical reinforcement) and T_g changes,[217] these are by no means universal. A clear understanding of the postulated relationship between these two quantities is an outstanding challenge in this area.

5.2. Magnetic NPs. Magnetic NPs (e.g., iron oxides such as maghemite γ-Fe_2O_3 or Fe_3O_4) can be used to make a new promising class of PNCs.[195,196,218−225] By taking the advantage of an external trigger such as a magnetic field, it has been demonstrated that the NP aggregation can be tuned during processing. Thus, the spatial anisotropy of the final morphologies in the polymer melt,[196,220] which is mainly governed by the dipolar forces between NPs, can be controlled. Hence, magnetic NPs can form chainlike structures oriented along the field leading to anisotropic mechanical properties of the corresponding nanocomposite materials.[196,220] These materials exhibit enhanced reinforcement in the magnetic field direction while it remains lower than the pure melt in the transverse direction. In extreme cases, for highly concentrated systems, the chainlike structure percolates and acts as a network along the field direction increasing considerably the mechanical reinforcement. Recent experiments have also shown the possibility of grafting polymer chains onto the magnetic NPs surface. A magnetic trigger may then offer an additional way to tune the NP spatial dispersion (as described above for silica NPs). In that particular case of grafted NPs, the balance of the repulsion forces between the grafted chains (which depends on the length and the grafting density) and the dipolar forces controls the final dispersion state.

5.3. Semicrystalline Polymers. Probably the most practically relevant application of polymer-grafted NPs is in the case of semicrystalline polymers. Here, we ask how the grafts affect the dispersion of the NP in the polymer above its melting point, how this is affected by crystallization, and how the presence of the NP affects the crystallization process itself. To our knowledge, this is a nascent field, and only recently have researchers even focused on the miscibility question.[226] Similarly, very little is known about how the NPs affect the nucleation and growth of crystalline domains in these polymers.[227] In the one case studied, silica NPs (14 nm in diameter) were grafted with PMMA and then mixed with poly(ethylene oxide). For this case, where we expect the brushes to be compatible with the matrix, at low NP loadings, we found that the crystallizing polymer "forces" the NP "defects" out of their way to crystallize in a minimally perturbed form. For higher loadings, the crystals become smaller in response to increased particle-induced confinement. In contrast to currently held views that the particles control the crystallization process, e.g., by providing heterogeneous nucleation sites, we find that the crystalline lamellae dominate; i.e., they manipulate the nanoparticle dispersion, especially at low loadings. While these conclusions are certainly interesting, very little systematic work exists in this area. We believe that this topic should be focused on, especially because it could be of critical practical relevance.

5.4. Block Copolymer Grafts. While ongoing work highlights the dramatic improvements that have been made in controlling the NPs spatial distribution by grafting homopolymers, more complicated situations offer the possibility of even greater control, but this is offset by the fact that our understanding of these situations is even more limited. For example, if the homopolymer attached to the surface is replaced by a block copolymer that can microphase-separate, then the competition between the interactions between the polymer components and the NP along with steric constraints imposed by the surface and the grafting density are likely to result in significantly altered mesoscale organization.[10] This is a significant area of interest for the development of non-centrosymmetric materials, and the parameter space in terms of nanoparticle shape, grafting density, and copolymer length and composition needs to be explored and compared to that of ABC triblock copolymers and their blends.[228,229] We expect significant progress in this area in the next few years.[230] In the same vein, another direction is to use a copolymer with two different T_gs to achieve an understanding of the relationship between the glass transition, chain dynamics and mechanical reinforcement.

5.5. Matrix with Different Chemistry than Brush. Almost all of the work reported to date has been in situations where the matrix polymers and the brushes are of the same chemical structure, but sometimes of different length. Work performed for grafted NPs in solvent, where the solvent is chemically distinct from the grafts, shows the formation of new morphologies like spheres and vesicles.[231] By extension, we

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expect that the use of different matrices might permit the formation of completely different morphologies, different from the essentially planar morphologies formed in the chemically identical case.[232] We believe that this should be a productive area of research that should be explored in ongoing work.

6. SUMMARY

This Perspective has focused on two aspects that are central to the outstanding problem of realizing the promised property improvements from polymer nanocomposites. These include (i) the factors that affect nanoparticle spatial distribution and (ii) how this spatial distribution affects properties. While considerable progress has been made in topic i, the relationship between nanoparticle spatial distribution and macroscopic properties remains at a nascent stage. We anticipate that ongoing work from many researchers will solve this central issue and lead to a quantum leap in the property improvements that have been promised by nanocomposites.

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Notes

The authors declare no competing financial interest.

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Brian Benicewicz received his PhD in polymer chemistry in 1980 from the Department of Chemistry and Institute of Materials Science at the University of Connecticut in Storrs, CT, working with Professor Sam Huang. He worked at Celanese Research Company, Ethicon, Inc., and Los Alamos National Laboratory before joining Rensselaer Polytechnic Institute in 1997 as Director of the Center for Polymer Synthesis and Professor of Chemistry. Since 2008, he has been in the Department of Chemistry and Biochemistry at the University of South Carolina where he holds the SmartState Chair in Polymer Nanocomposites. His research interests are focused on the development of high temperature polybenzimidazole membranes for fuel cells and electrochemical devices and reversible addition–fragmentation chain transfer (RAFT) polymerization, particularly for the preparation of multifunctional nanoparticles and polymer nanocomposites. His work on PBI membranes has been commercialized and is being used in fuel cell devices manufactured by multiple companies for portable and stationary applications. Benicewicz is a Fellow of the AAAS and cofounder of H2 Pump LLC which produces electrochemical hydrogen recycling equipment for industrial applications.

Tony Neely received his B.S. in chemistry from Furman University in 2006, staying on for his M.S. until 2008 when he started work for Oakwood Products. After the company downsized, he took the opportunity to obtain his PhD under the direction of Brian Benicewicz. His current research is focused on the modification of nanoparticle surfaces via RAFT polymerization.

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