

# Nanocomposites: Structure, Phase Behavior, and Properties

Sanat K. Kumar<sup>1</sup> and Ramanan Krishnamoorti<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Columbia University, New York, New York 10027; email: sk2794@columbia.edu

<sup>2</sup>Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77004; email: ramanan@uh.edu

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## Key Words

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## Abstract

It is well recognized that nanocomposites formed by adding nanoparticles to polymers can have significantly enhanced properties relative to the native polymer. This review focuses on three aspects that are central to the outstanding problem of realizing these promised property improvements. First, we ask if there exist general strategies to control nanoparticle spatial distribution. This is an important question because it is commonly accepted that the nanoparticle dispersion state crucially affects property improvements. Because ideas on macroscale composites suggest that optimizing different properties requires different dispersion states, we next ask if we can predict a priori the particle dispersion and organization state that can optimize one (or more) properties of the resulting nanocomposite. Finally, we examine the role that particle shape plays in affecting dispersion and hence property control. This review focuses on recent advances concerning these underpinning points and how they affect measurable properties relevant to engineering applications.

## INTRODUCTION

The addition of nanoparticles (nanospheres, nanotubes, nanorods, nanoplatelets, or sheets) to a polymer can result in materials with significantly improved properties (1–14). Although this principle seems to be well established, several issues that determine (a) the qualitative and quantitative description of the dispersion and organization of nanoparticles; (b) polymer properties, including chain conformation, local motions, and nonlocal dynamics; and (c) how these collectively affect the macroscale property improvements of the hybrids remain largely unresolved even from an empirical perspective. We organize our review around some of these unresolved questions:

1. Controlling particle dispersion: Are there general strategies to control the particles' dispersion and 3D arrangement? What relative roles do thermodynamics and dynamics play?
2. Particle dispersion and its role in properties: What role do particle dispersion and particle organization play in specific property enhancement? Can we predict a priori the particle dispersion and organization state that can optimize one (or more) properties of the resulting nanocomposite?
3. Particle shape: How does particle shape affect dispersion and property control?

Although the field of nanocomposites has been the focus of several authoritative reviews (15, 16), this one focuses only on current developments that impact potential applications. Thus, it is not comprehensive, and the interested reader is referred to several papers and reviews for a complementary and more complete picture of this rapidly evolving discipline (1–3, 12, 15–49).

A crucial question is if there are new physics that embody the behavior of polymers filled with nanoparticles, as compared with micrometer-sized (and larger) fillers, and how these physics affect the measurable material properties. Indeed, there has been at least one article titled “How nano are nanocomposites?” (50–53). Schaefer & Justice (52) decided that most of the resulting materials are not really nanocomposites, i.e., materials that are filled with individual nanometer-sized particles. Rather, the materials contain relatively large particle aggregates that behave effectively like micron-sized fillers. Whereas the presence of such larger agglomerates can be beneficial to certain properties, we nevertheless highlight the point that the dispersal of nanoparticles, which have very high specific surface area (and hence specific surface energy), into polymeric matrices remains an outstanding challenge. This situation is in direct contrast with the behavior found in colloidal systems, where dispersion is readily achieved by ensuring that the solvent's refractive index and density match those of the colloid: Whereas the former property ensures that there is no effective dispersion-based attraction between the particles, the latter ensures that sedimentation does not occur. Although sedimentation is not an important factor in dealing with nanoparticles, the challenge of balancing the dispersive attraction between nanoparticles remains open (34). This is a focus of discussion below.

Similarly, while nanoparticle 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 several, macroscale properties. Torquato and colleagues' work (54–56) on macroscale composites bolsters this point. Building on earlier research, they suggest that there exist cross-property bounds between different properties (e.g., electrical conductivity, mechanical reinforcement) of a macroscale composite. Thus, knowledge of the composite's mechanical properties places bounds on its electrical conductivity. These bounds also allow for the prediction of the optimal phase dispersion state to maximize one or multiple properties of the composite. Thus, if one “phase,” say *A*, of a binary composite is both mechanically reinforcing and electrically conducting (whereas the other, *B* phase, is not), then both the macroscale mechanical and electrical conductivity are optimized if the *A* phase is percolating. In contrast, if only the *A* phase were mechanically reinforcing, whereas only the *B* phase were conducting, then either property is optimized if the appropriate phase is

percolating. However, to optimize simultaneously both the electrical and mechanical properties of the composite requires that the two “phases” be connected in a triply periodic fashion, i.e., that both be simultaneously percolating. This immediately suggests that optimizing one versus two properties of a composite can require very different morphologies. Although this idea is new and unproven in the field of nanocomposites, it suggests that the creation of multifunctional composites requires exquisite control over nanoparticle spatial distribution (57). Such understanding, which is currently only at a nascent stage in the field of nanocomposites, is crucial to the end use of these materials in a variety of ubiquitous contexts, e.g., in strong, flame retardant fabrics; mechanically sound gas and water purification membranes; and highly refractive yet transparent soft materials that are wear resistant. Making such connections between nanoparticle dispersion and how it affects macroscale properties is the second focus of this review.

A final aspect we touch on here is the roles played by nanoparticle size and shape. Whereas spherical nanoparticles and their agglomerates (e.g., fumed silicas, carbon blacks) were the first fillers explored in the context of nanocomposites (as early as the 1940s), interest has switched more recently to platelets (clays and graphene), nanotubes (carbon based and others), and nanorods, primarily because it is believed that these anisotropic nanoparticles can achieve mechanical and electrical percolation at even lower loadings. Thus, the belief is that these additives can be used at “fairy dust” levels to result in extremely large changes in properties, with barrier properties, flame retardancy, and electrical conductivity being the most notable. Similarly, the role of particle size has also been a topic of discussion for the past 50 years, but it has not received as much attention as particle shape. Although we therefore shall not spend much space on this topic, in the limit of large sizes, the increase in specific nanoparticle surface area with decreasing diameter improves properties. Previous researchers have conjectured that this effect is counteracted by a reduction in the thickness of the adsorbed “bound” polymer layer with decreasing size, which leads to decreased interparticle “coupling.” A balance of these factors is speculated to lead to a particle size in the nanoscale (~100 nm) with optimum properties (58–63). The evolving understanding of the roles of particle shape on nanoparticle properties is thus the third focus of this review.

