Nanocomposites: Structure, Phase Behavior, Properties

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Abstract

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1. Paper Goals and Brief Context

It is now an accepted fact that the addition of nanoparticles (nanospheres, nanotubes or nanorods, nanoplatelets or sheets) to a polymer can result in materials with significantly improved properties, e.g., mechanical, electrical, barrier and flame retardant properties (15, 43, 76, 79, 81, 84, 86, 100, 104, 109, 124, 152, 158, 171). While this principle seems to be well established, several issues that determine the particle dispersion and organization and their quantification, the polymer properties including chain conformation and their local and non-local dynamics, and how they affect the macroscale property improvements of the hybrids remain largely unresolved even from an empirical perspective. We organize our review around these unresolved questions and specifically focus our attention on:

(i) <u>Controlling Particle Dispersion:</u> Are there general strategies to control the particle dispersion and their three-dimensional arrangement? What relative roles do thermodynamics and dynamics play?

(ii) <u>Particle Dispersion and Its Role on Properties:</u> What role does particle dispersion and particle organization play in specific property enhancement?. Can we predict apriori the particle dispersion and organization state that can optimize, one or more, properties of the resulting nanocomposite?

(iii) <u>Particle Size</u>: What is the role of particle size? Is there a size where a particular nanocomposite property is optimized?

(iv) <u>Particle Shape</u>: What role does particle shape (anisotropy) play in dispersion and property control?

In this context we note that, while the field of nanocomposites has been the focus of several reviews (4, 161), this particular review focuses only on current developments in the field which impact their potential applications. Thus it is not expected to be comprehensive and the interested reader is referred to several relevant papers and reviews for a complementary, and more complete picture of this rapidly evolving science and engineering (2-4, 10, 13, 15, 17-19, 21, 23, 28, 32, 38, 41-46, 53, 54, 59, 61, 66, 73, 74, 76, 79, 80, 89-92, 112, 116, 137, 154, 161).

A crucial question is if there are new physics that embody the behavior of polymers with included nanoparticles, as against more conventional fillers (in the micrometer size scale and larger) and how these affect the ultimate properties of the materials. Indeed, there have been articles that have posed the question: "How nano are nanocomposites ?" (64, 108, 126, 167). These works, especially that of Schaefer, decide that most of the resulting materials are not really nanocomposites, i.e., materials that are filled with individual nanometer sized particles. Rather, there are relatively large particle aggregates that behave effectively like micron-sized fillers. While the presence of such larger agglomerates can be beneficial to certain properties, it nevertheless highlights the point that dispersing nanoparticles, with their very high specific surface area (and hence specific surface energy), into polymeric matrices is probably the biggest outstanding challenge in this field. This situation is in direct contrast with the behavior found in the case of colloidal systems, where dispersion is readily achieved by ensuring that the solvent's refractive index and density matches that of the colloid: while the former ensures that there no effective dispersion based attraction between the particles, the

latter ensures that sedimentation does not occur. While sedimentation is not an important factor when one deals with nanoparticles, the challenge of balancing the dispersive attraction between nanoparticles is one that remains open at this time (92). This is one focus of our discussions below.

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 all) macroscale properties. To bolster this message, we point to relevant work of Torquato (65, 145, 146) on macroscale composites which is sketched schematically in Figure 1. Following earlier research, these workers suggest that there exist cross-property bounds between different transport properties (e.g., electrical conductivity, mechanical reinforcement, gas permeation) of a macroscale composite. Thus, knowledge of the effective mechanical properties of a composite immediately places bounds on its electrical conductivity or gas permeation behavior. Using these bounds allows them to predict the phase dispersion state that optimizes one or multiple properties of the composite. Thus, if one "phase", say *A*, of a binary composite is both mechanically reinforcing and electrically conducting (while the other, *B* phase, is not), then the macroscale mechanical and/or electrical conductivity is optimized if the *A* phase is percolating. In contrast, if only the *A* phase were mechanically reinforcing, while only the *B* phase were conducting, then, either property is optimized if the appropriate phase is percolating. However, to simultaneously optimize 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 *vs.* two properties of a composite can require very different

morphologies. While 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 (148). Such understanding, which is currently only at a nascent stage, 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 high refractive yet transparent soft materials which are wear resistant. Making such connections between nanoparticle dispersion and their organization with macroscale properties is then the second important focus of this review.

A final aspect we touch on here are the roles played by nanoparticle size and shape. While spherical nanoparticles and their agglomerates (e.g., fumed silicas, carbon blacks) were the first fillers explored in the context of nanocomposites (as early as in the 1940s), interest has switched to platelets (clays and graphene) and more recently 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 which can result in extremely large changes in properties, barrier properties flame retardancy and electrical conductivity being the most notable. In the same vein the role of particle size has also been a topic of continuing discussion for the last fifty years. 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 (30, 103, 119, 131, 132, 135). The evolving understanding of the roles of particle size and shape on nanoparticle properties are then the third focus of this review.

