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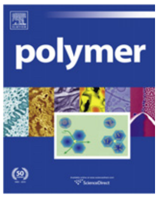

Feature Article

Current issues in research on structure–property relationships in polymer nanocomposites

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A B S T R A C T

The understanding of the basic physical relationships between nano-scale structural variables and the macroscale properties of polymer nanocomposites remains in its infancy. The primary objective of this article is to ascertain the state of the art regarding the understanding and prediction of the macroscale properties of polymers reinforced with nanometer-sized solid inclusions over a wide temperature range. We emphasize that the addition of nanoparticles with large specific surface area to polymer matrices leads to amplification of a number of rather distinct molecular processes resulting from interactions between chains and solid surfaces. This results in a “non-classical” response of these systems to mechanical and electro-optical excitations when measured on the macroscale. For example, nanoparticles are expected to be particularly effective at modifying the intrinsic nano-scale dynamic heterogeneity of polymeric glass-formation and, correspondingly, recent simulations indicate that both the strength of particle interaction with the polymer matrix and the particle concentration can substantially influence the dynamic fragility of polymer glass-formation, a measure of the strength of the temperature dependence of the viscosity or structural relaxation time. Another basic characteristic of nanoparticles in polymer matrices is the tendency for the particles to associate into extended structures that can dominate the rheological, viscoelastic and mechanical properties of the nanocomposite so that thermodynamic factors that effect nanoparticle dispersion can be crucially important. Opportunities to exploit knowledge gained from understanding biomechanics of hierarchical biological protein materials and potential applications in materials design and nanotechnology are among future research challenges. Research on nanocomposites formed from block copolymers and nanoparticles offers huge promise in molecular electronics and photovoltaics. The surface functionalization of nanoparticles by the grafting of polymer brushes is expected to play important role in the designing of novel organic/inorganic nanocomposite materials. The formation of bulk heterojunctions at the nanometer scale leads to efficient dissociation of the charge pairs generated under sunlight. Based on the presentations and discussion, we make recommendations for future work in this area by the physics, chemistry, and engineering communities.

1. Introduction

Polymer nanocomposites offer the possibility of substantial improvements in material properties – such as shear and bulk modulus, yield strength, toughness, film scratch resistance, optical properties, electrical conductivity, gas and solvent transport, among many – with only very small amounts of nanoparticles

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(NPs) dispersed in the polymer matrix. It has been known for about a century that the addition of nanofillers such as carbon black to rubbery polymers has a strong impact on the properties of these materials [1,2]. Similar effects have been reported in literature for polymer glasses [3–6] as well as for semicrystalline polymers [7] filled with NPs over wide temperature and composition range. For example, polymer nanocomposites can attain a substantially greater stiffness, strength, thermal stability and barrier properties at very low nanofiller content compared to plastics filled with traditional micrometer-sized particles. In addition to mechanical and rheological properties, the development of nanocomposites filled with carbon nanotubes and graphene sheets is particularly effective in modifying electrical properties of nanocomposite materials [8,9]. However, despite the large volume of literature published on the relationships between the nano-scale structural variables and macroscale physical and mechanical properties of polymer nanocomposites over the last 15 years, the understanding of the basic physical origin of these large property changes remains in its infancy. This is partly due to the complexity of polymer nanocomposites, requiring re-considering the meaning of some basic polymer physics terms and principles, and partly by the lack of reliable experimental data. In addition to detailed knowledge of molecular structure of the polymer matrix, the theory also requires a sufficient description of particle dispersion, self-assembly phenomena, particle–chain interactions and nanocomposite preparation processes. In an attempt to facilitate work in this field, we review state of the art of research in the field of polymer nanocomposites with an eye on critical issues that require further theoretical work and for creating a knowledge base for practical applications based on our existing limited understanding. Next, we consider some general observations that motivate the focused investigations of nanocomposite properties discussed below.

Of the many affected “macroscopic” properties, changes in the glass transition temperature, T_g, have been particularly emphasized in the literature, since changes in T_g are correlated with changes in diverse transport phenomena as well as chain relaxation behavior [10–15]. Specifically, both experimental and theoretical studies have indicated a tendency for highly attractive or repulsive NP interactions to increase or decrease T_g, respectively [16,24,25]. This phenomenon has been rationalized in terms of the influence of the NP boundary interactions on the dynamics of polymers within an interfacial “layer” near the NP surfaces. In particular, polymer chains in direct contact with the NP shows a slowing down (increased T_g) or acceleration of dynamics (decreased T_g) when the polymer–NP interactions are attractive or repulsive, respectively [17,24,25]. This observation also led to the suggestion that the inter-particle distance, related to the particle concentration for uniformly distributed NP, plays a role analogous to film thickness in thin polymer films [18]. One has to bare in mind the relative size of a polymer chain compared to micrometer and nanometer-sized particle (Fig. 1). The dramatically larger chain–particle interface area in the case of nanocomposites compared to microcomposites makes effects appearing negligible in microcomposites very prominent in nanocomposites [19].

The state of the dispersion of NPs in the polymeric matrix often has a large impact on the properties of polymeric materials. Unfortunately, it often has proved difficult to form uniform and stable dispersions of NPs in polymer matrices resulting in large variations in properties for systems of the same composition prepared using different techniques. Additionally, the NPs geometry – such as plate or sheet-like particles, nanotubes, or polyhedral nanoparticles – can also have a large impact on property changes, since it can affect both surface energetics and surface to volume ratio [20–23]. The possible underlying mechanisms for nanoparticle clustering have been investigated, considering the roles played by phase separation, as well as self-assembly that may occur before, or *in lieu* of phase separation [24]. In addition, the way, in which the state of NPs clustering and the NPs shape both affect material properties are important for applications and processing [25,26].

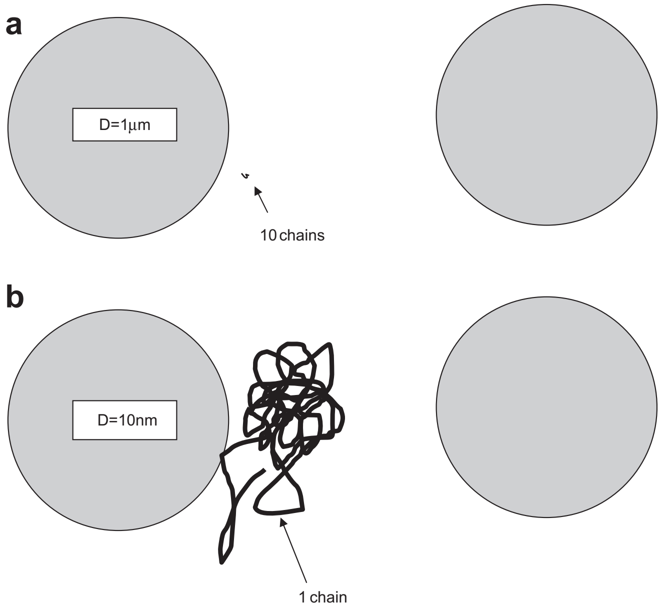


Fig. 1. Simplified view of the relative size of a single polymer chain with $R_g = 5$ nm and particles with diameter $D = 1$ μm at 7 vol.% of the filler, when the average distance between regularly arranged particles is about 2 particle diameters. (b). Simplified view of the relative size of a single polymer chain with $R_g = 5$ nm and particles with diameter 10 nm at 7 vol. % of the filler, when the average distance between regularly particles is about 2 particle diameters.

There has been considerable interest in utilizing particle self-assembly as a “bottom-up” route to new material assembly [27–35]. Such particle self-assembly is of interest because it might, for example, allow us to construct improved polymer nanocomposites with “dialed-in“ properties. Specifically, the ability to assemble particles into desired morphologies should allow us to dramatically increase the electrical conductivity of typically insulating polymers. Similarly, this ability to control particle self-assembly might permit us to synthesize a range of biomimetic materials. As an illustrative example, we point to biomimetic systems where spherical nanoparticles of hydroxyapatite (HA) are used to create tooth enamel and bone mimics. In the former case, it is conjectured that the HA particles are organized by the biological systems into “lines”. These “lines” are then stabilized by a matrix, which subsequently hardens and “freezes in” this organization. In contrast, bone has a uniform dispersion of HA particles in the matrix. Our unique ability to control nanoparticle organization might thus allow us to build such bioinspired systems for an entirely new range of synthetic applications. It has also been shown that structural proteins such as collagen can undergo self-assembly process resembling first-order thermodynamic transitions in forming micro-fibrils which controls to a great extent the mineralization process to form basic building blocks of bones [36,37].

From a rheological point of view, a direct consequence of incorporation of fillers in molten polymers is a significant change in their steady shear viscosity behaviour and the viscoelastic properties [38,39]. Due to the possibility to achieve thermodynamic equilibrium conditions, measurements of composition and condition dependencies of viscoelastic properties in the molten state are generally useful for theoretical analysis of the structure–property relationships in these materials. As the filler nanostructure, the inter-particle and polymer–filler interactions can all strongly influence both linear and non-linear viscoelastic behavior, rheology appears to be a useful technique to obtain reliable experimental data on polymer nanocomposites. Unlike experiments in the glass state below T_g measuring the behavior under non-equilibrium conditions, rheological measurements provide data in a state close to the thermodynamic equilibrium making them more suitable for comparison with theoretical models and computer simulations. On the other hand, ability to predict mechanical properties of solid nanocomposites is indispensable for future design and commercial use of these materials.

Reliable models capable of linking macroscale mechanical properties of solid polymer nanocomposites with their nano-scale structural variables are scarce and not generally accepted. However, the need to establish reliable predictive algorithms for large-scale mechanical properties required for structural applications of composite materials engineered at the nano-scale is highly desired (Fig. 2a). In order to bridge the gap between the discontinuous nano-scale structure and continuum macroscale models, it is recognized that physics-based bridging laws are needed (Fig. 2b, c). In composite micromechanics, the assumption of statistical homogeneity is usually made allowing application of classical continuum mechanics to obtain constitutive equations [40]. If this assumption fails, non-local coupling between stress and strain tensors takes place [41]. In such a case, the ergodicity fails and ensemble and volume averages do not coincide.

As a result, classical continuum mechanics cannot be applied when the length scale of heterogeneity is below 20 nm [42,43]. On the other hand, molecular dynamics (MD) simulations are limited to nano-scale and cannot deal with the micro-scale sized bodies. In order to bridge between nano- and micro-scale, the MD studies assume local nature of the stress–strain relationship which in turn requires that the length scale for internal stress inhomogeneity infinitely exceeds molecular inhomogeneity. This assumption is not valid for glassy polymers containing heterogeneities smaller than 20 nm and, thus, its use leads to considerable errors in reducing experimental data into structurally interpreted properties [44].

The macroscale experiments represent some kind of “averaging/homogenization” of contributions from cooperatively relaxing domains with their “statistical weight” proportional to the total volume fraction of domains relaxing in the same manner. Structural interpretation of these experiments is correct when the length scale of the structural variables is substantially shorter compared to the characteristic length scale of the variation in stress field. i.e., for ergodic systems. In models relating the nanometer structural details to the macroscale properties, the characteristic structural domains are non-ergodic. Thus, much more detail is required to adequately describe and correct bridging algorithms are needed to model their structure–property relationships.