## STRUCTURE AND PHASE BEHAVIOR

### Phase Behavior

The dispersion state of nanoparticles in a polymer matrix is thought to crucially affect the properties of the resulting nanocomposite. A central player in this equation, then, is the thermodynamic miscibility of the nanoparticles with the polymers. At the level of Flory theory, this miscibility is comparable in difficulty with mixing two large polymers. Thus, enthalpic effects typically dominate this situation with entropy playing only a weak role.

**Enthalpic control.** The miscibility of nanoparticles with polymers has been a topic of recent intense theoretical interest (15, 34, 41, 64–88). In contrast, experimental work has lagged, in part owing to the lack of well-defined nanoparticles and adequate characterization methodologies. In the case of bare nanoparticles, Mackay et al. have suggested that the relative sizes of the nanoparticles and the chemically similar melt polymer chains (measured by the radius of gyration,  $R_g$ ) determine miscibility (34). Miscibility occurs when the chains are bigger than the nanoparticles. The theoretical basis for this intriguing result, which is speculated to be entropic in origin, is the focus of ongoing work. However, it is fair to say that the experimental situation is still unclear because the initial state of nanoparticle dispersion or aggregation, which crucially affects the final nanoparticle dispersion state after annealing, is sensitively dependent on sample preparation. Thus,

even this canonical case of entropically driven miscibility between nanoparticles and polymers remains unresolved.

For anisotropic rod- and plate-like nanoparticles, following Onsager (89), the nanoparticles form nematic, smectic, and columnar phases beyond a critical volume fraction that scales approximately as  $1/x$  ( $x$  being the aspect ratio) in the absence of strong matrix-nanoparticle attractive interactions. Such ideas have been refined using theoretical methods and indicate that to obtain well-dispersed, anisotropic nanoparticles at modest to high concentrations requires significant efforts to reduce particle-particle attraction and increase particle-matrix attractive interactions. Thus, at modest concentrations of anisotropic nanoparticles, entropic effects will not result in a dispersion of the nanoparticles (90, 91).

Enthalpic effects can also be used to control miscibility between polymers and nanoparticles (9). Poly(2-vinylpyridine) mixes readily with spherical silica nanoparticles because of favorable hydrogen bonding interactions. Poly(ethylene oxide) (PEO) readily intercalates the galleries of unmodified smectite clays, presumably owing to the formation of crown ethers with the charge-balancing interlayer counterions and to an additional entropic gain by releasing confined water molecules previously bound to the metal counterion (92). Similarly, there have been many efforts to modify the surface functionality of particles with short ligands to improve miscibility with polymers; the most notable examples are efforts to increase the miscibility of organically modified clays and covalently functionalized carbon nanotubes (CNTs) with a variety of commercial thermoplastics and thermosets (43, 93). Such ligands reduce particle-particle attractive interactions in a manner analogous to the steric stabilization of colloids and provide additional avenues to improve enthalpic interactions between the matrix and the nanoparticle. A variation on this idea uses zwitterionic surfactants that act as compatibilizers between CNTs and poly( $\epsilon$ -caprolactone); the surfactant forms hydrogen bonds with the polymer and favorably interacts with the nanotubes through ionic interactions with nanotube defects (94).

**Grafted nanoparticles.** There has also been considerable interest in using polymer-grafted nanoparticles to improve miscibility with a matrix polymer. For large colloidal particles Hasegawa et al. (73) found that immiscibility only occurs if the free matrix chains are higher in molecular weight than the brush. Because both the matrix and the brush have the same chemical structure, this immiscibility is entropic in origin and attributable to the concept of brush autophobicity (9, 66, 76, 83, 85, 95). Similar ideas appear to apply for nanoparticles (88, 96). Apparently, controlling the length of the grafted chains versus the matrix chains of the same chemistry can serve as a very sensitive handle for miscibility in these cases. However, the role of processing has not been well explored in this context and remains an open question.

The situation for nanotubes and clays is less well understood. The use of end-grafted polyolefins of modest molecular weight as compatibilizers has failed to produce true stable nanocomposites (97, 98). However, the use of lightly functionalized (such as maleic anhydride treated) polyolefins, although not resulting in optimized dispersions of the nanoparticles, yields significantly improved mechanical properties and therefore commercial applications (50, 51). Mixing and dispersing with flow fields (especially shear) as well as infiltration of aerogels or xerogels of dispersed nanoparticles have been used to prepare polymer nanocomposites with highly dispersed nanoparticles (99, 100). The use of shear to exfoliate clays and nanotubes in enthalpically favorable or neutral polymers is critical for the integration of nanocomposite manufacturing using polymer processing equipment. Paul and coworkers have hypothesized (50, 51, 100), and Vaia et al. have used computer simulations to verify (101), that a layer-by-layer exfoliation is the dominant mechanism for such dispersion, at least for the enthalpically favored case. The stability (post-shear) of such dispersions is highly dependent on the nature of the

polymer–nanoparticle interactions, i.e., the thermodynamic stability, the viscosity of the polymer matrix, and the ability of the nanoparticles to percolate and form a kinetically trapped network (102, 103). In this context, a significant challenge is to garner a true understanding of the relationship between percolation, orientation, particle size and shape, and polydispersity, and this remains an area of continued interest. Nevertheless, for thermodynamically stable dispersions, such structural relaxation is strongly non-Brownian, extremely slow for high molecular weight polymer matrices, and likely to be trapped in metastable states.

## Structure

Here we focus on (*a*) the spatial distribution of the nanoparticles, namely whether they are well dispersed, agglomerated, or assembled into superstructures; and (*b*) chain conformations in the presence of the nanoparticles.

**Characterizing the structure of nanocomposites.** Quantitative characterization of the dispersion and orientation states of nanoparticles and the polymer matrix are critical for developing fundamental structure–property correlations. However, such efforts are difficult, partly because of the range of length scales associated with such nanocomposites, but also owing to the polydispersity and heterogeneity of the nanoparticles (and their collections). Typically, structural characterization tools include force, optical, and electron microscopy; X-ray, neutron, and light scattering; chemical spectroscopic methods; electrical and dielectric characterization; and mechanical spectroscopy. Depending on the details of the nanoparticle and the polymer matrix, each of these methods can provide unique information on the dispersion state and polymer and nanoparticle arrangement over size scales ranging from nanometers to millimeters; these are often used in combination to provide detailed information on the hierarchical morphology in nanocomposites (3).