2. **Structure & Phase Behavior**

2.1 Phase Behavior

The phase behavior, namely the miscibility of nanoparticles with polymers has been topic of intense theoretical interest in the last decade (4, 6, 28, 29, 51, 56, 58, 62, 67, 68, 70, 72, 75, 92, 95-97, 110, 113, 139, 142, 143, 155, 160, 162, 164, 165, 168). While the theoretical interest in these systems has been high, experimental work has lagged in part due to the lack of well-defined nanoparticles and adequate characterization methodologies to quantify such phase behavior. In the case of <u>bare nanoparticles</u>, Mackay et al have suggested that miscibility is determined by the relative sizes of the nanoparticles and the melt polymer chains. Miscibility appears to occur when the chains are bigger than the nanoparticles. The theoretical basis for this intriguing result, which is speculated to being 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 the solvent casting conditions used to prepare the samples. Thus, even this most canonical case of entropically driven miscibility between nanoparticles and polymers remains unresolved at this time.

For anisotropic rod and plate like nanoparticles following the arguments of Onsager it is clear that beyond a critical volume fraction that scales $\sim 1/x$ (x being the aspect ratio), in

the absence of strong matrix-nanoparticle attractive interactions, the nanoparticles form nematic, smectic and columnar phases. Such ideas have been refined using self-consistent and field theoretical methods and indicate that in order 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, for anisotropic nanoparticles, at modest concentrations of nanoparticles (because of the low percolation threshold and overlap concentration), entropic effects will not result in a dispersion of the nanoparticles.

In addition to this entropically driven miscibility, enthalpic effects can also be favorably used to control miscibility (124). Poly(2-vinylyridine) mixes easily with spherical silica nanoparticles because of the favorable hydrogen bonding interactions between the polymers and the substrate. Poly(ethylene oxide) readily intercalates the galleries of unmodified smectite clays, presumably due to the formation of crown ethers with the charge-balancing interlayer counter-ions and an additional entropic gain by releasing confined water molecules previously bound to the metal counterion (151). Similarly, there have been many efforts to modify the surface functionality of the particles with short ligands so as to improve miscibility, the most notable being the miscibility of organically modified clays and covalently functionalized carbon nanotubes with a variety of commercial thermoplastic and thermosets (41, 98). Such ligands reduce particle-particle attractive interactions analagous to steric stabilization of colloids and provides additional avenues to improve enthalpic interactions between the matrix and the nanoparticle. A variation on this idea is through the use of zwitterionic surfactants that act as compatibilizers between carbon nanotubes and poly(ε-caprolactone), with the

surfactant forming hydrogen bonds with the polymer and favorable interactions with the nanotubes through ionic interactions with defect sites along the nanotube (99).

There has also been considerable interest in using polymer grafted nanoparticles to affect the miscibility between polymers and nanoparticles. Early work of Hasegawa et al. (58) have considered this case for large colloidal particles, and found that miscibility occurs as long as the free matrix chains are lower in molecular weight than the brush chains. Since both the matrix and the brush chains have the same chemical structure, this change in miscibility is entropic in origin and attributable to the concept of "brush autophobicity" (57, 67, 97, 124, 162, 168). Recent work by Green and Mewis (52) and by Wang et al. (155) have extended these ideas to the case of nanoparticles and have found similar results. It thus appears clear that controlling the length of the grafted chains vs. the matrix chains of the same chemistry can serve as a very sensitive handle on the miscibility of grafted nanoparticles into polymer matrices. The technological implications of such brush autophobocity is quite dramatic – the concept of using either end-grafted polyolefins of modest molecular weight as compatibilizers for polyolefins and clays and nanotubes has failed to produce true stable nanocomposites with significantly improved properties (93, 156). On the other hand, the use of lightly functionalized (such as maleic anhydride treated) polyolefins, while not resulting in optimized dispersions of the nanoparticles, has resulted in significantly improved mechanical properties and therefore commercial applications (64, 108).Lastly, mixing and dispersing with flow fields (especially shear) and infiltration of aerogels or xerogels of dispersed nanoparticles have been used to prepare polymer nanocomposites with highly dispersed nanoparticles (11, 31). The use of shear to exfoliate clays and nanotubes in enthalpically favorable or neutral polymers has been demonstrated and is

critical for the integration of nanocomposite manufacturing using polymer processing equipment. Paul and coworkers have hypothesized (31), and Vaia et al have used computer simulations to verify (136), that a layer-by-layer exfoliation is perhaps the dominant mechanism for such dispersion at least for the enthapically favored case. The stability (post-shear) of such dispersions is highly dependent on the nature of the polymer nanoparticle interactions i.e., thermodynamic stability, the viscosity of the polymer matrix and the ability of the nanoparticles to percolate and form a kinetically trapped network (82, 118). In this context, a significant challenge is to garner a true understanding of the relationship between percolation, orientation, particle size and shape and perhaps polydispersity, and 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.