Traditionally, a representative volume element (RVE), used for homogenization in microcomposite modeling, only needed properties of reinforcement, matrix, and some boundary condition based descriptor of the interface [45]. In nanocomposites, the drastic change of local chain dynamics at the nanoparticle interface and change in spatial distribution of relaxation times govern the material response over a broad range of length and time scales. When considering amorphous polymers filled with nanometer-sized solid inclusions, the relationship between stress and strain becomes highly non-local and, thus, reducing the size of the RVE below certain length scale limits applicability of the classical continuum mechanics. This has been proven when considering deformation response of a single macromolecule where force and displacement controlled experiments provided different results [46,47].

Important polymer characteristics needed for developing reliable theoretical models also include more precise description of chain conformation statistics, especially, the effects of the presence of arrays of solid nanoparticles has on it. From this point of view, the number average molecular weight and details regarding the molecular weight distribution, as well as any chemical functionality that can interact with the nanoparticle surface are needed for developing useful models. In addition, to derive suitable bridging laws, the nature of chain entanglements is also of pivotal importance and should be reconsidered for understanding the chain stiffening mechanism, especially, when considering response of polymer nanocomposites over a wide time and temperature scales. Similarly to the corpuscular-wave particle dualism in quantum mechanics, entanglements can be envisioned either as topological constraints expressed using the tube model for solid polymers and as dynamically changing domains of cooperatively relaxing chains expressed in terms of dynamic fragility for polymer liquids [48,49].

Important structural characteristics of the nano-scale reinforcement include more detailed description of the chemical texture of the surface, information regarding the local curvature of the particles in relation to the chain stiffness, and their specific surface area. Latest theoretical modeling suggests that the spatial and time distributions of inter-particle distances in real nanocomposite systems with randomly packed particles are of crucial importance for the experimentally observed enormous chain stiffening. For reinforcement by spherical NPs, more detail regarding the radial size distribution is important for refined predictive model development. Thus, more appropriate descriptors of the specific surface area, distribution of surface curvature and radial distribution of the filler particles are important, since the scale of the response is correlated to the scale of the local perturbation caused by the nanoparticles. Similarly, for anisotropic particles, more detailed descriptors are necessary, including information about spatial and time distribution of particle orientation. It was also agreed that multi-scale descriptions and characterizations at a range of length scales are still needed so that each can be modeled with appropriate governing physics. On a contrary note, it was generally acknowledged that the stiffness and strength of the reinforcing nanoparticles is secondary when considering the bulk mechanical, rheological, and physical properties of this class of nanocomposites.

More critical characteristics are associated with the polymer behavior in the interphase region which prevails over the bulk at very low nanoparticle content even in the case of spherical particles (Fig. 3(a)). Needless to point out that the traditional meaning of the interphase as a continuum layer existing between the particle surface and some distance in the polymer bulk [50,51] becomes no longer valid at the nano-scale. Experiments as well as theoretical simulations suggest that the “thickness of interphase” does not scale with particle size [52], as often proposed [53]. In a simple case of regular cubic lattice of monodisperse spheres, the average inter-particle distance reaches particle diameter D for about 7 vol. % of the filler (Fig. 3(b)), while for random packing of the same spheres, this limit is reached at 2.6 vol% of the filler. For spherical particles with $D = 10$ nm and common amorphous polymer with radius of gyration R_g equal to about 5 nm, at this volume content, all the chains are in contact with particle surface and there is no bulk polymer. Moreover, interphase layer is usually described as a layer with properties distinct from both filler and the polymer bulk or with a property gradient. Such a description is no longer valid at the length scale of a single macromolecule and becomes even more complicated in the case of entangled chains.

Two international workshops on physics and mechanics of polymer nanocomposites were held at Brno University of Technology (Czech Republic) on September 4–5, 2008 and May 27–29, 2009. The aim of the first workshop workshops was to find the bridge between macroscopic properties of polymer nanocomposites and their nano-scale structural variables and to ascertain

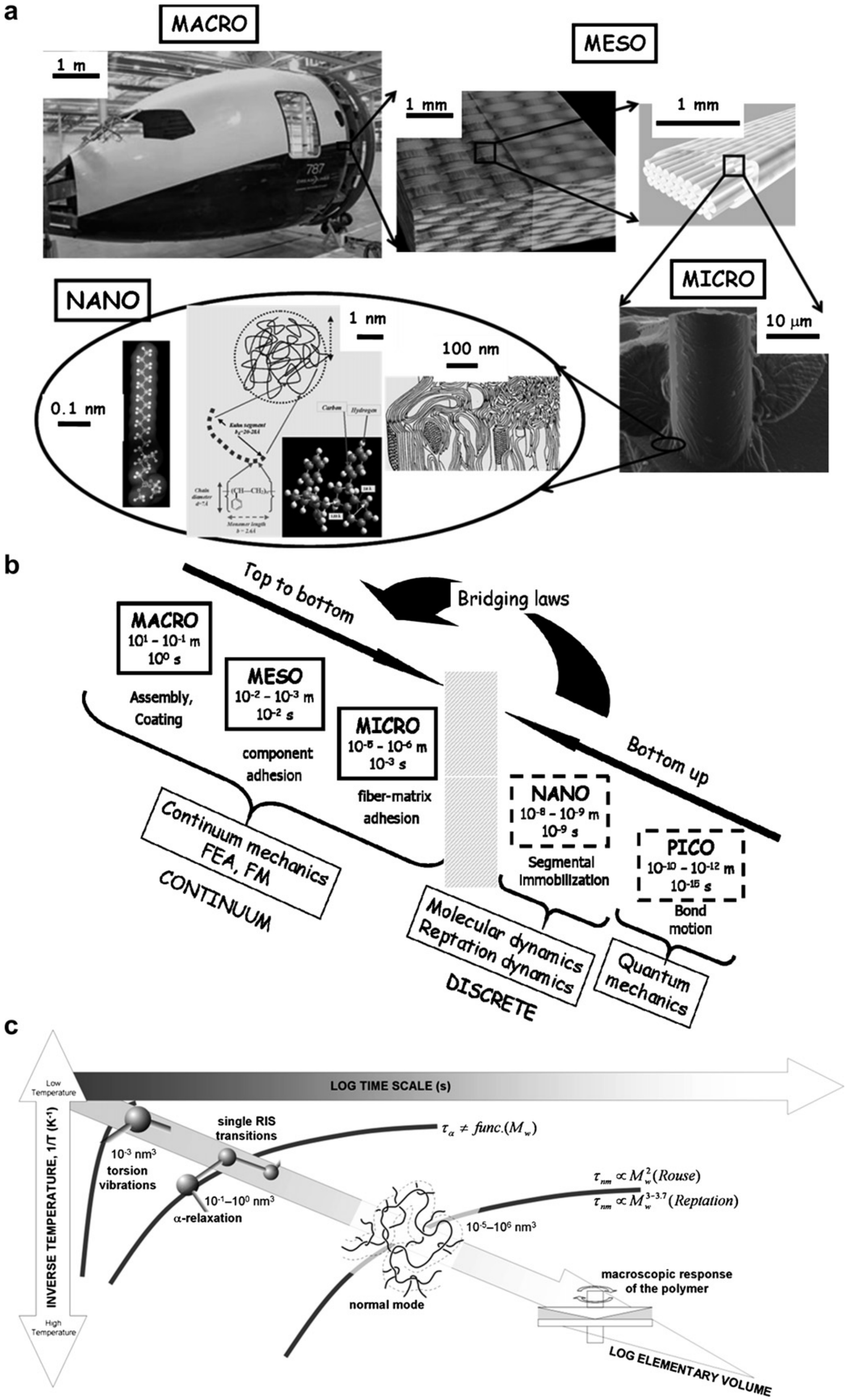


Fig. 2. Hierrachical nanocomposite material structure. Part of the fuselage of Boeing 787 Dreamliner can serve as an example of a large man-made multi-scale composite structure. This polymer composite structure has been designed using the engineering top–bottom methodology within the framework of continuum mechanics. No functional hierarchy exists between the various length scales. (b) Dependence of the matrix modulus, $M_m^* = E_c/f(V_f)$, on the logarithm of the specific interface area, S_f, above T_g using the Guth model (a) and below T_g using the Kerner–Nielsen model (b).(c) Microscopic relaxation processes on the background of the time, temperature and characteristic volume scale.

mechanisms leading to the observed "non-classical" structure–property relationships. The main theme of the second workshop was to address controversies in recent understanding of the effects of polymer–particle interactions on behavior of polymer nanocomposites on both sides of the T_g and on the nature of TD transitions in polymers. Although polymer nanocomposites are under investigation more than forty years (tires, coatings, etc.), we are still far from fully understanding molecular mechanisms responsible for the observed behavior. Research in nanostructured polymers renewed interest in phenomena such as the glass transition, fundamentals of molecular mobility below the glass transition temperature, nature of the chain entanglements, etc. As a result of the workshop discussions, discussion leaders of both workshops have reviewed the outstanding issues in the research of physics of these systems and identified some of the important fundamental issues to be addressed in further research on polymer nanocomposites. We now turn to more focused summaries of the issues discussed above as they were described at the meetings.

2. Effects of nanoparticles on the glass-formation in polymer nanocomposites

There is a number of mechanisms that have been identified by which nanoparticles influence the properties of the polymer matrix to which they are added. The formation of self-assembled clusters or aggregate formation provides a common effect. The 'bridging interactions' between polymer chains mediated by the particles play the role of effective polymer cross-links. This later effect is particularly important in connection with the Payne effect where the cross-links can 'lock in' the otherwise transient entanglements of the polymer melt. These effects were also considered in the case of microcomposites, however, due to small interface area, the number of affected chains was negligible up to very large filler volume fraction [54]. Moreover, the moment of inertia of the micrometer-sized inclusions is several orders of magnitude greater than that of the individual polymer chain. In polymer nanocomposites, both of these assumptions become invalid. The present section focuses on a more subtle effect of the NPs on organization of molten polymer chains in the presence of the particles, an effect hard to understand from the continuum theory of filled polymers.

Changes of T_g, while informative, provide only a limited understanding of how NPs affect the properties of glass-forming polymer melts. It is also natural to expect that strength of the temperature dependence of the dynamic properties such as shear viscosity, η, upon approaching T_g, referred to as the "fragility" of glass-formation, might also be altered so that the very nature of the glass transformation process changes with the nano-sized additive. Fragility changes with adding NPs are expected on theoretical grounds, based on the finding that any factor that influences the molecular packing in the glass state ($T < T_g$) alters the fragility of glass-formation. The NP studied by our molecular dynamics simulation should be particularly effective at modifying molecular packing since their size is roughly commensurate with the heterogeneity scale of fluids near their T_g (i.e., 2 nm–3 nm in real glass-forming liquids).

The new simulation studies [17] for unassociated NP corroborate that the addition of NP can change the fragility of glass-formation and, moreover, multiple measures of fragility all consistently indicate that fragility increases or decreases depending on the nature of the polymer–NP interaction. Attractive NP made the system become more fragile, while repulsive interactions made the nanocomposite a stronger glass-former and that this effect becomes more pronounced with increasing NP volume faction, V_f.