Electron and force microscopy have been used most extensively to determine the nanoscale dispersion in different nanocomposites and, with the aid of image analysis of several tens of such micrographs for each sample, to quantify the dispersion and orientation of the nanoparticles (50, 104). Developments in 3D reconstruction, stereology, and high resolution transmission electron microscopy (TEM) and scanning electron microscopy (SEM) methods are significantly improving the understanding of the 3D distribution and dispersion of nanoparticles (3). On the other hand, radiation scattering methods provide an ensemble average of the dispersion and orientation state, but require model development for quantification. The efforts of Vaia & Maguire and Schaefer & Justice to develop such modeling tools have allowed for a more thorough quantification of the dispersion state of nanocomposites (10, 52). Significant efforts toward the development of rapid experimental tools and robust modeling tools to interrogate and quantify the dispersion and orientation state at various scales is an open challenge.

**Grafted-particle dispersion in polymer melts.** As discussed above, multiple experimental and theoretical reports suggest that particles with grafted chains can be readily “mixed” with polymer melts of the same chemical structure (40, 72, 73, 95, 96, 105–118). There is growing consensus that the composite will have well-dispersed nanoparticles if the matrix polymer is shorter than the brush but will be immiscible otherwise. Whereas variables such as the graft density and particle radius can also play a role, the overall point is that only phase separation phenomena are observed/predicted in this context. Thus, we can obtain the extremes of either particle aggregation into large spheres or uniform particle dispersion. These researchers apparently have obtained no other, intermediate, structures. Exceptions to this statement are recent findings that densely grafted particles apparently

crystallize when present in large concentrations in a lower molecular weight matrix, as discussed below (118–121).

In contrast, we now consider hydrophilic nanoparticles grafted with hydrophobic chains. In the limit of low grafting densities, spherical silica nanoparticles isotropically grafted with polymers have been found to self-assemble into a range of superstructures when they are dispersed into the corresponding homopolymer (3, 34, 49, 95, 96, 122) (**Figure 1**). Theory and simulation (39, 123) show that this assembly 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) (124). As expected, we find the extremes of phase separation and well-dispersed particles in the two limits of no grafting and dense grafting, whereas intermediate structures occur at intermediate grafting densities. To gain a better understanding of these results, an analytical theory that contains two essential ingredients was developed. First, it was assumed that there is an extremely short range (“point”) interparticle attraction. Second, the entropy of distorting the polymer brush chains when two particles approach each other counteracts this attraction. The minimization of the resulting free energy yields a morphology diagram that is similar to the simulations. These results are also consistent with recent simulations of fullerenes with multiple PEO grafts that are uniformly distributed on the particle surface. These are found to assemble into string-like and branched polymers (39, 125–129). Both theory and simulation thus show that polymer-grafted particles readily assemble into block copolymer-like morphologies, which balance core-core attractions and brush entropy.

In contrast, undiluted functionalized nanoparticles with chains grafted at higher grafting densities form cubic structures, as has been anticipated for highly functionalized star polymers (118). The conformations of the chains are consistent with the mean-field predictions of Daoud & Cotton (130) and indicate that the chains, when long enough, adopt ideal conformations because of space filling (131). Furthermore, these hybrid nanoparticles with high grafting density behave as soft spheres. The intersphere interaction is a repulsive potential that is deduced from rheology experiments to scale as  $\sim r^{-12}$ .

The dilution of such grafted nanoparticles with homopolymers (so that the mean interparticle spacing is up to several times the grafted chain length) does not alter the ordered structure down to approximately 25 vol% of grafted nanoparticle; below this the particles have liquid-like ordering. Furthermore, blending the particles with matched molecular weight homopolymers leads to chain size scaling that is consistent with good solvent conditions.

Although these works highlight the dramatic improvements that have been made in controlling the spatial distribution of nanoparticles, these ideas are still in a nascent stage. More complicated situations offer the possibility of even greater control, but 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 situation becomes much more interesting. The competition between the interactions of the polymer components and those between the polymer components and the nanoparticle, along with the steric constraints imposed by the surface and the grafting density, is likely to result in significantly altered mesoscale organization, as recently shown (10). Nevertheless, this is a significant area of interest for the development of noncentrosymmetric materials, and the parameter space in terms of nanoparticle shape, grafting density, and copolymer length and composition needs to be explored and compared with that of triblock copolymers composed of three different chemical constituents (denoted as ABC copolymers in the literature) and their blends (132, 133). We expect significant progress in these areas in the next few years, and this will provide us with significantly more control over the property enhancements that nanofilled polymers can provide.



**Structure of nanocomposites with anisotropically shaped particles.** The structure of nanocomposites containing anisotropic nanoparticles is complicated by the different length scales associated with the individual nanoparticles and their ability to organize themselves into mesoscale structures, either disordered or ordered. A crucial issue that emerges for many anisotropic nanoparticles is their intrinsic lack of rigidity when fully exfoliated and dispersed in a solvent or polymer matrix. The most notable examples of such layer flexibility are seen in exfoliated graphene through electron microscopy and in exfoliated layered silicates and single walled CNTs through scattering measurements (52, 134–136). Several groups have reported large persistence lengths in CNTs, which might be a result of either their observation in vacuum (without an interacting solvent) or rigidification owing to the template surrounding the nanotube (as in DNA-stabilized CNTs). Such flexible anisotropic nanoparticles can have a significant effect on the property enhancement sought in mechanical, barrier, and electrical applications and in some cases can severely limit the extent to which property enhancement can be achieved.