2.2 Structure

When one thinks about the structure of polymer nanocomposites two points are implied. They are (i) the spatial distribution or morphology of the nanoparticles, whether they are well dispersed, agglomerated or assembled into superstructures; and (ii) the conformations assumed by the polymer chains in the presence of the nanoparticles.

2.2.1 Grafted - Particle dispersion in polymer melts: As discussed above, there are multiple experimental and theoretical reports which suggest that particles with grafted chains can be readily "mixed" with polymer melts with the same chemical structure as the brush (1, 7, 8, 17, 39, 47-49, 52, 57, 58, 87, 94, 122, 123,

141, 163, 165, 169). A growing consensus is that the composite will have well dispersed nanoparticles if the matrix polymer is shorter than the brush, but immiscible otherwise. While variables such as the graft density and particle radius are also predicted to play a role, the overall point is that only phase separation phenomena are observed/predicted in this context. Thus, all of the works to date apparently suggest that we can obtain the extremes of either the particles being aggregated into large spheres or uniform particle dispersion. No other, intermediate, structures appear to have been obtained by any of these workers. Exceptions to this statement are recent findings that densely grafted particles apparently crystallize (presumably into an FCC lattice) when present in large concentrations in a lower molecular weight matrix (47, 101, 105, 106).

In contrast to these past works, there is simulation and experimental work which considers the behavior of fullerene nanoparticles grafted with a relatively low grafting density of polyethylene oxide chains. When a fullerene is functionalized with only one PEO chain and placed in water, it behaves analogous to a traditional amphiphile since the fullerene is hydrophobic while the PEO is hydrophilic (85). Experimentally, such "linear" amphiphiles assemble into cylinders, sheets etc. following well developed ideas in this field (40, 170). For fullerenes with multiple PEO grafts which are uniformly distributed on the particle surface, assembly into string-like and branched polymers has been found in computer simulations (13, 40, 114, 115, 138). These simulations suggest the following physical picture: even though the particles are uniformly grafted with

the chains, there is a strong propensity for the hydrophobic particle cores to contact each other to shield themselves from the water. Due to the relatively low grafting density, this process is achieved by forcing the PEO chains "out of the way", resulting in an anisotropic effective interparticle potential, and hence anisotropic self-assembly.

Experimentally, in the limit of low grafting densities it was found that spherical silica nanoparticles isotropically grafted with polymers self-assemble into a range of superstructures when they are dispersed into the corresponding homopolymer (12, 52, 57, 79, 80, 92). The results shown in Figure 2, which are based on TEM, are corroborated by independent x-ray and neutron scattering. Theory and simulation (see Figure 3) (13, 60) 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) (37). 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. Both theory and simulation thus show that the polymer grafted particles readily assemble into "block copolymer-like" morphologies, which balance core-core attractions and brush entropy.

In contrast to these low grafting density results, the behavior at higher grafting densities leads to the formation of cubic structures for the undiluted functionalized nanoparticles as has been anticipated for highly functionalized star polymers (47). Curiously, the conformations of the chains in such hybrids, are consistent with the mean-field predictions of Daoud and Cotton and indicate that in such concave brushes, the chains, when long enough, because of space filling adopt ideal conformations (153). Further, these hybrid nanoparticles with high grafting density behave as soft-spheres, with a repulsive potential extracted from the scaling of the equilibrium modulus that scales as roughly r^{-12}.

Structurally, dilution of such grafted nanoparticles with homopolymers (upto several times the grafted chain length) does not alter the ordered structure down to roughly 25 vol % of grafted nanoparticle and below which a liquid-like ordering for the nanoparticles (not a gaseous dispersed state). Further, for blending with matched molecular weight homopolymers leads to chain size scaling that is consistent with good solvent conditions. On the other hand, for cases where the free homopolymer is thrice as long as the grafted chains, the chain size scaling is consistent with that of chains in a poor solvent.

The situation is vastly complicated when the homopolymer that is attached to the surface is replaced by a block copolymer that can microphase-separate. The competition between the interactions between the polymer components and between the polymer components and the nanoparticle along with steric constraints imposed by the surface and the grafting density are likely to result in

significantly altered meso-scale organization, as recently shown (152). Nevertheless, 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 need to be explored and compared to that of ABC triblock copolymers and their blends (36, 50).