An examination of these fragility and glass transition temperature changes shows that the presence of the particles perturbs both the local and global polymer matrix dynamics. The presence of the attractive or repulsing polymer–NP interaction led to an increase or decrease of the particle relaxation time relative to the pure polymer in a 'layer' about the particles, respectively, and these changes were correspondingly reflected in both T_g and fragility increasing. Changes in the local force constant fluctuations in these mixtures implicate changes in the elastic constant fluctuations, which are presumably related to fluctuations in the local molecular packing within the polymer matrix. These observations indicate that the NP can 'polarize' the configurational state of the polymers to alter the nature of the molecular packing about the particles and thereby alter the intrinsic breadth of the glass transition process. Evidence supporting this scenario was discussed, although it is pointed out that the observed trends may be more complicated in polymer matrices involving hydrogen bonding polymers where self-assembly competes with the glass transformation process. Taken together, these results nonetheless indicate that the NP can induce large non-continuum effects on the nanocomposite materials, even in the regime of good dispersion. This effect is quite apart from those involving particle-induced cross-linking and self-assembly.

3. Mechanisms for nanoparticle clustering and effects on material properties

In this section, we review underlying mechanisms for NPs clustering, considering the roles played by phase separation, as well as self-assembly that may occur before, or in lieu of phase separation. In addition, we discuss how the state of NPs clustering and the NP shape both affect material properties important for processing and applications. The simulations discussed were performed in an equilibrium state, i.e., substantially above the matrix T_g.

The existence of thermodynamically phase-separated states is ubiquitous in mixtures. NP clustering via phase separation is particularly common if there are unfavorable polymer–NP interactions, relative to the NP–NP interactions. Indeed, when polymer–NP interactions are highly unfavorable, there may be no thermodynamically stable NP dispersion. Here, we focus on situations where a stable dispersion is possible, and examine the NP clustering process. The state of dispersion is affected by a number of factors, including particle loading, inter-particle interactions, and temperature. We have found that the specific heat can be a reliable metric to determine the state of dispersion, since specific heat is sensitive to energy fluctuations related to particle dispersion. Specifically, when particles are in a stable dispersion or clustered state, there are little fluctuations in energy, since the "phases" are highly stable. However, between the limiting assembled and dispersed states, particles can aggregate into small, short-lived clusters, resulting in large fluctuations energy, and hence large specific heat. To illustrate this, we plot specific heat as a function of temperature for several loading fractions and find a pronounced maximum at intermediate loading (Fig. 4). The peak in specific heat defines the crossover between dispersed and assembled states, and the energy determines that the assembled state occurs at low temperature (also identifiable by visual inspection). If dispersion were to be analogous to the phase separation of a binary mixture, we would expect that energy and specific heat would exhibit a discontinuity, provided we do not follow a path through the critical point. Additionally, if the transition were first-order, we would expect hysteresis in the vicinity of the transition, i.e., in a narrow region near the transition our results would depend on which direction we approach the transition. We tested this possibility, and found no evidence of hysteresis. These results suggest the transition is not first-order.

If the crossover between clustered and dispersed states is not a simple phase transition, how can we characterize it? We use the specific heat data to calculate the "clustering diagram". Specifically, for each, we define the approximate boundary temperature, T^*,

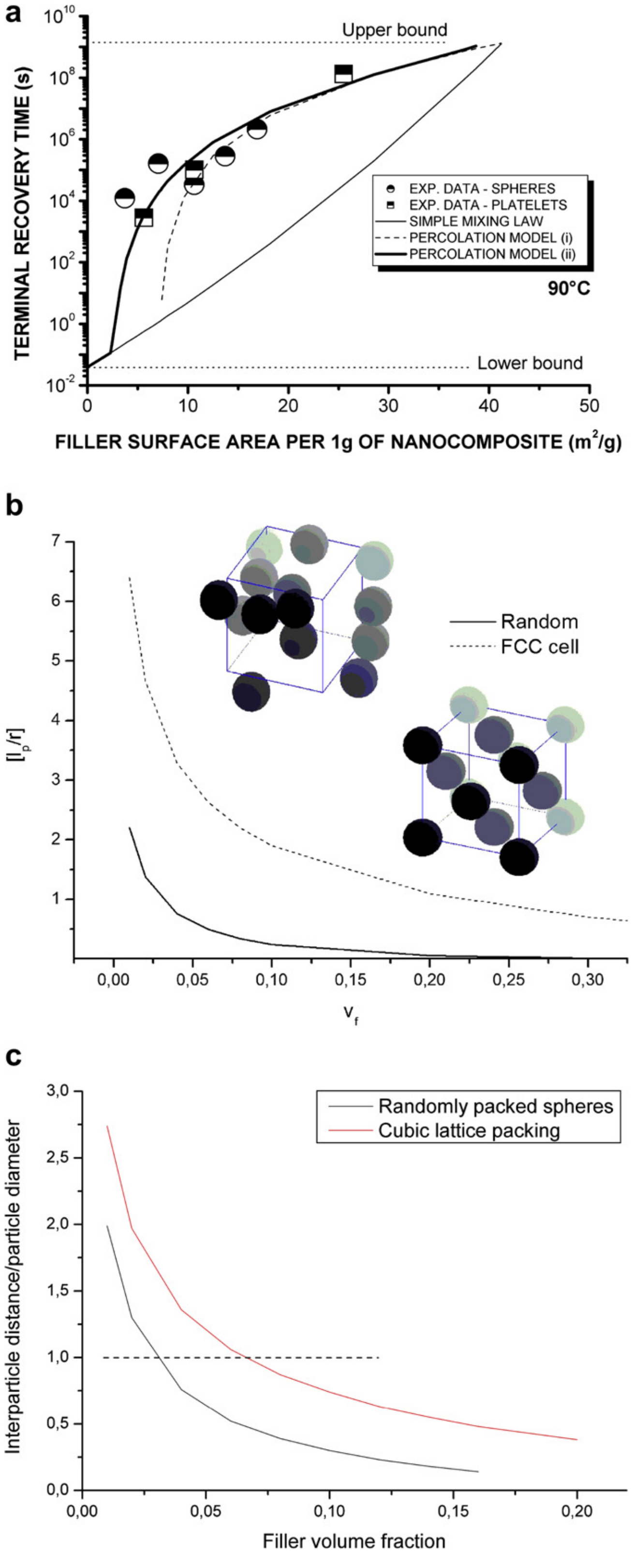


Fig. 3. Surface area, packing and inter-particle spacing. (a) Terminal modulus recovery time *vs*. filler–matrix contact area dependence for the PVAc/HAP nanocomposite. Experimental data are correlated with results from calculations based on rule of mixtures and percolation model. For the system investigated, all matrix chains became stiffened by the filler particles at the interface area of 42 m^2/g. Average inter-particle spacing calculated using a 3 particle (Kalfus et al, submitted for publication) (b) and 1000 particle, (c) model as a function of the volume fraction of monodisperse spheres.

between clustered and dispersed states by the location or the peak of specific heat. The boundary is positively sloped, indicating that clustering occurs for large volume fraction V_f and low T. Comparing the behavior of the amplitude and location of the maximum specific heat provides us with further evidence against phase separation via a first-order transition. From the shape of the boundary shown in Fig. 5, we see that, if the clustering mechanism were analogous to binary phase separation, the critical point must be at some $V_f > 0.3$; at a critical V_f^{crit}, specific heat must diverge, although the divergence can be quite weak. However, we can see from Fig. 4 that the amplitude of the peak in specific heat decreases and becomes broader as we increase toward the possible critical value of V_f. For a binary system with a first-order phase transition, the amplitude of the peak in specific heat should increase as we approach the critical concentration. The decrease in the amplitude of the specific heat peak with increasing V_f is consistent with the predicted behavior for an associating system [56]. The model of equilibrium polymerization [56] specifically predicts that the loci of specific heat maxima should shift location according to:

$$V_f^{\text{crit}} \approx \exp\left(-E/kT^*\right) \tag{1}$$

The exponential temperature dependence derives from an underlying Arrhenius temperature dependence of the rate constants describing the association and dissociation rate constants of the equilibrium particle association. We plot the clustering boundary in the inset of Fig. 5 to test for consistency with equation (1). Within the limits of uncertainty in our data, the clustering boundary can be described by equation (1), from which we obtain $E = 6.9$. These findings suggest that the clustering transition in our system, and presumably in many similar real nanocomposite systems, is controlled by the same mechanism as simple associating systems. This observation provides a framework for rationalizing the behavior of many nanoparticle systems, which should in turn aid in the control of dispersion and nanocomposite properties.

We next examine the effect clustering on the viscosity η. We examine η as a function of the NP–polymer interaction strength, ε_{mp}, for fixed $V_f = 0.172$. Fig. 6(a) shows that η appears to approach nearly constant values at $\varepsilon_{\text{mp}} = 1$ and 1.5, with a gradual crossover around $\varepsilon_{\text{mp}} \approx 1.3$. In addition, we show the specific of the sheared systems in Fig. 6(b), indicating the crossover in clustering behavior occurs in the same range of ε_{mp} that η changes between asymptotic regimes. Hence our results suggest that η is more sensitive to the state of particle clustering than to ε_{mp}. Interactions must play a role in η, but this effect is less obvious. Why should particle dispersion result in increased viscosity? From hydrodynamic

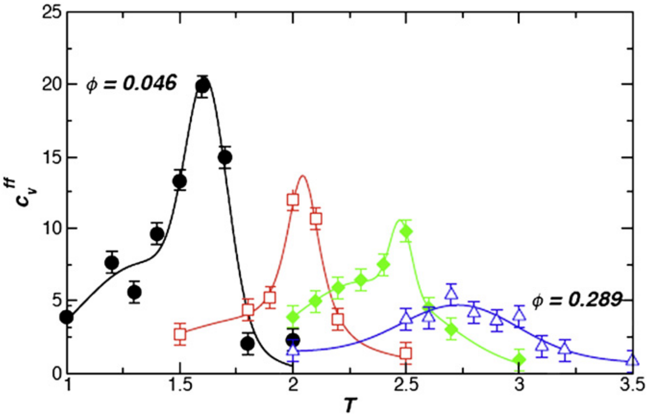


Fig. 4. Temperature dependence of the specific heat for filler volume fraction ranging from 0.046 to 0.289.