Increasing the concentration of nanoparticles in well-dispersed nanoparticle hybrids results in changes in the structure of the nanocomposites as well as in their rheological and mechanical (and possibly electrical) properties. The formation of sample spanning percolated network structures dominates these changes. The percolation threshold scales inversely with the effective aspect ratio of the nanoparticle and can occur at concentrations significantly smaller than those found in their isotropic counterparts. In semidilute (at concentrations well above the percolation threshold) and concentrated dispersions of both isotropic and anisotropic nanoparticles in polymers, the nanoparticles form hierarchical fractal structures with the formation of flocs that are micrometers in size and consist of a mesh of dispersed nanoparticles. Such fractal-like behavior results in universal scaling (dependent only on the relative magnitudes of the interactions between the nanoparticles and the interactions between flocs) of the linear elastic network modulus and in time-temperature-composition superpositioning of the critical strain for shear thinning and of the damping function that characterizes the nonlinear behavior. The fractal exponent typically ranges from 1.7 to 2.4, with the higher values consistent with the formation of diffusion-limited aggregates. In the case of anisotropic nanoparticles with strong intrafloc interactions, the elastic strength scales with the number of nanoparticle–nanoparticle contacts and is therefore a good measure of the dispersion quality (33, 137). At high concentrations, as has been demonstrated for CNTs, the nanoparticles form liquid crystalline domains that exhibit all of the optical characteristics associated with small molecule and polymeric liquid crystals (7).

Such structural hierarchy affects the shear rheology properties. Ren et al. observed several features in the steady shear behavior of layered silicate nanocomposites in the semidilute regime (138; see also 103): (a) The steady shear viscosity was significantly lower and exhibited a weaker shear rate dependency than the linear oscillatory properties; i.e., the data do not conform to the empirical Cox–Merz rule that is applicable to homopolymers; (b) at comparable shear rates, the nanocomposites exhibited a lower first normal stress difference than the pure polymer. However, when compared at the same shear stress values, the data collapsed onto a single master curve; (c) a stress overshoot occurred during the onset of steady shear in a polymer matrix that does not demonstrate such overshoots on its own. Kharchenko and coworkers (139) have reported the flow-induced properties of a multiwalled nanotube network in a polypropylene matrix in which significant shear thinning and, more importantly, large and negative normal stress differences were observed. The negative normal stress differences result in die-contraction properties and presumably arise from the large-scale deformation of the network and the local deformation of nanotubes under shear. The stress overshoot observed and the failure of the Cox–Merz rule (with the steady shear viscosity being lower than the oscillatory shear viscosity) are manifestations of the changes in the fractal network structure upon imposition of continuous shear (both shear-induced

formation of stress-bearing bonds and shear-induced breakdown of stress-bearing contacts) and alignment of the nanoelements within the floc (140). It has been conjectured that under steady shear, the flocs locally rearrange in response to the applied deformation, which results in cluster-cluster collisions and jamming of the network elements that in turn give rise to the observed stress overshoot. Under continuous shearing, when the local stress exceeds the yielding stress, the network bonds break and the network flows; under steady state conditions an equilibrium between bond formation and bond breaking occurs.

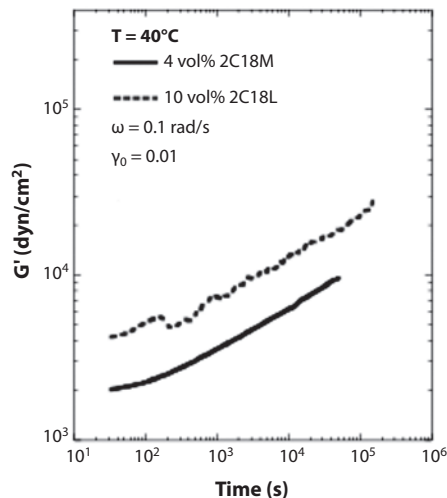
Processing using external fields such as large amplitude oscillatory shear flow significantly impacts the structure and properties of such nanocomposite materials and, in particular, can lead to the development of oriented materials in the case of anisotropic nanoparticle dispersion. Such flow fields can remove the kinks and folds observed in the dispersed nanoparticles and, when they are trapped in a crystallized or vitrified polymer matrix, recover some of the property enhancements sought (141). However, in materials that naturally incorporate layering, such as multiwalled CNTs and silicic acid-based platelets, the individual nanoparticles are several nanometers thick (their smallest dimension) and become significantly rigid with large persistence lengths (52, 135, 136).

Polymer nanocomposites can be considered to be soft colloidal dispersions, the rheology of which has been studied in great detail recently. The structure of soft colloidal dispersions has been conjectured to be intrinsically metastable and disordered. This structural disorder creates energy barriers that Brownian forces alone cannot overcome. Upon application of a stress, the energy landscape changes and the system takes on a new metastable structure. This analogy to glass formation has allowed the interpretation of the viscoelasticity of these dispersions in terms of physical aging (see sidebar, Soft Glasses, below). Cloitre and coworkers have demonstrated that microgel pastes exhibit a stress response analogous to physical aging with rejuvenation occurring at large stresses and metastability achieved upon removal of the stress (142). On the other hand, Bonn and coworkers showed that anisotropic laponite-based colloidal suspensions exhibit many of the same aging and rejuvenation characteristics observed in their isotropic counterparts (143). Polymer nanocomposites containing anisotropic nanoparticles exhibit many of the characteristics common to soft colloidal dispersions such as weak low-frequency dependency of the quiescent state moduli and logarithmic scaling of the disorientation of parallel aligned layers (**Figure 2**)

## SOFT GLASSES

The topic of “soft glasses” centrally impacts the field of nanocomposites, especially the mechanical reinforcement achieved when nanoparticles are added to a polymer. Apparently, in nanocomposites that show mechanical reinforcement, the nanoparticles form a percolated, slow-relaxing structure. This phenomenology tracks that of reversible gels, such as cytoskeletal networks, that show solid-like mechanical properties at relatively short time scales but liquid-like behavior at long time scales. To understand this behavior, consider that a soft-glassy material has a liquid-like structure, but its dynamics become exponentially slower with decreasing temperature because the molecules have sticky interactions. The time between attempts to break sticker pairs also increases exponentially with decreasing temperature. Because the fraction of “open” stickers decreases dramatically with decreasing temperature (presumably in an Arrhenius fashion), the now “unpaired” stickers cannot find an open sticker with which to pair and thus return to their original partner. The combination of these two factors leads to a rapid increase in relaxation times with decreasing temperature, in analogy to liquids close to their glass transition. These ideas thus indicate that nanocomposites can show aging effects and that their processing can play a crucial role in the properties that result.