2.2.2 Structure of Anisotropic Nanoparticle Based Nanocomposites

The structure of nanocomposites with anisotropic nanoparticles is complicated by the range of length scales associated with the individual nanoparticles and their ability to organize themselves into mesoscale structures that can either be 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 flexibility of the layers is seen in exfoliated graphene through electron microscopy, and in exfoliated layered silicates and single walled carbon nanotubes through scattering measurements (125-127, 140). We note that there have been several reports for large persistence lengths in carbon nanotubes and these might be a result of either their observation in vacuum (without an interacting solvent) or rigidification due to the template surrounding the nanotube (as in DNA stabilized CNTs). Such flexible anisotropic nanoparticles can have significant effect on the property

enhancement sought in mechanical, barrier and electrical applications and in some cases severely limit the extent to which property enhancement can be acheived. Processing, especially the use of flow fields such as extensional and shear fields, can remove the kinks and folds observed in such dispersed nanoparticles and when they are trapped in a crystallized or vitrified polymer matrix, recover some of the property enhancements sought (25). On the other hand, materials that naturally incorporate layering such as in multi-walled carbon nanotubes and silicic acid based platelets, the individual nanoparticles are several nanometer thick for their smallest dimension and become significantly rigid with large persistence lengths (125-127).

Starting from well dispersed (i.e., individualized) nanoparticle hybrids, with increasing concentration of nanoparticles, the structure of the nanocomposites along with their rheological and mechanical (and possibly electrical) properties are dominated by the formation of sample spanning percolated network structures. The percolation threshold scales inversely with effective aspect ratio of the nanoelement and can occur at concentrations significantly smaller than those of their isotropic counterparts. In semi-dilute dispersions (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 microns in size and consisting of a mesh of dispersed nanoparticles. Such fractal like behavior results in "universal" scaling (dependent only on the relative magnitude of the

interactions between the nanoelements and the interactions between flocs) of the linear elastic network modulus and time-temperature-composition superpositioning, of the critical strain for shear-thinning and of the damping function that characterizes the non-linear 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 intra-floc interactions, the elastic strength scales with the number of nanoparticle – nanoparticle contacts and therefore a good measure of the dispersion quality (22, 23). At high concentrations, as has been demonstrated for the case of carbon nanotubes, the nanoparticles form liquid crystalline domains that exhibit all of the optical characteristics associated with small molecule and polymeric liquid crystals (100).

Such structural hierarchy affects the shear rheology properties and is manifested in several important findings summarized here. Ren et al observed several features in the steady shear behavior of layered silicate nanocomposites in the semi-dilute regime (82, 117): (i) The steady shear viscosity was significantly lower and exhibited a weaker shear rate dependence than the linear oscillatory properties i.e., the data do not conform to the empirical Cox-Merz rule that is applicable for homopolymers; (ii) 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 on to a single mastercurve; (iii) Observation of a stress overshoot during the onset of steady

shear in a polymer matrix that does not demonstrate such overshoots on its own. Kharchenko and coworkers have reported the flow-induced properties of MWNTs network in polypropylene matrix where significant shear thinning and more importantly large and negative normal stress difference 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 naneoelements within the floc (24). It has been conjectured that under steady shear, the flocs locally rearrange in response to the applied deformation and result in cluster-cluster collisions and jamming of the network elements that gives rise to the observed stress overshoot. With continuous shearing and when the local stress exceeds the yielding stress, the network bonds break and the network flows until a final steady state is reached where 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 for the case of dispersion of anisotropic nanoparticles. Polymer nanocomposites 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 the structure is intrinsically metastable and disordered. This 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. 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 (27). On the other hand, Bonn and coworkers have demonstrated that anisotropic laponite based colloidal suspensions exhibit many of the same aging and rejuvenation characteristics observed in their isotropic counterparts (16).

Polymer nanocomposites with anisotropic nanoparticles exhibit many of the characteristics common with soft colloidal dispersions such as weak low-frequency dependence for the quiescent state moduli, and the logarithmic scaling of the disorientation of parallel aligned layers (Figure 4) (118, 147, 153). However, these nanocomposites do not exhibit the crucial similarity to the aging in soft colloidal dispersions: the viscoelastic data indicate liquefaction with increased waiting time rather than increased solidification with increased waiting time (16, 27). Importantly, for such anisotropic materials, any theoretical development has

to account for the orientation or orientability of the dispersed particles. Further these indicate that the processing of these materials is non-trivial and suggest that quiescent holds rather than pre-shearing can improve processability.

2.2.3 Characterizing Structure of Nanocomposites

Quantitative characterization of the dispersion and orientation state of nanoparticles and the polymer matrix are critical towards fundamentally being able to develop structure – property correlations. However, such efforts are stymied partly because of the range of length scales associated with such nanocomposites but also due to polydispersity and heterogeneity of the nanoparticles. 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 state of dispersion and arrangement of the polymer and nanoparticles over size scales ranging from nm to μm, and are often used in combination to provide detailed information on the hierarchical morphology usually present in such nanocomposites (79).