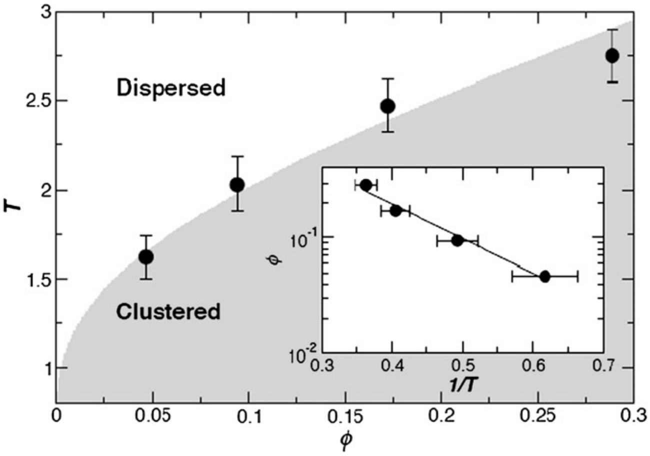


Fig. 5. “Clustering diagram” of the nanoparticles, as a function of *T* and filler volume fraction, φ. The boundary of the shaded region is determined by fitting the points using Eq. (1), shown in the inset.

considerations, one expects the opposite effect—that a large or extended rigid body embedded in a fluid results in a greater viscosity than a disperse collection of small rigid bodies. However, we previously showed that the clusters formed are dynamic in nature, and hence are not rigid. Moreover, changes in the polymer dynamics near the nanoparticle surface are known to play an important role in viscosity changes. We know that attractive surface interactions lead to a slowing of dynamics near the surface, which in turn results in an increased viscosity. For a fully dispersed configuration, the amount of exposed nanoparticle surface grows linearly with the number of nanoparticles. If clustering occurs, the amount of exposed surface grows sub-linearly relative to the number of particles. Therefore, if the changes in η are proportional to the amount of exposed nanoparticle surface, then η should be larger for well-dispersed configurations than for clustered configurations. The correlation with the exposed surface area A – which we estimate by the fraction of nanoparticle force sites in contact with a chain – is demonstrated by Fig. 6(c). We point out that the large change in A does not match exactly with the large change in η, suggesting that there are additional effects, which we touch on in the next section.

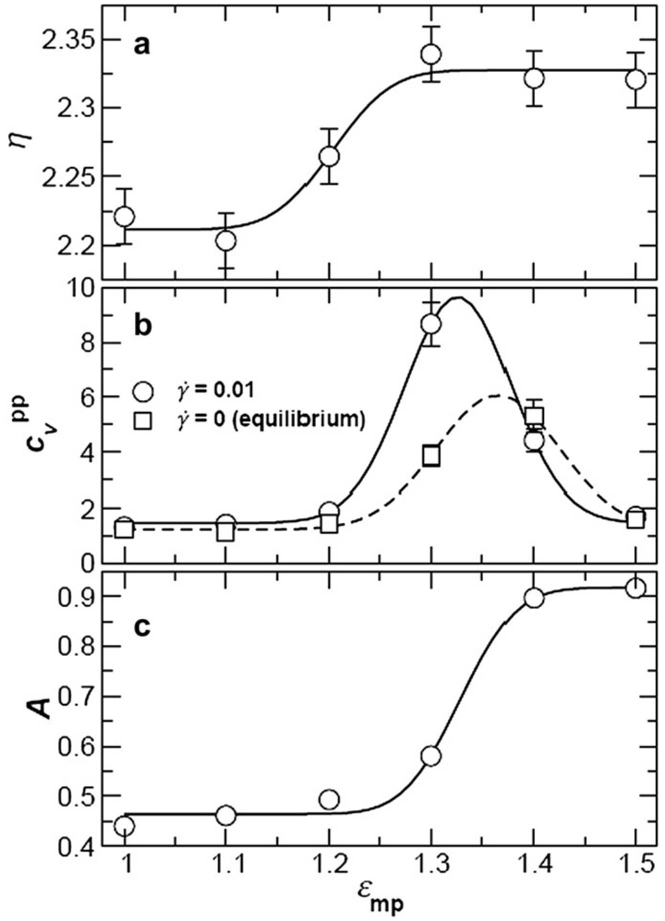


Fig. 6. Dependence of nanoparticle properties on the strength of the nanoparticle–polymer interaction. (a) Viscosity η, as a function of the ε_{mp} at fixed $T = 2.0$ and $V_f = 0.172$. (b) Specific heat for the shared configurations (circles, solid line) and equilibrium configurations (squares, broken line). (c) The fraction of nanoparticle force sites in contact with a chain, an estimate of the exposed area, A.

It is generally appreciated that highly asymmetric nanoparticles have the potential to be even more effective than spherical (or nearly spherical) nanoparticles in changing the properties of the polymer matrix to which they are added. In addition to the large enhancements in viscosity and shear modulus expected from continuum hydrodynamic and elasticity theories, extended nanoparticles can more easily form network structures both through direct interaction between the nanoparticles, or through chain bridging between the nanoparticles, where a “bridging” chain is a chain in contact with at least two different nanoparticles [55,186]. These non-continuum mechanisms are believed to play a significant role in property enhancement in polymer nanocomposites compared to more “classically” behaving microcomposites. In this section we discuss the role of nanoparticle shape in determining the viscosity η, and the ultimate material breaking stress. Fig. 7 shows representative images of the icosahedra, rods, or sheet nanoparticles that we examine. Fig. 8(a) shows the effect of varying the chain length N on η. But normalizing η by the value of the pure melt, we obtain the reduced viscosity η_r which demonstrates an enhancement of η through the addition of nanoparticles. An increase in η with increasing N is expected from basic polymer physics, since the chain friction coefficient increases with N. Interchain interactions and “entanglement” interactions enhance this rate of increase, since the friction coefficient of each chain increases linearly with N. However, Fig. 8(b) shows that if we normalize by the pure system and plot the reduced viscosity $\eta_r = \eta(V_f)/\eta(V_f = 0)$, the origin of the increase must be more complex than simply increasing N. Needless to point out that the $\eta_r = \eta(V_f)/\eta(V_f = 0)$ normalization assumed only the effect of filler volume and did not account for possible change in matrix chains dynamics, thus, it is of only limited validity.

To better understand the increase of viscosity, we test for a correlation between η and chain bridging. We define a “bridging chain” as a chain that is simultaneously in contact with two or more nanoparticles. Fig. 9 shows the fraction of bridging chains, f_B, as a function of N. The trend in f_B is consistent with η, showing an increase in f_B with increasing N as well as a clear ordering between systems for every chain length. Hence, the fraction of bridging

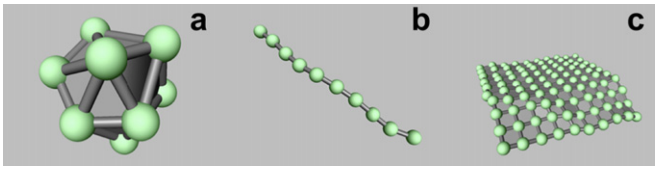


Fig. 7. Simulated nanoparticle shapes: (a) icosahedron, (b) rod and (c) sheet. The nanoparticle force sites are rendered as spheres connected by cylinders representing FENE bonds.

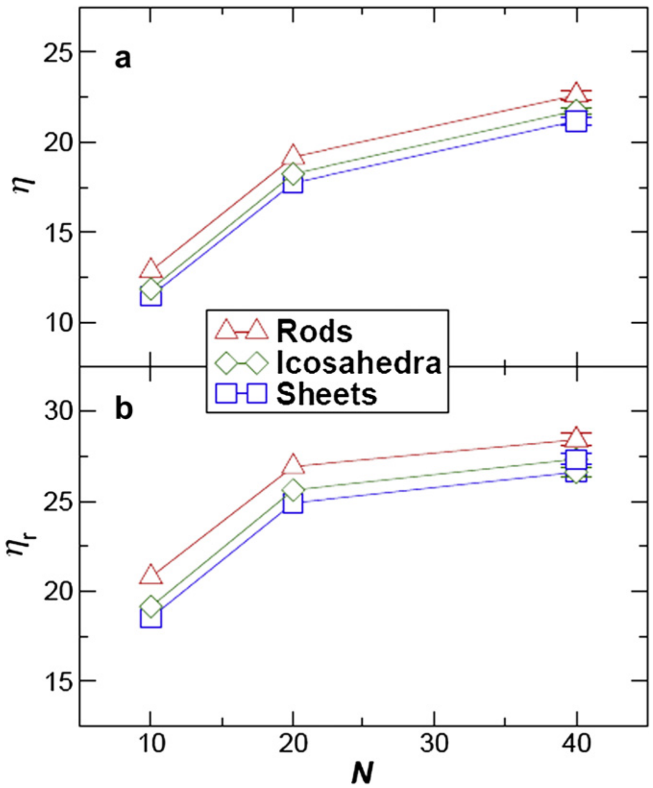


Fig. 8. The (a) suspension viscosity η and (b) reduced viscosity η_r as a function of chain length N at a constant shear rate and NP content.

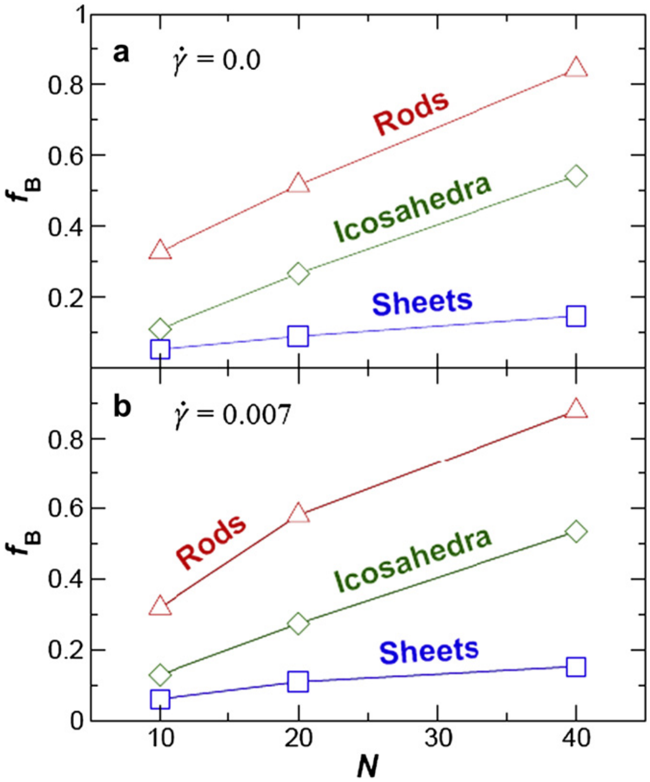


Fig. 9. The of chain length N on a fraction of bridging chains f_b in each of the nano-particle systems.

chains seems to be a useful “order parameter” for characterizing the polymer–nanoparticle interactions. If the polymer–nanoparticle interactions were sufficiently small, the bridging would not be expected to play significant role, and it is likely that the continuum hydrodynamic approach would be applicable. However, Sternstein et al. [3] and Kalfus et al. [4] have shown that for rubbery matrices, even in the case of weak NP–chain interaction, the chain stiffening can become enormous due to perturbation of entanglement mobility resulting in “trapped” entanglements.

We next consider how the NP shape affects the ultimate isotropic tensile strength τ of a material, defined as the maximum tension a homogeneously stretched material can sustain before fracture not accounting for the stress field heterogeneity as discussed in the Introduction. We calculate τ as a function of N in Fig. 10. For the pure polymers, we find that τ decreases with increasing chain length. This is nontrivial, since one might naively expect longer chains to exhibit more interchain coupling. This is the same trend with chain length as observed in Ref. [57] for n-alkanes. Most importantly, Fig. 10 shows that the addition of the nanoparticles reverses the N dependence of τ when compared to the pure system. Thus, while the presence of icosahedral or rod-like nanoparticles decreases the material strength for most chain lengths studied, the trend of τ is increasing, and if this continues, τ will surpass the pure melt for all nanoparticle shapes at large enough N. Indeed, τ for the icosahedra nanocomposite already exceeds that of the melt at $N = 40$.