**Figure 2**

Small amplitude oscillatory elastic moduli ( $G'$ ) monitoring of the recovery after shear alignment for two hybrids of laponite (22 wt% 2C18L) and montmorillonite (8.5 wt% 2C18M) dispersed in an elastomer matrix. Recovery measurements were performed at  $T = 40^\circ\text{C}$ , frequency  $\omega = 0.1 \text{ rad s}^{-1}$  and strain amplitude  $\gamma_0 = 0.01$ . The values of linear viscoelastic  $G'$  at  $\omega = 0.1 \text{ rad s}^{-1}$  for the quiescent unaligned hybrids are  $\sim 4.5 \times 10^5 \text{ dyn cm}^{-2}$  for the 2C18M-based and  $\sim 1.2 \times 10^6 \text{ dyn cm}^{-2}$  for the 2C18L-based hybrids.

(102, 131, 144). However, these nanocomposites do not exhibit the crucial similarity to the aging of soft colloidal dispersions; the viscoelastic data indicate liquefaction rather than further solidification with increased waiting time (142, 143). Importantly, for such anisotropic materials any theoretical development must account for the orientation or orientability of the dispersed particles. Furthermore, these previous works indicate that the processing of these materials is nontrivial and suggest that quiescent holds rather than preshearing can improve processability.

**Chain structure.** The perturbation of polymer chain configurations by nearby surfaces has been studied for many years. Two different situations have been experimentally addressed: polymer thin films and polymer nanocomposites. Fairly conclusive results have been obtained for the behavior of the polymer radius of gyration,  $R_g$ , in thin films as a function of film thickness (145). For example, small angle neutron scattering (SANS) measurements have demonstrated that polystyrene (PS) molecules, when confined in thin films, exhibit changes in their conformations when the film thickness becomes thinner than the unperturbed radius of gyration of the polymer,  $R_g$ . These changes primarily occur in the direction perpendicular to the film (or interface) plane, while in the tangential direction the radius of gyration is relatively unperturbed. Such a clear picture of the behavior of  $R_g$  is lacking for polymer nanocomposites. Polymer chain expansion, contraction, and no change have been found in the few experimental studies that have been conducted (146–148). These studies, however, differed in the types of nanoparticles dispersed in the host polymer, the nanoparticle size, and the quality of the nanoparticle dispersion. In the two cases in which the host polymer was PS, the polymer chains expanded when the nanoparticles were composed of cross-linked PS—soft spheres—but did not change when the nanoparticles were silica—presumably, hard spheres. For the soft PS nanoparticles the dispersion quality could be characterized only indirectly by SANS because there is no TEM contrast. TEM visualization

in Reference 146, however, showed that the dispersions of “hard” silica nanoparticles were not of high quality. Thus, the dramatically different findings of these two studies could be a result of differences in dispersion quality. This uncertainty suggests that we do not fully understand even this fundamental aspect of polymer nanocomposite behavior. In recent simulations Termonia (149) shows that chain size is unaffected if the chains are smaller than the interparticle spacing; as the chains are made bigger, initially they shrink but then they expand, similar to chains in the presence of obstacles. This intriguing prediction still needs to be verified, but it may provide us with the best possible framework from which we can understand chain dimensions in the presence of nanoparticles.

On the other hand, studies of polymers confined between anisotropic nanoparticles or in anisotropic pores have indicated significant changes in chain conformations. For instance, PS (in toluene) confined to 7 nm diameter pores of Vycor glass exhibited smaller radii of gyration than in the bulk material (150). Interestingly, the molecular weight dependency for the reported radius of gyration changes from  $M^{-0.54}$  for the bulk solutions to  $M^{-0.44}$  for the confined polymer chains. When confined between plates (with confining distances of  $\sim 2$  nm) either in the melt or with good solvents for the polymer, polymer chains form two-dimensional random walks with no interpenetration. Such structures might have significant consequences for the topological arrangement and barriers that intimately govern the macroscopic polymer mobility and stress-transfer mechanisms. Clearly, systematic studies of chain conformations and their dynamics with increasing distance between confining surfaces are needed to truly understand the nature of confinement in such nanocomposites.

## PROPERTIES, APPLICATIONS, AND CHALLENGES TO INTEGRATION

### Mechanical Properties

Mechanical property enhancement and especially the intriguing possibility of overcoming the traditional trade-off between toughness and stiffness associated with filled polymers has caused significant interest in the use of nanoparticles to reinforce polymers (151, 152). The first demonstrated example of a thermomechanically reinforced polymer nanocomposite was nylon-6 layered silicate hybrids prepared by Toyota Central Research. This material demonstrated simultaneous improvements in stiffness and heat distortion temperature without affecting impact properties (153). Synergistic property enhancements also have been observed in model SWNT-reinforced networks of an amine-terminated poly(dimethyl siloxane) (PDMS) as well as in networks of poly(propylene fumarate), a biodegradable polymer used for tissue engineering applications, with dispersed nanotubes (154–156). A functionalized nanotube [with a  $\text{CO}_2(\text{CH}_2)_{10}\text{OH}$  functional group] was used to reinforce the polymer. The tensile stress versus strain for one such nanocomposite and a comparable PDMS network with roughly the same cross-link density (based on solvent swelling) are shown in **Figure 3**. A comparison of the tensile modulus and the elongation-at-break for a series of nanocomposites is shown in **Figure 4**. These results are remarkable because the tensile modulus and strength are considerably increased while the strain-at-break is largely unchanged, and therefore the toughness is significantly increased.

From a macroscopic viewpoint, much of the enhancement observed in stiffness can be understood in terms of macroscopic models such as the Halpin-Tsai and Mori-Tanaka descriptions (51). Following the finite-element modeling efforts of Boyce and coworkers and the experiments of Thomas et al. (157, 158), it has become clear that nanoparticles, especially anisotropic ones, can lead to stress concentration near the leading edge of the particle. This, along with the ability to finely tune the thermal properties (and hence mechanical properties) of polymers near the

surface of nanoparticles, has led to recent interest in tailoring the interface between the polymer and the nanoparticle to maximize property enhancement (9, 159–162). Issues that remain to be understood include the role of the nanoparticle and the interactions between polymers and nanoparticles in long-term fatigue life and physical aging characteristics. Recent reports suggest that the nanoparticles cause a slowing down of long-term aging, presumably because in the cases studied the incorporation of nanoparticles somewhat elevated the glass transition temperature of the polymer. There have also been indications that nanoparticles result in heterogeneity of populations and environments in such nanocomposites, a finding that is motivated by the emergence of an extra, rapid relaxation process that might cause significant aging prior to the slow process. Because aging has significant consequences on the long-term use of polymer nanocomposites, systematic studies to unravel the details of aging clearly are required.