Electron and force microscopy has been most extensively used to determine the nanoscale dispersion in different nanocomposites, and with aid of image analysis of several tens of such micrographs for each sample, quantify the dispersion and

orientation of the nanoparticles (64, 166). The development of 3 dimensional reconstruction, stereology and high resolution TEM and SEM method are significantly improving the understanding of the three-dimensional distribution and dispersion of the nanoparticles (79). On the other hand, radiation scattering methods provide an ensemble average of the dispersion and orientation state and require the development of analytical models to quantify the dispersion and orientation. The efforts of Vaia, Schaefer and Pederson to develop such modeling tools has allowed for a more thorough quantification of the dispersion state of nanocomposites (126, 152).

While significant improvements in the quantification of the dispersion and orientation state of nanocomposites has been achieved, it is clear that significant more efforts and the development of rapid experimental tools and robust modeling tools to interrogate and quantify the dispersion and orientation state at various scales is necessary.

Chain Structure: The perturbation of polymer chain configurations by nearby surfaces has been studied for many years. Two different situations have been experimentally addressed in the past: 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 (71). For example, 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, or no change, have all been found from the few experimental studies that have been conducted (102, 130, 149)! These studies, however, differed in the types of nanoparticle dispersed in the host polymer, the nanoparticle size and the quality of the nanoparticle dispersion. In the two cases where the host polymer was polystyrene, 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 only be characterized indirectly by SANS since there is no TEM contrast. TEM visualization in ref. (130), on the other hand, showed that the dispersions were not of high quality. Thus, the dramatically different results of these two studies could be due to 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 (144) shows that chain size is unaffected if the chains are smaller than the interparticle spacing; as the chains are made bigger, initially they shrink after which they expand, in a manner similar to chain in the presence of obstacles. This intriguing prediction still needs to be verified, but it may provide us with the best possible means of understanding chain dimensions in the presence of nanoparticles.

On the other hand, the studies of polymers confined between anisotropic nanoparticles or in anisotropic pores has indicated significant changes in the chain conformations. For instance for the case of polystyrene (in toluene) confined to the pores of vycor glass (with pores of 7 nm diameter) exhibited smaller radii of gyrations than in the bulk (83).

Interestingly, the molecular weight dependence for the reported radius of gyration goes from $M^{\sim0.54}$ for the bulk solutions to $M^{\sim0.44}$ for the confined polymer chains. Polymer chains when confined between plates (with confining distances of $\sim$ 2 nm) in either the melt or with good solvents for the polymer, form two-dimensional random walks with no interpenetration. Such structures might have significant consequences in terms of the topological arrangement and barriers that intimately govern macroscopic polymer mobility and stress-transfer mechanisms. Clearly, systematic studies of chain conformations and their dynamics with increasing distance between confining plates are needed to truly understand the nature of confinement in such nanocomposites.

(ii) **Properties & Applications & Challenges to Integrate**

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 (5, 128). The first demonstrated example of thermomechanically reinforced polymer nanocomposite was that of nylon-6 layered silicate hybrids prepared by Toyota Central Research and demonstrated simultaneous improvements in stiffness and heat distortion temperature while not affecting the impact properties (150). Recent demonstrations of these synergistic property enhancement have been observed in a 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 (34, 133, 134). A functionalized nanotube (with a $CO_2(CH_2)_{10}OH$ functional group) was used to reinforce

the polymer and the tensile stress vs. strain for one such nanocomposite along with a comparable PDMS network with roughly the same cross-link density (based on solvent swelling) are shown in Figure 5. Comparison of the tensile modulus and the elongation – at – break for a series of nanocomposites is shown in Figure 6. 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 or the Mori-Tanaka models (108). Following the finite-element modeling efforts of Boyce and the experiments of Thomas et al (20, 55), it has become clear that the nanoparticles, and especially anisotropic ones, can lead to regions of stress concentration near the leading edge of the particle. These along with the ability to finely tune the thermal properties (and hence mechanical properties) of polymers near the surface of nanoparticles, has led to a recent interest on understanding and tailoring the interface between the polymer and the nanoparticle in order to maximize property enhancement (111, 120, 121, 124, 129). Outstanding issues that remain to be understood are the role of the nanoparticle and the interactions between polymers and nanoparticles on long-term fatigue life and the physical aging characteristics. Preliminary hints about the significantly altered aging characteristics have recently been reported for nanocomposites and suggest that the nanoparticles cause a slowing down of the long-term aging characteristics presumably because in the cases studied the glass transition temperature of the polymer was somewhat elevated by the incorporation of nanoparticles. There has also been indications that the nanoparticles cause the appearance of a rapid relaxation process that

might cause significant aging prior to the slow process and suggest a heterogeneity of populations and environments in such nanocomposites. While having signifgicnat consequences on the long term use of polymer nanocomposites, it is clear that systematic studies to unravel the details of aging are required.