4. Nanoparticle self-assembly

It has been suggested by many previous workers, that nanoparticle shapes and their mutual interactions as well as interactions with chains determine the superstructures that they can assemble into [58–68]. The geometry of the assemblies is, thus, largely encoded at the level of a single particle. Similarly, flow effects can also be used to assemble particles into anisotropic structures [69,70]. Surfaces have routinely been used to assemble particles into a variety of structures. It was found that C_{60} particles will preferentially segregate to a surface of a thin polymer film. This result is attributed to entropic effects – the system loses less entropy when the particles segregate to the surface. The idea that nanoparticles will spontaneously migrate to surfaces has been used to spontaneously heal cracks that might appear in polymer film's surface.

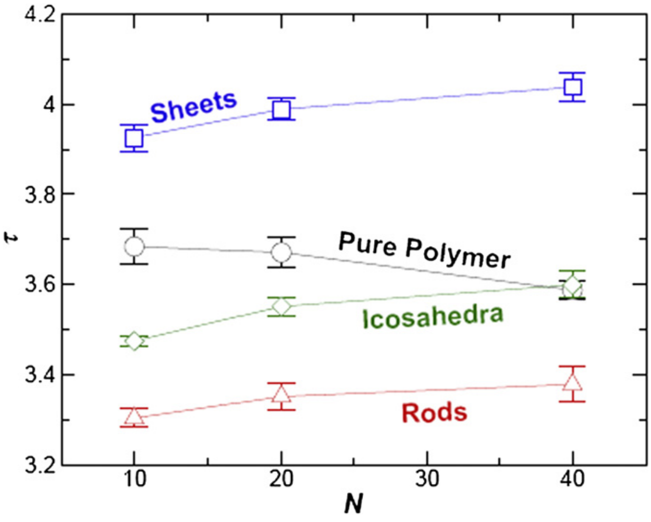


Fig. 10. The shear strength τ as a function of chain length N for the neat polymer and three nanocomposites.

Obtaining controlled dispersion of NPs in polymer matrices is a significant challenge in achieving the dramatic property improvements promised by polymer nanocomposites [71]. However, it is often difficult to achieve this goal since inorganic particles are typically immiscible with an organic phase [72–75]. One strategy to overcome this difficulty is to "shield" the particle surface by grafting it with the same chains as the matrix polymer [96–98]. While this approach for particle dispersion is successful in some cases, we find instead that the particles can exhibit self-assembly into highly anisotropic structures [76]. This process arises because the immiscible particle core and grafted polymer layer attempt to phase separate but are constrained by chain connectivity— this is evidently analogous to "microphase separation" in block copolymers and other amphiphiles. Similar to these amphiphiles, these particles with a "polarizable" segmental cloud can self-assemble under a broad range of conditions into a variety of superstructures. Recent MD simulations on aqueous solutions of hydrophobic fullerenes uniformly grafted with hydrophilic polyethyleneoxide chains also verify this behavior. That is, the particles form chains, branched objects and other anisotropic structures emerge at equilibrium (Fig. 11). These results were interpreted as arising from the propensity for the hydrophobic particle cores to contact each other to shield themselves from water. This process is evidently facilitated by two particles forcing the PEO chains "out of their way", resulting in an effective "dipolar" inter-particle potential, and anisotropic self-assembly.

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. It was suggested [77–80], 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 us 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 [81–85]. 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 but transparent polymers which are wear resistant. Making such connections between nanoparticle dispersion and organization with macroscale properties is then a crucial aspect that is only now beginning to be considered.

5. Relationships of macroscopic rheological and mechanical properties to nano-scale structural variables

Elastomers filled with nanoparticles show a solid-like behavior response which includes a non–terminal zone of relaxation, apparent yield stress and a shear-thinning dependence of viscosity on particle concentration and/or dispersion. This particular rheological behavior arises from the presence of a network structure. Actually, the controversial discussion, or at least the main debate in the open literature, is about the origin of this network structure: Polymer–particle or/and particle–particle interactions. The strain-dependence of the dynamic viscoelastic properties, often referred to as the Payne effect [1], is well known in elastomers for forty years. There are experimental data [86,87] suggesting that the mechanical reinforcement of crosslinked rubbers is mainly related to the secondary structure of filler particles and others [4,38] suggesting chain stiffening due to the rubber filler interactions is the primary reinforcing mechanism. Intensive discussions have been held on the nature of this effect, but the exact causes of this non-linear behavior are still a matter of investigations and controversial discussions.

In one approach [86], the level of filler dispersion is expected to play a major role in determining the filler effects on non-linear responses of nanocomposites while the other considers the chain stiffening due to reversible trapping of entanglements to be the primary cause of the observed behavior [3]. For example, it is well known that rubber-like materials exhibit an appreciable change in their mechanical properties (stress softening) resulting from the first tensile experiment. This phenomenon is well recognized to be caused by the following mechanisms (see Fig. 12): i) physical disentanglement of rubber chains, ii) decrease in the interactions between polymer molecules and filler surfaces, iii) filler network breakdown and iv) chain scission of rubber molecules. A number of research papers and reviews have been dedicated to this behavior termed Payne and Mullins effects [1,2]. Although different theories have been proposed, it is essential to understand the filler superstructure at different length scales.

First of all, the comparison of viscoelastic behavior of fumed silica and clay nanocomposites leads to an apparent paradox (see the scheme in Fig. 13). Actually, both percolation threshold and limit of linearity decrease with increasing the exfoliation state of organo-clays platelet whereas they increase with the dispersion of fumed silica by surface grafting of end-tethered chains. More precisely, Fig. 14 shows the disappearance of the solid-like behaviour of PS/SiO_2 nanocomposite with increasing the dispersion of the fumed silica from cluster structure (virgin fumed silica) towards primary particles. Note that the transmission electron microscopy (TEM) clearly showed that the micrometer-sized domains of stringy-shaped aggregated silica particles are partly destroyed after polymer grafting and the silica particles appear regularly distributed within the polymer matrix. Regarding the organo-clays, the critical deformation decreases with increasing the exfoliation rate as shown in Fig. 15. Interestingly, such trend has already been observed for carbon nanotube (CNT) composites. Actually, the percolation threshold for CNT in polymer composites can range from 0.0005 vol% to several vol % depending on the CNT "miscibility" in polymers, i.e., when improving CNT/chain attraction. From these results on thermoplastic nanocomposites, one could conclude that the filler networking is the primary structural variable controlling their viscoelastic properties. Reversibility of the observed behavior, however, puts serious doubts on such an interpretation. Moreover, in the case of elastomers, i.e., polymers with long chains and some times with particular viscoelastic behaviour, the filler network appears to be a second-order structural parameter affecting the viscoelastic response of the nanocomposite. This last mechanism is generally described analysing the modulus recovery experiments. It is assumed to be based on change in chain dynamics near the filler–matrix interface and, consequently, interpreted in terms of the physics of entangled chains. For example, Kalfus and Jancar [4] showed that the modulus recovery time was governed by the chain relaxation processes in the polymer matrix near the filler surface. This process was successfully interpreted using

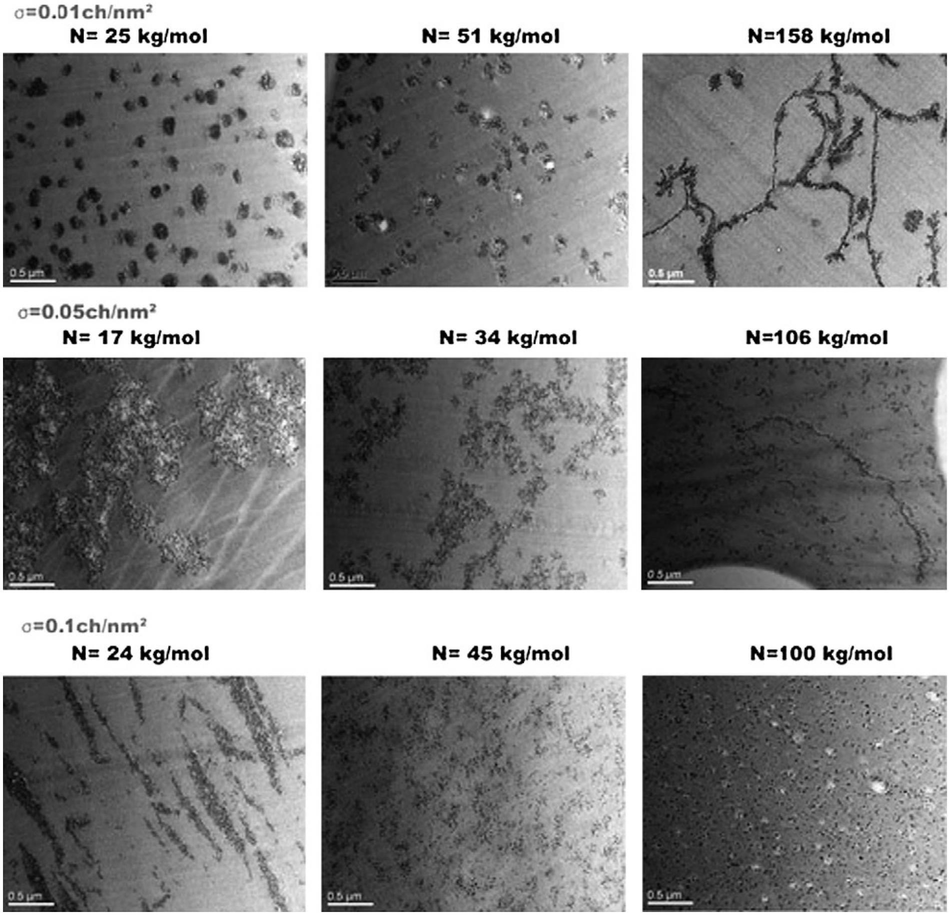


Fig. 11. Self-assembled nanoparticles with grafted polymer layers in a polymer melt matrix. TEM of 14 nm silica particles functionalized with a polystyrene brush with molecular mass and grafting density as shown in the figure. These particles are placed in a polystyrene matrix with molecular mass of 142 kg/mol. The samples, with 5 mass% silica, were annealed for 5 d at 150 °C.

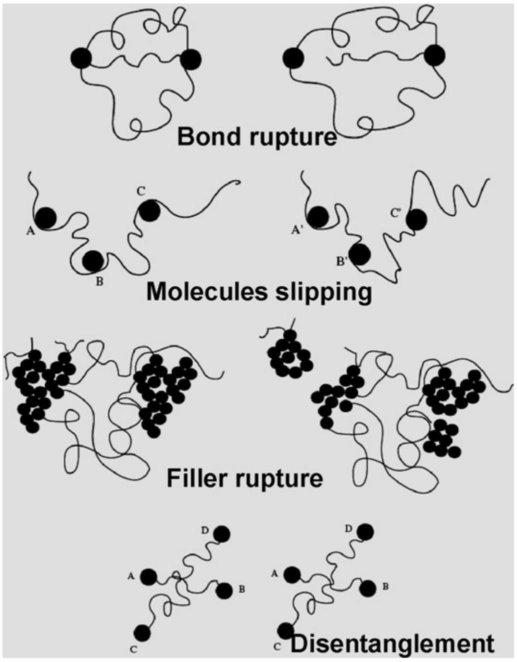


Fig. 12. Schematic physical explanations of the Mullins effect.

the reputation concept of molten entangled chains. Consequently in this study, filler agglomeration and/or network is less important representing only a second-order contribution to the non-linear viscoelastic response of a nanocomposite.