The thermomechanical reinforcement observed in several thermoplastic-based hybrid systems, including the nylon-6 layered silicate hybrids prepared by Toyota Research (153), has been attributed to the ability of nanoparticles to alter crystalline morphology, such as by changing polymorphs, providing nucleation and templating surfaces, or stabilizing the amorphous phase. Most notably, for the case of nylon-6–clay nanocomposites, the clays stabilize the usual high-temperature  $\gamma$ -phase polymorph at all temperatures, avoiding the Brill transition, and therefore fundamentally alter the thermomechanical properties of the nylon (163). Similarly, for the case of poly(vinylidene fluoride) (PVDF), well-dispersed clays stabilize the piezoelectric  $\beta$ -phase without any of the flow-processing that is usually required (151). The formation of the  $\beta$ -phase leads to not only an electroactive material but also a material that is significantly more ductile than the  $\alpha$ -phase-based PVDF. The significant improvements observed in the reinforcement of poly( $\epsilon$ -caprolactone) nanocomposites with dispersed single walled CNTs is thought to occur owing to the nucleation of polymer crystals by the highly aligned nanotubes, which results in a “shish-kebab” structure with three-dimensionally aligned structures from the unit cell to the polymer lamellae to the nanotubes (141). Finally, such dispersed nanoparticles can also lead to a breakdown of the crystallinity of the polymer, as has been observed in nanocomposites of high molecular weight PEO with dispersed CNTs in which the melting point of PEO decreased by more than 30°C with the incorporation of less than 1% nanotubes (164).

Orientation and texturing of the nanoparticles can lead to highly improved and often tailorable anisotropic mechanical properties in such nanocomposites (141). Methods for orientation and texturing include the use of various external fields, most notably shear and elongational flow, as well as electric, magnetic, optical, and interfacial effects. However, strategies for optimizing such reinforcement remain somewhat elusive, with challenging questions as to how the pioneering work of Torquato and others translate to such nanoparticles and furthermore how to understand the role of the polymer–nanoparticle interface in dictating such property changes. Gusev and coworkers have shown through theoretical calculations that a web-like morphology is capable of significantly improving the shear moduli to a greater extent than a comparable random or hexagonal ordered structure of isotropic particles (165). Yakobson et al. have suggested that to truly exploit the mechanical properties of nanotubes, they need to be arranged in a superlattice that is highly interpenetrating and can optimize between two alternative routes of brittle bond breaking and plastic relaxation (166).

## Electrical Properties

Owing to the significant contrast between the electrical and dielectric properties of many nanoparticles and typical polymers, polymer nanocomposites have been attractive to the development of lightweight materials with potential applications in electrostatic discharge, electrical

interconnects, conductive coatings, and electromagnetic shielding with conductivities tailored between  $10^{-6}$  to  $100 \text{ S cm}^{-1}$ . Nanotubes and metallic nanorods are typically dispersed in polymer matrices for the development of conductive nanocomposites. Vaia et al. developed conductive elastomers with the incorporation of carbon nanofibers (167) or multiwalled CNTs (168) and have shown that such materials exhibit significantly improved mechanical properties and electrical conductivity and therefore represent the development of a new generation of stimuli-responsive materials. Nevertheless, the critical issues to consider include the development of the nature of the percolative structures; the formation of hierarchical structures (i.e., fractals) and their impact on percolative behavior; the orientation state of nanoparticles, their mesoscale ordered structures, and their consequences on electrical conductivity; and finally the junction resistance between matrix and nanoparticle and between nanoparticles. These intriguing concepts still require significant theoretical understanding before they can be practically realized on a routine basis. Functionalization of nanotubes and nanorods, often used to improve dispersion, also results in a significant disruption of the conductive pathways and leads to a significant decrease in the measured conductivity as compared with theoretically expected values. Orientation of the nanoparticles can also lead to significant anisotropy in the electrical conductivity of such nanocomposites. Recently, Forest and coworkers (169) examined the role of nanoparticle orientation in the anisotropic percolation of nanorods and demonstrated theoretically the ability to transform these structures, at a fixed loading of nanoparticles, from a 3D to a 2D to a 1D percolating structure by changing the orientation state, in their case by the application of shear.

A particularly interesting application is that of metallic nanorods, which are highly oriented but internally interrupted in an insulating polymer matrix. Such materials can demonstrate a dielectric strength in excess of  $10^5$  at concentrations (and orientations) that are close to the percolation. This could result in their use in ultrahigh capacitors. Development of robust processing techniques and extension of such structural paradigms to dielectric nanoparticles can lead to significant advances in actuators and sensors.

On the other hand, pristine layered silicates (naturally occurring with a negative charge) with charge-balancing cations in the intergallery have been suggested as possible motifs for single ion conductors for potential Li-ion battery applications with solvent-free PEO-alkali metal salt complexes as solid electrolytes (170). Significant efforts have been directed toward the preparation of PEO-lithium/sodium montmorillonite for such applications. The ether-based polymers are capable of forming crown-ether complexes with the lithium and allow for rapid mobility of the lithium ion. Significant challenges remain in the preparation of such materials, which require highly oriented films that contain more than 70 wt% inorganic material and can resist cracking.

## Gas Permeation

The inclusion of nanoparticles, especially anisotropic ones, can significantly alter the barrier properties of polymers for three underlying reasons: (a) The increased physical “tortuosity” of the diffusion path because of the well-dispersed nanoparticles; (b) changes in the local and segmental mobilities and the glass transition temperature of the polymer; and (c) alterations in the sorption resulting from competitive interactions between the penetrant molecules, nanoparticles, and the polymer matrix. The increased tortuosity dominates the changes in barrier properties observed for polymer nanocomposites; these are largely described by continuum based models such as those suggested by Cussler et al. (171) and improved by Bharadwaj (172). The orientation of the anisotropic nanoconstituents is critically important to the increase in tortuosity, and Bharadwaj has captured theoretically the effect of orientation on permeability. Nanocomposites of exfoliated clays in poly(ethylene terephthalate) show a 10- to 15-fold reduction in oxygen permeability with

1 to 5 wt% clay addition that is largely attributable to the increased tortuosity: these are beginning to find commercial applications. Recent work incorporating nanoporous layered aluminophosphates or silicates (that permit transport of protons while blocking methanol) in Nafion membranes maintains proton conductivity close to that of neat Nafion while reducing methanol permeability by an order of magnitude (173) and offers significant improvements for membranes in fuel cell applications.