The thermomechanical reinforcement observed in several thermoplastic based hybrid systems, including the nylon-6 layered silicate hybrids prepared by Toyota Research (150), have been attributed to the ability of the nanoparticles to alter crystalline morphology including changes in polymorphs, providing nucleation and templating surfaces or providing a stabilization of the amorphous phase. Most notably, for the case of nylon-6 clay nanocomposites, the clays stabilize the usual high-temperature γ-phase polymorph at all temperatures, avoiding the Brill transition, and therefore fundamentally alter the thermomechanical properties of the nylon (88). Similarly, for the case of PVDF, well-dispersed clays stabilize the piezoelectric β-phase, without the use of any flow-processing that is usually required to stabilize it (5). The formation of the β-phase leads to not only an electroactive material but also a material that is significantly more ductile than the α-phase based PVDF. The significant improvements observed in the reinforcement of poly(ε-caprolactone) nanocomposites with dispersed single walled carbon nanotubes is thought to occur from the nucleation of polymer crystals by the highly aligned nanotubes resulting in a "shish-kebab" structure with three-dimensionally aligned structures from the unit-cell to the polymer lamellae to the nanotubes (25). Finally, such dispersed nanoparticles can also lead to a breakdown of crystallinity of the polymer as has been observed in nanocomposites of high molecular weight poly(ethylene oxide) with dispersed carbon nanotubes, with the melting point of PEO reduced by over 30 ºC with the incorporation of less than 1% nanotubes (26).

Orientation and texturing of the nanoparticles can lead to highly improved and often tailorable anisotropic mechanical properties in such nanocomposites (25). Methods for orientation and texturing include the use of various external fields, most notably shear and elongational flow, electric, magnetic, optical and interfacial effects. However, strategies for optimizing such reinforcement remain somewhat elusive with the challenging ideas remaining as to how the pioneering work of Tarquato and others translate to such nanoparticles and further to understand the role of the polymer – nanoparticle interface in dictating such property changes. Gusev and Rozman have shown through theoretical calculations that a web-like morphology is capable of significantly improving the shear moduli than a comparable random or hexagonal ordered structure of isotropic particles (9). Yakobson has suggested that in order to truly exploit the mechanical properties of nanotubes, they need to be arranged in a super-lattice that is highly interpenetrating and can optimize between two alternative routes of brittle bond breaking and plastic relaxation to maximize mechanical properties (33).

Electrical Properties:

Due to the significant contrast between the electrical and dielectric properties of many nanoparticles and many commodity polymers, one of the attractions in the preparation of polymer nanocomposites has been in the development of lightweight materials with potential applications in electrostatic discharge to electrical interconnects to conductive coatings to electromagnetic shielding with conductivities tailored between 10^{-6} to 100 S/cm. Nanotubes and metallic nanorods are typically dispersed in polymer matrices for the development of conductive nanocomposites. Vaia and others developed conductive elastomers with the incorporation of carbon nanofibers (78) or multi-walled carbon nanotubes (77) and have shown that such materials exhibit significantly improved

mechanical properties along with electrical conductivity and therefore the development of a new generation of stimuli responsive materials. Nevertheless the critical issues to consider include, the development of nature of the percolative structures, formation of hierarchical structures (i.e., fractals) and their impact on percolative behavior, the orientation state of nanoelements and their mesoscale ordered structures and their consequences on electrical conductivity, and finally the junction resistance beween matrix and nanoparticle and between nanoparticles, and still require significant theoretical understanding and practical manifestation of intriguing concepts. Functionalization of nanotubes and nanorods, often used to improve dispersion, also result in a significant disruption of the conductive pathways and leads to a significant decrease in the measured conductivity as compared to the theoretically expected values. Orientation of the nanoparticles can also lead to significant anisotropy in the electrical conductivity of such nanocomposites. Recently, Forest and coworkers have examined the role of orientation of nanoparticles on the anisotropic percolation of nanorods and have demonstrated theoretically the ability to transform these structures, at a fixed loading of nanoparticles, from a three-dimensional to a two-dimensional to a one-dimensional percolating structure with changing orientation state, caused in their case by the application of shear.

A particularly interesting application is that of metallic nanorods, highly oriented but internally interrupted in an insulating polymer matrix, that can demonstrate a dielectric strength in excess of 10^5 at concentrations (and orientations) that are close to the percolation and could result in their potential 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 inter-gallery, 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 (159). Significant efforts have been directed towards the preparation of poly(ethylene oxide) – lithium/sodium montmorillonite for such applications. The ether based polymers are capable of forming crown-ether complexes with the lithium and allows for rapid mobility of the lithium ion. Significant challenges remain in the preparation of such materials that require highly oriented films with over 70 wt % inorganic material that can resist cracking.