Finally, mechanisms consisting of entanglement–disentanglement of polymer chains and the breakdown of silica aggregates can be considered. The respective contribution of each mechanism to the linear and non-linear viscoelastic properties of the nanocomposite is balanced by the type and extent of silica surface treatment. This means that the linear and non-linear rheological properties of polymer nanocomposites are consistent with a network structure of weakly agglomerated particles, combined with a mechanism of polymer chain relaxation at the filler surface vicinity governed by the polymer–particle interactions. These conclusions are consistent with previous studies on elastomer reinforcement and experimental results from the rubber industry. Even though, the industrial approach prefers to control compounding so as to obtain optimal dispersion of fillers without completely suppressing their aggregation into larger structures. In other words, a fractal filler structure is considered commercially more viable way to optimize the best balance of the properties of rubbery nanocomposites.

6. Length scale limits for using continuum mechanics in interpretation of mechanical properties of polymer nanocomposites below T_g

A number of papers have been published describing effects of the presence of solid nanoparticles on the chain statistics and

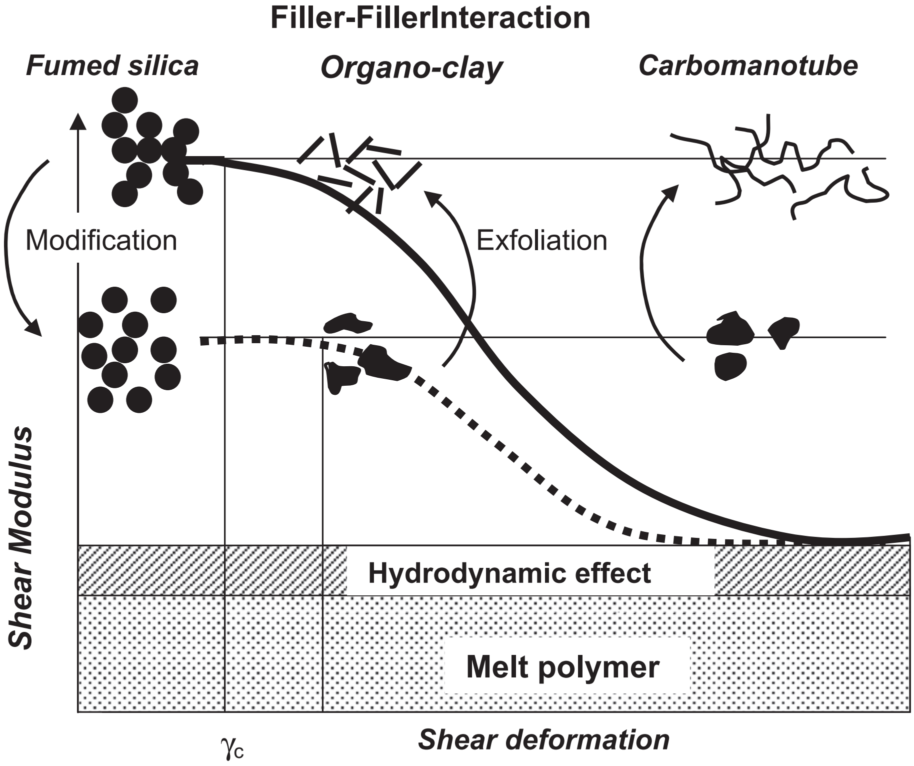


Fig. 13. Contributions to the complex shear modulus *vs.* strain for elastomers filled with different types of filler at two level of dispersion.

dynamics near the polymer T_g. At the same time, attempts to develop theoretical understanding of the molecular mechanisms underlying thermal transitions in glass-forming polymer liquids, chain relaxations, and the nature of entanglements near solid nanoparticles in polymer liquids has advanced greatly. Despite significant success obtained in the nano-scale and macroscale interpretations, the bridging laws between these vastly differing length scales have been far less successful. In this part, the relationship between the measured global properties and the nano-scale local structural variables is reviewed for amorphous polymers near and below T_g. The effects introduced by strongly attractive or repulsive nanoparticles affecting greatly the amplitude of heterogeneity of the localized chain relaxations are also discussed. Possible algorithms capable of capturing physically sound averaging procedures transforming the response of the variety of local nano-scale structures discrete in nature into the global response of mesoscale continuum are also reviewed. The need to include time scale into considerations of bridging laws is also proposed.

In agreement with the theory of glass-forming liquids reviewed earlier, it has been suggested that the view of entanglements as dynamically changing clusters of cooperatively moving chain sequences provides suitable framework for theoretical description of the effects of chain length, polarity and backbone stiffness on the thermal transitions in polymer nanocomposites above T_g. Below T_g, for chains directly interacting with nanoparticle surface, this model framework can be coupled with reputation theory considering change in spatial and time distribution of the effective tube

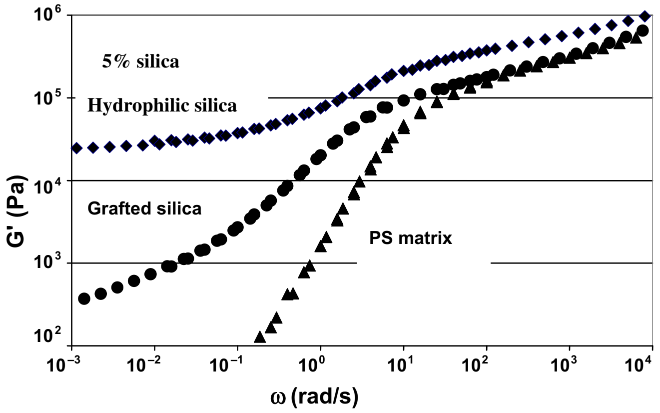


Fig. 14. Variation of storage modulus *vs.* frequency of PS nanocomposite filled with 5vol % of silica and PS-grated silica nanoparticles.

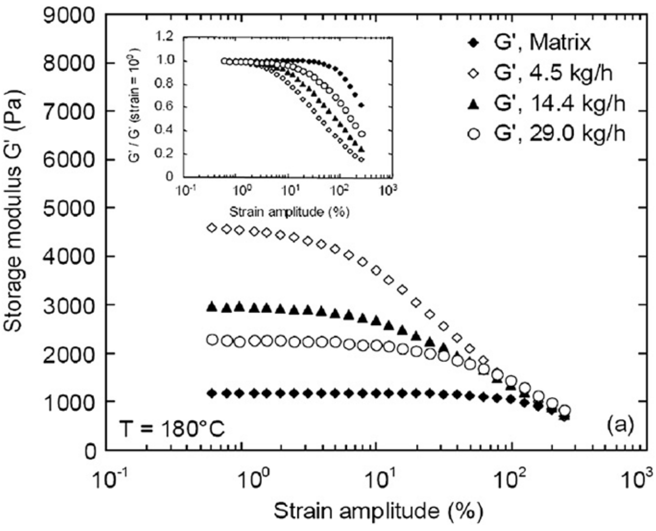


Fig. 15. Strain-dependence of PP/montmorillonite nanocomposite on the exfoliation quality. From a processing point of view, the exfoliation degree is expected to decrease with increasing the flow rate in the extruder.

diameters due to the presence of solid NPs to predict the effect of solid nanoparticles on the surface chain normal mode dynamics, i.e., chain stiffening [4].

It was recommended that the M_n is a more appropriate parameter describing the chain statistics when modeling the chain dynamics at this length scale compared to M_w. It was also agreed that evidence suggests that the long-time chain dynamics may be more, or, as affected as the short-time dynamics in some nanocomposites. In these cases, the particles may serve to lock entanglements in or to stabilize them, especially, when the chain–particle interactions are weak. The nanoparticles can polarize the structure of the polymeric medium to which they are added, altering the molecular packing and dynamics *near* the particle, which can indirectly change the packing and dynamics *far away* from the particle. These effects result in highly non-local coupling of stress and strain tensors. Nanoparticles can have this powerful effect because the intrinsic heterogeneity of glass-forming liquids is nanometric in scale and the nanoparticles, being nearly commensurate in size with this heterogeneity, can effectively perturb this structure intrinsic to glass-formation. Thus, the very character of glass-formation is changed which may affect the measured T_g. Because of the relaxation character of the glass transition, the structural interpretation of the shifts in T_g with nanoparticle content experimentally observed under given conditions and reported often in literature does not have suitable support in the current physics of these systems.

The reinforcement of the filled amorphous polymers consists of a contribution related to the volume of the rigid filler and a contribution due to the molecular stiffening caused by the interaction between particle surface and matrix chains [116]. The first one is dominating for particles with small surface to volume ratio, S/V, while the second one prevails for particles with large S/V. Common$M_c = M_m^* f(V_f)$ ly used models inherently assume modulus of the matrix independent of particle content and size, i.e., [88]:

$$\frac{M_c}{M_m^o} = M_r = f\left(V_f\right) \tag{2}$$

The steep increase of the elastic modulus of polymers filled with relatively small amount of NPs is generally ascribed to the molecular stiffening [3] with its extent proportional to the specific filler–matrix interface area, S_f, thus, should be particle size dependent [19]. In this case, the composite modulus can be expressed phenomenologically as:

$$M_c = M_m^* f\left(V_f\right) \tag{3}$$

where

$$M_m^* = M_m^o \phi\left(S_f\right) \tag{4}$$

is the modulus of the matrix in the presence of particles which differs from that for the neat polymer, M_m^0. The $\Phi(S_f)$ is an unknown dependence of the extent of molecular stiffening on the specific interface area and the strength of the filler–matrix interactions. For large particles, i.e., $r >> R_g$, and large V_f, the $\Phi \to 1$ and $M_m^* \approx M_m^0$. For small V_f and $r \approx R_g$, the $f(V_f) \to 1$ and the reinforcement is predominantly due to the matrix stiffening, i.e., $M_c \approx M_m^*$. Since the molecular stiffening is pronounced the most for highly mobile chains, the effect of particle size on the elastic modulus has been investigated near the neat matrix T_g. In agreement with the proposed hypothesis, $M_m^* \approx M_m^0$ for particles larger than 1 μm and became strongly dependent on particle content for particles smaller than 50 nm, increasing approximately linearly with log (S_f) for both temperatures investigated (Fig. 16). Needless to point out that the scale of matrix stiffening below T_g is only about 1/8 of that above the T_g. Even though the proposed simple model does not describe the actual molecular mechanism of chain stiffening, it can provide a simple framework for analyzing the experimental data correctly.