## Flame Retardancy

Polymer nanocomposites based on nanoplatelets and nanotubes have been suggested for improved flame resistance because of reduced gas transport, the radical scavenging activity of high surface area nanoparticles, increased melt viscosity, and stable char formation and therefore prevention of continuous surface regeneration of fuel for the combustion process (2). Critical to stable char formation is the presence of a percolated filler network structure to provide a mechanical framework of high-temperature stable nanoparticles (174). Cone calorimetric studies of polymer nanocomposites indicate that when the nanoparticles are dispersed and form percolated networks, there is a significant reduction in the peak heat release, thereby reducing the potential for flame propagation to adjacent areas. This reduction in peak heat release rate is strongly correlated with increased char formation and the creation of percolated networks of nanoparticles. Changes in the degradation mechanism of the polymer in nanocomposites through the amount and types of degradation products can also significantly improve fire retardancy, as has been observed for several polymers including PS, polyamide-6 (PA-6), and ethylene-vinyl acetate (EVA) copolymers. This change has been ascribed to secondary reactions (e.g., hydrogen abstraction, radical recombination, extensive random scission, various intermolecular reactions) that can lead to new polymeric products that must again undergo thermal degradation. Radicals that have a substantial stabilization energy, e.g., styryl radical from PS, thus will exist and be retained in the nanocomposite long enough to participate in additional reactions, whereas radicals lacking this stabilization energy, e.g., a methacrylate radical from poly(methyl methacrylate), are not long lived and will not recombine (175).

Because many of the nanoparticles are organically modified, often through ionic interactions, it has become imperative to use “designer” functional groups when dealing with flame retardancy applications, which makes the cost quite prohibitive for only marginal improvements in properties. The passive nature of nanoparticle-enabled retardancy, combined with stricter controls on the use of halogenated compounds and the cost issues, has led to increased awareness that a new nano-based active flame retardancy needs to be pursued. A promising route for new materials is the use of traditional phosphorous-based additives with nanoparticles to not only provide both active and passive fire retardancy, but also to exploit synergistic improvements by providing a scaffold for the phosphorous additives to be best dispersed in the polymer matrix.

## Multifunctionality: Piezoelectric/Flexoelectric Response; Magnetostrictive Materials

One of the most exciting developments in the generation of multifunctional nanocomposite materials has emerged from the recent study of size-dependent electromechanical coupling and significant size-dependent flexoelectricity in nanomaterials. Sharma and coworkers (176, 177) have recently adapted the original work of Cross to nanoscale materials and have shown that the theoretical origins of piezoelectricity in nonpiezoelectric materials and the notion of giant piezoelectricity at the nanoscale emerge from flexoelectricity with a nonvanishing, but small, flexoelectric coefficient and from the development of large strain gradients in the case of mechanically mismatched

polymer nanocomposite materials. The experimental manifestation of such piezoelectricity from nonpiezo components is an outstanding problem owing to the requirement of noncentrosymmetric shape for the nanoparticles and their periodic arrangement on macroscopic length scales. Flexoelectricity is likely to play a significant role in the area of high energy density nanocapacitors, which continue to elicit significant scientific interest.

Nanoparticle-enhanced electric field-activated electroactive polymers (EAPs) are an attractive class of smart materials that exhibit electromechanical coupling conversion and can be applied as solid-state actuators and motion or pressure sensors. Current EAPs require high actuation voltages and have low blocked stresses and low operating temperatures. These current limitations are linked to inherent polymer properties such as low dielectric constant and low modulus. Addition of nanoparticles can significantly improve the thermomechanical properties of EAPs (without significant increase in the weight) and further cause the field distribution to become nonuniform. Recently Ounaies and coworkers have developed an electrostrictive material from amorphous polyimide nanocomposites by addition of small quantities of CNTs (178). Most importantly, the improvements achieved by these workers were achieved at much lower actuation voltages and were accompanied by increases in both mechanical and dielectric properties.

## SUMMARY

This review has focused on three aspects that are central to realizing the promised property improvements from polymer nanocomposites. These include (a) which factors affect nanoparticle spatial distribution, (b) how this spatial distribution affects properties, and (c) what role particle shape plays in this context. Whereas considerable progress has been made in topics (b) and (c), the control of nanoparticle spatial distribution remains at a nascent stage. We anticipate that ongoing work by many researchers will solve this central issue and lead to a quantum leap in the property improvements that nanocomposites have promised.

## FUTURE ISSUES

1. Morphological requirements (i.e., nanoparticle distribution and organization) for optimizing multifunctional nanocomposites need to be developed.
2. The role of processing in optimizing the structure of dispersions of polymer-grafted nanoparticles in like and unlike polymer matrices needs to be better understood.
3. The relationship between percolation, orientation, particle size, shape, and polydispersity needs to be better understood.
4. Rapid experimental tools and robust modeling tools need to be developed to interrogate and quantify the dispersion and orientation state of nanoparticles at various scales.
5. Systematic studies are needed of chain conformations and dynamics as functions of confining distance, confining nanoparticle shape, and size.
6. Understanding aging and fatigue in polymer nanocomposites and relating them to the dispersion of nanoparticles and the interaction between polymer and nanoparticle are important challenges.



## DISCLOSURE STATEMENT

Both S.K. and R.K. have ongoing NSF funding. S.K. has one patent pending, and R.K. has PCT/US04/20108, PC7/US04/19769, and two other patents pending.

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**137. Discusses the formation of a fractal nanotube network in polymer nanocomposites and how this affects properties.**

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165. One of the first theoretical works, based on a macroscale finite element technique, to relate mechanical reinforcement in nanocomposites to particle structuring.