Gas Permeation:

The barrier properties of polymers can be significantly altered by the inclusion of nanoparticles, and especially anisotropic ones, for three underlying reasons: (i) The increased physical "tortuosity" of the diffusion path because of the well-dispersed nanoparticles; (ii) Changes in the local and segmental mobilities and the glass transition temperature of the polymer; and (iii) Alterations in the "sorption" due to competitive interactions between the penetrant molecules, nanoparticles and the polymer matrix. The increased tortuosity dominate the changes in barrier properties observed for polymer nanocomposites and are largely described by continuum based models such as those suggested by Cussler (35) and improved by Bharadwaj (14). Orientation of the anisotropic nanoconstituents is critical important in the increase in tortuosity and the effect of orientation on the permeability has been captured theoretically by Bharadwaj. Nanocomposites of exfoliated clays in poly(ethyelene terephthalate) have shown 10 to 15

fold reduction in oxygen permeability with 1 to 5 wt % clay addition, largely attributable to the increased tortuosity, are beginning to be find commercial applications. On the other hand, recent work of incorporating nanoporous layered aluminophosphates or silicates (that permit transport of protons while blocking methanol) in Nafion membranes results in maintaining proton conductivity close to that of neat Nafion while reducing methanol permeability by an order of magnitude (63).

Flame Retardancy:

Polymer nanocomposites based on nanoplatelets and nanotubes (and nanorods) have been suggested to provide a paradigm for improved flame resistance because of reduced gas transport, radical scavenging activity of the high surface area nanoparticles, increased melt viscosity, and stable char formation and therefore prevention of continuous surface regeneration of fuel for the combustion process (43). Critical to the stable char formation is the presence of a percolated filler network structure to provide a mechanical framework of high-temperature stable nanoparticles (157).   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 and thereby reducing the potential for flame propagation to adjacent areas. This reduction in peak heat release rate is strongly correlated with the increased char formation and the creation of percolated networks of the nanoparticles. Changes in the degradation mechanism of the polymer in nanocomposites, through the amount and types of degradation products, can also significantly improve fire retardance as has been observed for several polymers including polystyrene (PS), polyamide-6 (PA-6) and ethylene-vinyl acetate copolymers (EVA). This change has been ascribed to secondary

reactions (hydrogen abstraction, radical recombination reaction, extensive random scission, various intermolecular reactions etc) that can lead to new polymeric products which must again undergo thermal degradation. Radicals have a substantial stabilization energy, e.g., styryl radical from polystyrene or an allylic radical from EVA, will exist and be retained in the nanocomposite long enough to participate in additional reactions, while radicals which do not have this stabilization energy, e.g., a methacrylate radical from poly (methyl methacrylate) or a radical adjacent to a nitrile, from SAN, are not long lived and will not recombine (69).

Since 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 and making 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 the increased awareness that a new nano-based active flame retardancy needs to be pursued. A promising route for new materials include 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.

<u>Multifunctionality: Piezoelectric / flexoelectric response; Magnetorestrictive materials</u>

One of the most exciting developments in the generation of multifunctional nanocomposite material has emerged from the recent study of size-dependent electromechanical coupling and significant size-dependent flexoelectricity in nanomaterials. Sharma and coworkers have recently adapted the original work of Cross

to nanoscale materials and shown that the theoretical origins of piezoelectricity in non-piezoelectric materials and the notion of giant piezoelectricity at the nanoscale emerges from flexoelectricity with a non-vanishing, but small, flexoelectric coefficient and the development of large strain gradients in the case of mechanically mismatched polymer nanocomposite materials. Experimental manifestation of such piezoelectricity from non-piezo components is an outstanding problem due to the requirement of non-centrosymmetric shape for the nanoparticle and their periodic arrangement on macroscopic lengthscales. One of the areas where flexoelectricity is likely to play a significant role is in the area of high energy density nanocapacitors and continues 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, 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 non-uniform. Recently Ounaies and coworkers have developed an electrostrictive material from amorphous polyimide nanocomposites by addition of small quantities of carbon nanotubes (107). Most importantly, these improvements were achieved at much lower actuation voltages, and were accompanied by increase in both mechanical and dielectric properties.