To describe quantitatively the molecular stiffening leading to the steep increase of elastic modulus with nanofiller content above the T_g of neat matrix, the model of trapped entanglements [3] has been proposed. It has also been shown that the spatial distribution of trapped entanglements is related to the spatial distribution of inter-particle spacing shorter than the average entanglement length [89,90] and, thus, should be related to the particle size distribution and uniformity of particle dispersion. In contrary to the continuum mechanics approach, it has also been shown that the extent of stiffened chains due to interaction with nanoparticles scales with the matrix–filler interface area being inversely proportional to particle diameter for a given V_f [4,52]. It is generally agreed that a key element of the overall response of the macroscopic solid made of polymer nanocomposite is associated with how and to which extent the local chain dynamics is affected by the strength and extent of interactions between chain segments and large specific surface area particles of varying surface chemistry and how this local response is "averaged" over the structurally

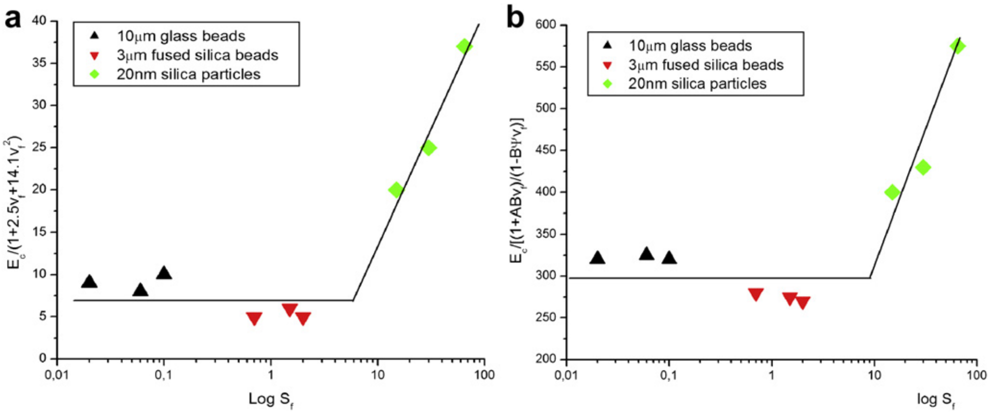


Fig. 16. Dependence of the matrix modulus, $M_m^* = E_c/f(V_f)$, on the logarithm of the specific interface area, S_f, above T_g using the Guth model (a) and below T_g using the Kerner–Nielsen model (b).

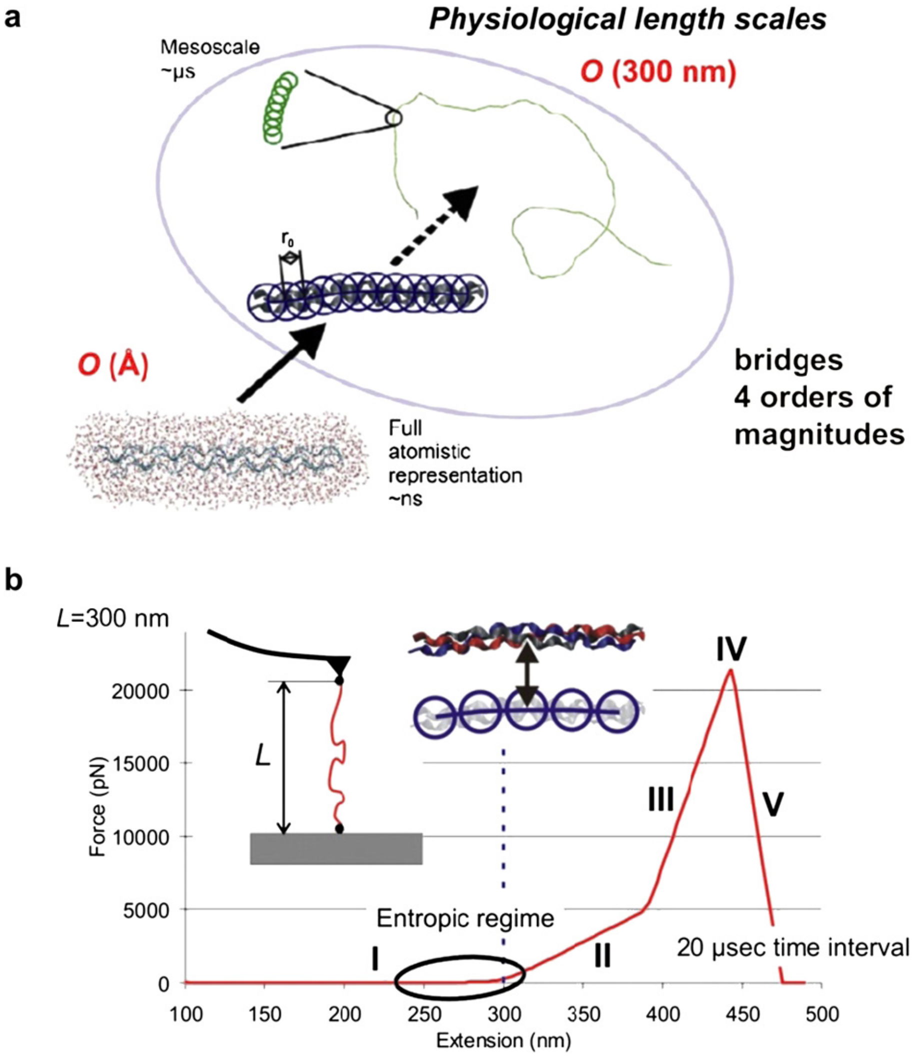


Fig. 17. (a) Illustration of coarse-graining approach for a simple one-dimensional fibrillar protein filament (single tropocollagen molecule). This schematic image illustrates how a full atomistic representation is coarse-grained and used in a mesoscale model formulation. The mesoscale model formulation enables one to reach much larger time and length scales. The systematic parameterization from the bottom-up provides a rigorous link between the chemical structure of proteins (for example, through their amino acid sequence) and the overall functional material properties. This computational approach is a key component, as it provides us with the ability to reach microsecond- and micrometer length scales. (b) Example application of this approach in elucidating the force–extension behavior of a 300 nm long tropocollagen molecule.

heterogeneous nanocomposite volume into measured properties of mesoscale continuum specimens.

In heterogeneous materials, there are characteristic length scales associated with the compositional heterogeneity and length and time scales related to the relaxation heterogeneity of the polymer phase (Figs. 16 and 2c). Traditional continuum mechanics modeling of composites usually rests on use of a Representative Volume Element (RVE) with simplified description of the compositional heterogeneity, whereupon the properties are homogenized with an appropriate equilibrium constitutive model assuming locality of the stress–strain relationships. With discrete dynamical systems like that near the particle–polymer interface, ascribing a traditional RVE seems to be inadequate. Moreover, phenomenological stress and strain parameters have to be replaced with forces and displacements, and, in addition, the coupling between displacement and forces becomes highly non-local (Fig. 17). Thus, it appears that the RVE must evolve over time as well as the associated boundary conditions. It was suggested that an approach might involve using an RVE spectra in an attempt to capture the material response over the necessary length and time scales. It was also agreed that many of the methods currently being attempted to perform multi-scale modeling either totally ignore or inadequately incorporate key characteristics of polymeric physical behavior. The current constitutive equations are based within the framework of equilibrium thermodynamics, or mechanics, which is not well suited for evolving systems. Also, a more detailed bridge between molecular dynamics and continuum mechanics is necessary and can only be developed by better modeling and designing critical experiments with the aim of elucidating the governing physics at each length and time scale.

Existence of a threshold length scale was proposed above which the nano-scale heterogeneities are averaged out and, thus, not reflected in the measured global properties. This critical length scale can be considered the minimal size of the RVE used in classical continuum mechanics. Due to the nature of polymer chains, the size of this critical RVE depends strongly on the structural heterogeneities as well as on temperature and time scale of the property investigated. Below this threshold RVE size, test geometry becomes important variable since the stress–strain relationship is highly non-local. Computer simulations and experimental data revealed that the critical RVE size is reached when one of its dimensions becomes smaller than approximately 50 nm. Below this length

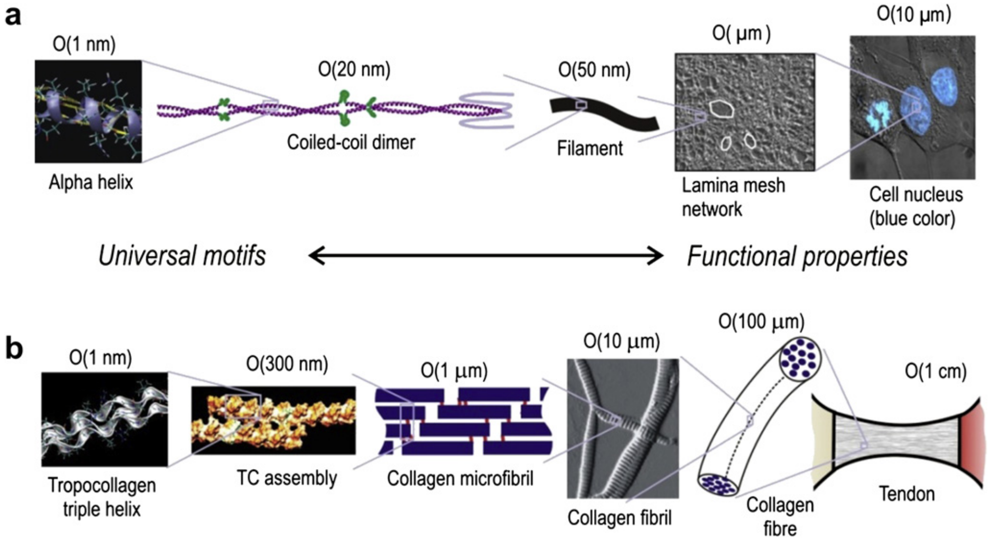


Fig. 18. Example hierarchical multi-scale structures of biological protein materials: lamin intermediate filaments (lamins), collagenous tissues (tendon), as well as the materials science paradigm for the analysis of biological protein materials. (a), Structure of lamins. (b), Structure of collagenous tissues, from nano-scale to macroscale.

scale, use of classical Euler continuum mechanics should be justified for each case.

7. Mechanics of multi-scale hierarchical nanostructured bio-composites

It has been proposed that advanced structural composites will benefit from new features, which can be designed modifying structure on the nano-scale. Biological protein materials such as bones feature hierarchical structural components to constitute a diverse range of tissues. The analysis of mechanical properties of protein materials is an emerging field that utilizes mechanistic insight, based on structure–process–property relations in its biological context, to probe deformation and failure phenomena at the molecular and microscopic level. This part discusses the integration of advanced multi-scale experimental, computational and theoretical methods that can be utilized to assess structure–process–property relations and to monitor and predict mechanisms associated with the properties of mineralized protein materials and structures composed of them. Based on the integration of scales with physical, biological and chemical concepts, opportunities to exploit knowledge gained from understanding biological protein materials and potential applications in materials design and nanotechnology will be highlighted.