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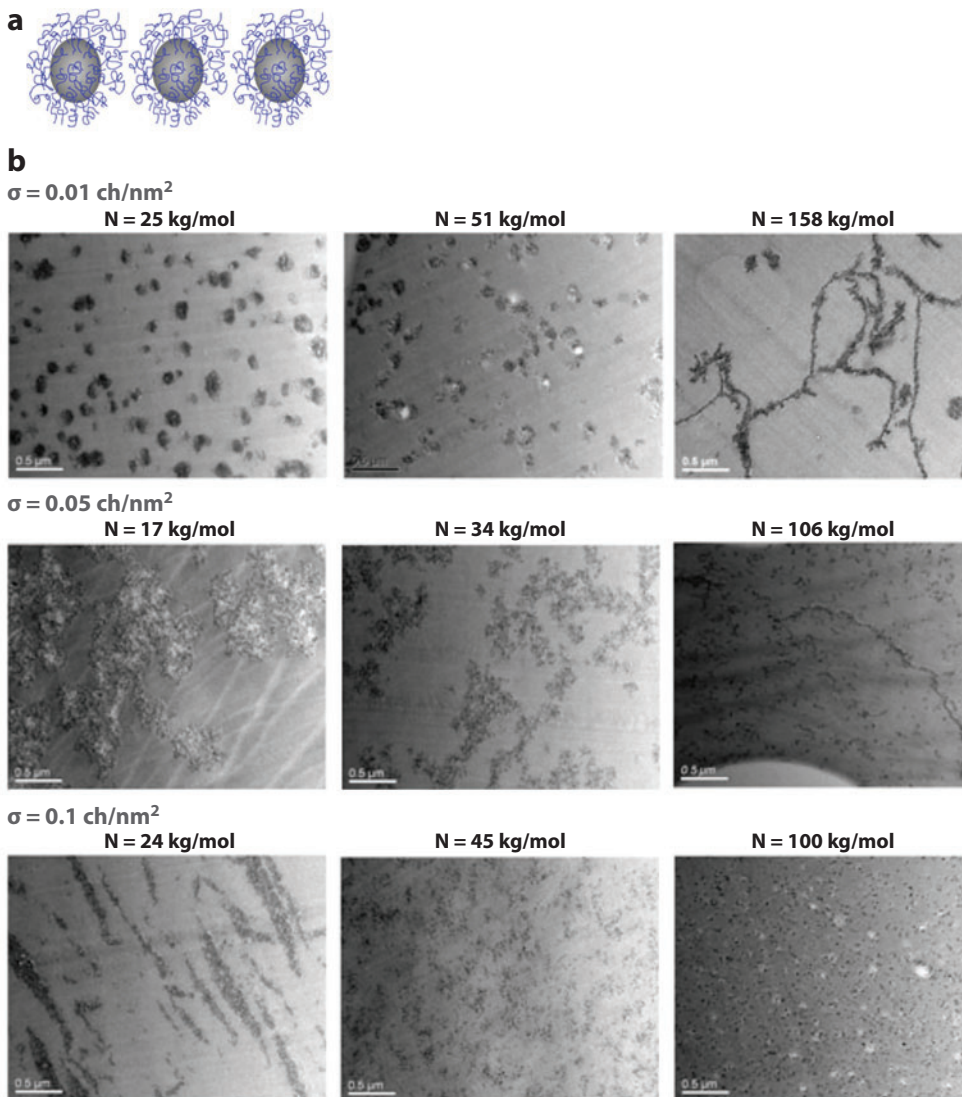


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174. Describes the role of particle structuring in flame resistance.

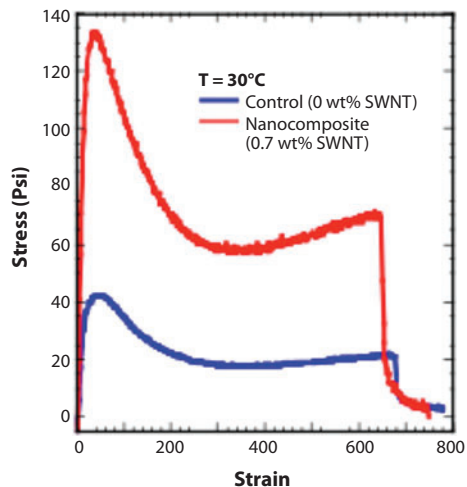
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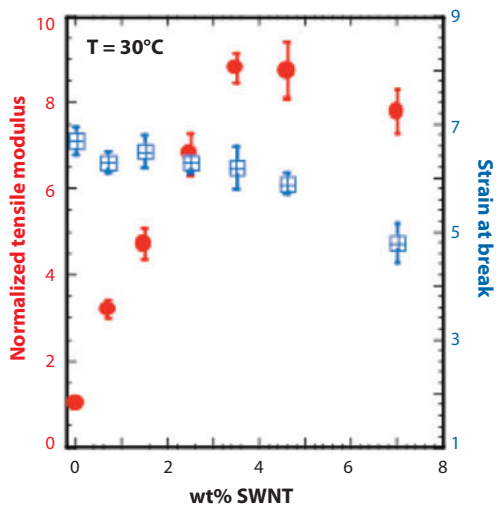
**Figure 1**

(a) A cartoon image of polymer-decorated nanoparticles. (b) Transmission electron microscopy (TEM) images of 14 nm silica particles functionalized with a polystyrene brush with molecular mass and grafting density as shown in the figure. These particles are placed in a polystyrene matrix with a molecular mass of  $142 \text{ kg mol}^{-1}$ . The samples, with 5 mass% silica, were annealed for 5 days at  $150^\circ\text{C}$ .



**Figure 3**

Tensile testing of 0.7 wt% single walled nanotube (SWNT) (functionalized) filled poly(dimethyl siloxane) (PDMS) nanocomposite compared with a similarly cross-linked PDMS network. The sample was stretched at a rate of  $2 \text{ mm min}^{-1}$  in a mini-Instron tester.



**Figure 4**

Composition dependency of the normalized tensile modulus and elongation-at-break for functionalized SWNT-PDMS networks.



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## Errata

An online log of corrections to *Annual Review of Chemical and Biomolecular Engineering* articles may be found at <http://chembioeng.annualreviews.org/errata.shtml>