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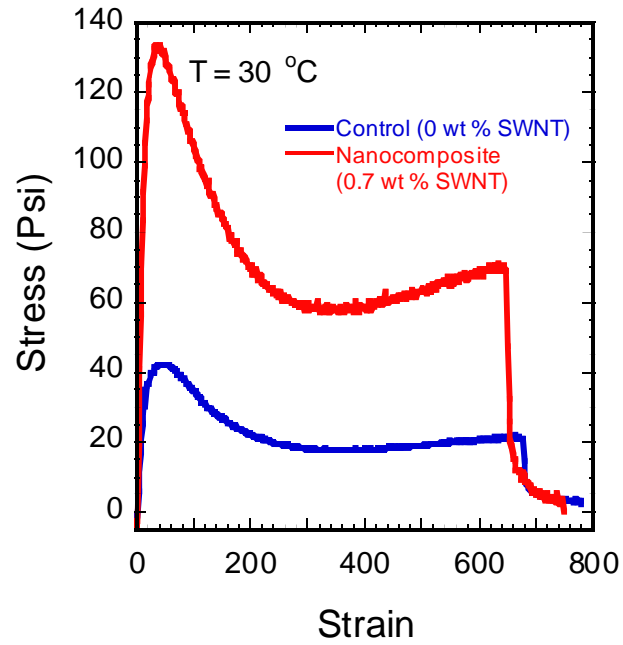
Figure 5: Tensile testing of 0.7 wt % SWNT (functionalized) filled PDMS nanocomposite compared to a similarly cross linked PDMS network. The sample was stretched at a rate of 2 mm / min in a mini-Instron tester.
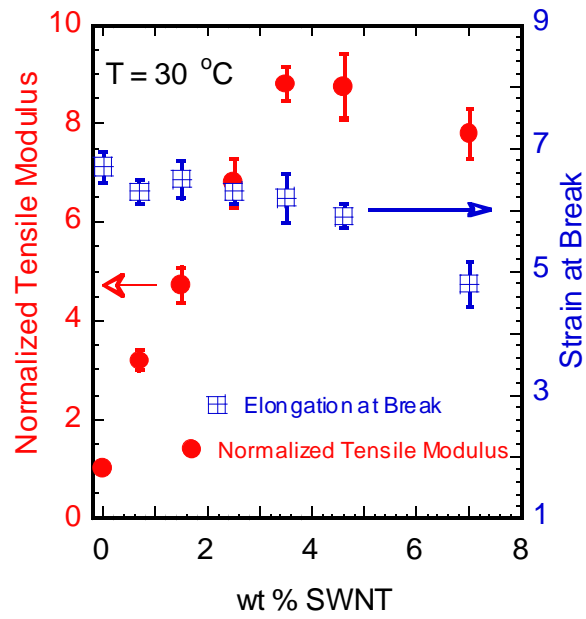
Figure 6: Composition dependence of the normalized tensile modulus and elongation- at

– break for functionalized SWNT-PDMS networks.
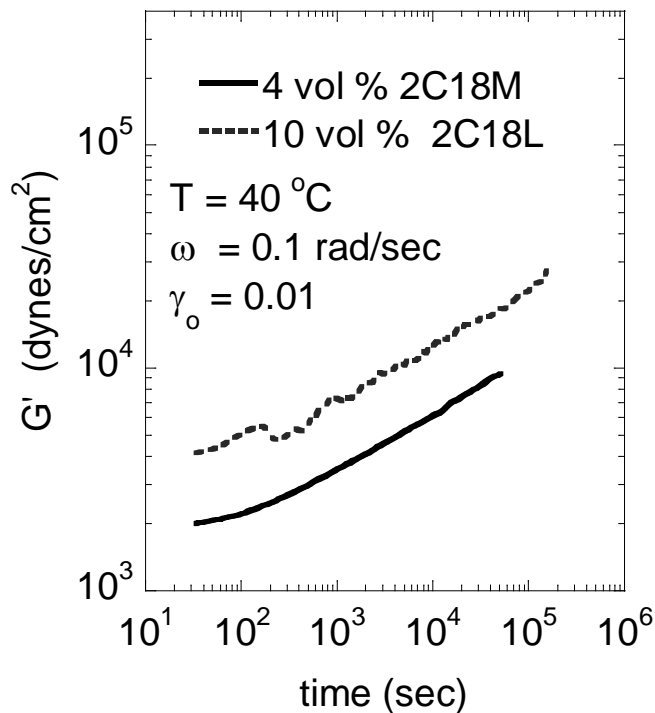
Figure 4. Small amplitude oscillatory elastic moduli (G') monitoring of the
recovery after shear alignment for the two hybrids of laponite (22 wt %
2C18L) and montmorillonite (8.5 wt % 2C18M) dispersed in an elastomer
matrix. Recovery measurements were performed at T = 40 °C, ω = 0.1
rad/sec and γ_o = 0.01. The values of linear viscoelastic G' at ω = 0.1
rad/sec for the quiescent unaligned hybrids are ~ 4.5 x 10^5 dynes/cm^2 for
the 2C18M and ~ 1.2 x 10^6 dynes/cm^2 for the 2C18L based hybrids.