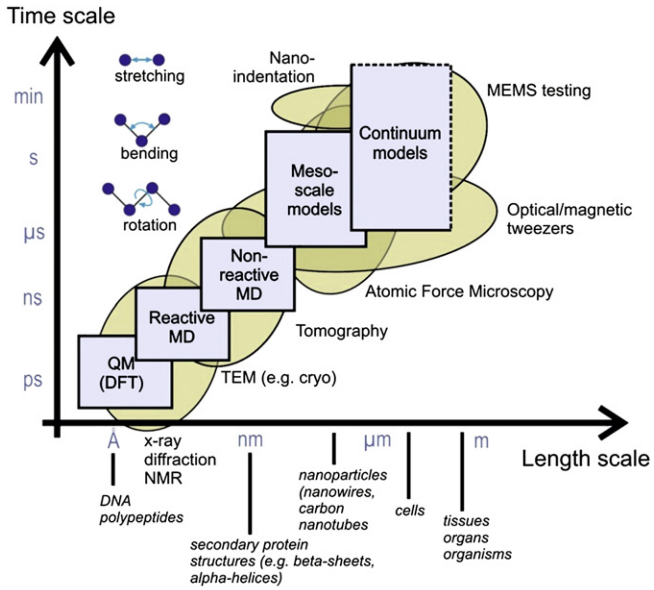


Fig. 19. Experimental, theoretical and computational tools for the characterization and modeling of deformation and failure of biological protein materials, plotted over their respective time and length scale domain of applicability. Experimental methods include X-ray diffraction, transmission electron microscopy (TEM), atomic force microscopy, optical/magnetic tweezers, as well as MEMS testing and nanoindentation. Theoretical and simulation tools include quantum mechanics/DFT, molecular dynamics, coarse-grained models, mesoscale atomistically informed continuum theories, as well as continuum models. The lower part of the figure indicates respective classes/scales of protein materials that can be studied with these types of techniques.

Proteins constitute critical building blocks of a diverse group of biological materials, ranging from spider silk to bone, tendon to the skin, all which play an important role in providing key functions to biological systems [91–98]. These materials are distinct from the conventional references to structure and material, as it connotes the merger of these two concepts through hierarchical formation of structural elements that range from the nano-scale to macroscale (Fig. 16) [99–103]. This merger of structure and material is critical for biological protein materials to reach superior properties, in particular for their ability to combine disparate properties such as toughness and stiffness or their intrinsic ability to adapt, change and remodel (Fig. 18).

The use of multi-scale modeling and simulation methods as shown in Fig. 19 has become a widely used strategy in furthering our understanding of biological protein materials. Specifically, the integration of multi-scale experimental and simulation tools has led to advances in appreciating the complex change of material properties across scales and hierarchy levels [104]. In such models, the elasticity of the polypeptide chain is captured by simple harmonic or anharmonic (non-linear) bond and angle terms, whose parameterization is informed from lower level higher fidelity models in the multi-scale scheme. Such methods are computationally quite efficient and capture for example shape dependent mechanical phenomena in large biomolecular structures [105], and can also be applied to collagen fibrils in connective tissue [106] as well as mineralized composites such as bone [107,108]. Results from such coarse-grained models can be used in larger-level models, for example in finite element simulations as demonstrated

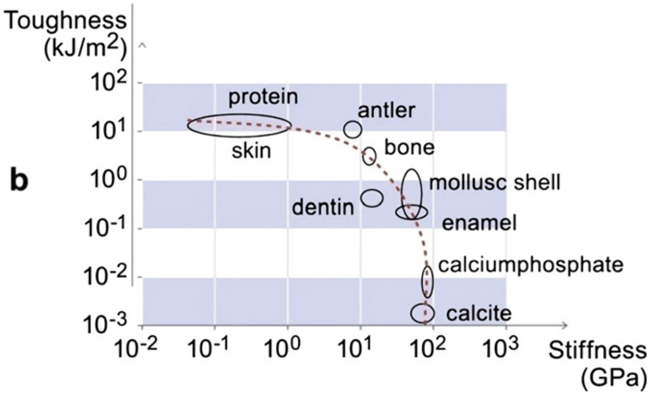


Fig. 20. Performance of biological materials in the stiffness–toughness domain. b, Comparison of toughness and stiffness properties for a number of biological materials.

for collagenous tissues [104]. The evolution of protein materials through genetic selection and structural alterations has resulted in a specific set of protein building blocks that define their structure [109–111]. A fundamental difference between engineered materials and naturally formed biological materials is that functionality in biology can be created by arranging universal building blocks in different patterns, rather than by inventing new types of building blocks, as in many engineered materials. The formation of hierarchical arrangements provides the structural basis to enable the existence of universality and diversity within a single material. This combination of dissimilar concepts may explain how protein materials are capable of combining disparate material properties, such as high strength and high robustness, together with multifunctionality (Figs. 18–20).

The approach of utilizing universal building blocks to create diverse multi-functional hierarchical structures has been successfully applied in current macroscale engineering paradigms. For example, in the design of structures such as buildings or bridges, universal constituents (bricks, cement, steel trusses, glass) are combined to create multi-functionality (structural support, living space, thermal properties, light harvesting) at larger length scales. The challenge of utilizing similar concepts that span to the nanoscale, as exemplified in biological protein materials (Fig. 18), through the integration of structure and material, could enable the emergence of novel technological concepts. A key obstacle in the development of new materials lies in our inability to directly control the structure formation at multiple hierarchical levels [112,113].

Fig. 21 shows the shear strength of clusters of H-bonds as a function of the size of the strand, showing a peak maximum shear strength of close to 200 MPa at a critical cluster size of 3–4 H-bonds [114]. This result illustrates that by utilizing a size effect, the fundamental limitation of H-bonds (which are mechanically weak) can be overcome. The occurrence of a strength peak at this characteristic dimension provides a possible explanation for several protein constituents, all of which display cluster of H-bonds at a similar size. Fig. 21 shows the geometry of a single alpha-helix, composed of 3H-bonds per turn, corresponding to the peak of the scaling shown in Fig. 21.

Up until now, the hierarchical nanostructural geometries have not yet been widely utilized for most engineering applications. This analysis further shows how high-performance materials can be made out of relatively weak constituents such as alpha-helices that

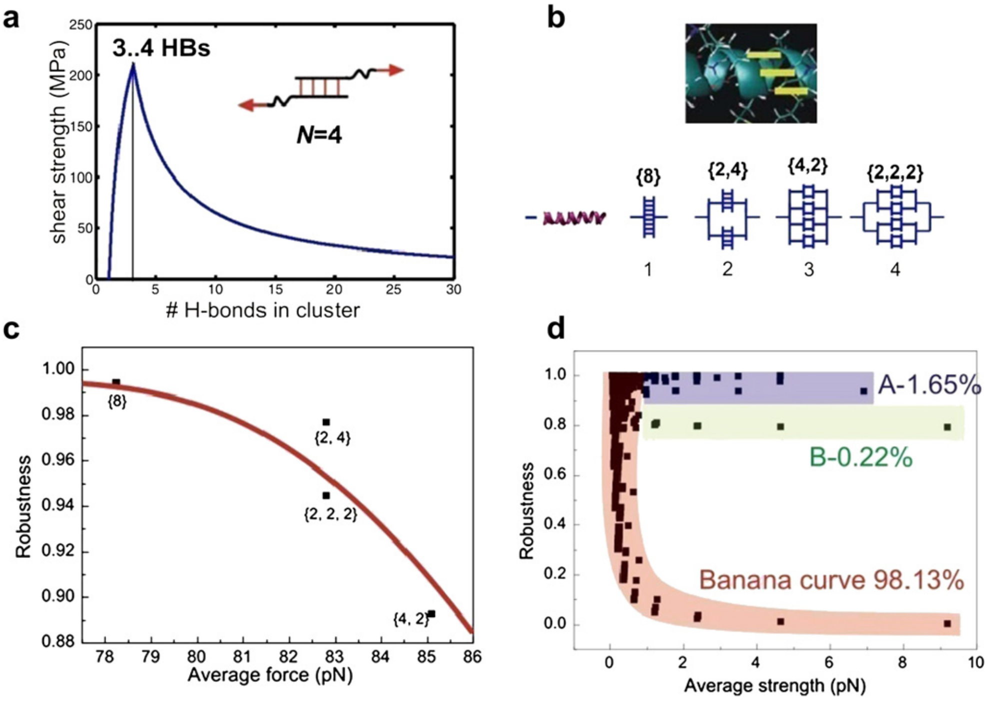


Fig. 21. Size effect and strength–robustness relation for alpha-helical protein filaments, composed out of clusters of H-bonds. (a) Shear strength of clusters of H-bonds as a function of the size of the strand, showing a peak maximum shear strength of close to 200 MPa at a critical cluster size of 3–4 H-bonds. By utilizing a size effect, the fundamental limitation of H-bonds of being mechanically weak can be overcome. (b) Geometry of a single alpha-helix, composed of 3–4 H-bonds per turn. We study how the performance in the strength–robustness domain changes if several alpha-helices are assembled in different hierarchical patterns, as shown schematically in the plot (for 8 alpha-helices). (c) Results for eight subelements in the protein filament arranged in all possible hierarchical patterns. The definition of subelements and their arrangement are those shown in panel b. (d) Results for 16,384 subelements in the protein filament. An analysis of the distribution of structures and their performance shows that most data points (>98%) in panel d fall onto the banana-curve. Only less than 2% of all structures lead to high strength and high robustness. This analysis shows how high-performance materials can be made out of relatively weak constituents such as alpha-helices that are bonded by mechanically inferior H-bonds.

are bonded by mechanically inferior H-bonds. Many biological materials may have developed under evolutionary pressure to yield materials with multiple objectives, such as high strength and high robustness, a trait that can be achieved by utilization of hierarchical structures. The use of these concepts may enable the development of self-assembled *de novo* bioinspired nanomaterials based on peptide and protein building blocks.

8. Issues related to blends of nanoparticles and block copolymers

Nanocomposites composed of block copolymers (BCPs) and nanoparticles have attracted much attention because BCPs organize into diverse multiphase structures with nano-scale periodicity and commercial interest [115–119] and because of the recognition that the properties of even ordinary polymers can strongly benefit from the addition of nanoparticles [119]. Fullerenes (C_{60}) are particularly attractive nanoparticle additives because of numerous proposed applications of C_{60} nanocomposites in the electronics, laser engineering, optics, and pharmaceutical industry [120]. The tunability of the optical properties of Au and CdSe and the conductivity of Au, Ag and other metal nanoparticles make these nanoparticles also attractive as BCP additives. Recent work has shown that the interfacial morphology of self-assembled BCP can be decorated with conductive nanoparticles, an effect of potential widespread application [119]. Nanoparticles within ordered BCP films have also been used as detectors of residual stresses in solution-cast BCP films through their influence on the BCP morphology [121].

A recurrent problem in the blending of BCP and nanoparticles is the propensity of nanoparticles to self-assemble into extended clusters that can greatly affect the BCP ordering morphology and the very nature of the BCP order–disorder transition. Thermal fluctuations in BCP materials characteristically drive the ordering phase transition order from second to first-order by the well known Brazovskii mechanism and there have been many observations of jumps in X-ray and neutron scattering intensity data at the order–disorder transition (ODT) that signal this phenomenon. However, the existence of quenched disorder associated with extensive nanoparticle clustering can be expected to destroy the ODT if their perturbing effect on the ordering process becomes sufficiently large. Yue et al. [122] have found this effect in the dispersion of C_{60} into a model (polystyrene-*block*-polyisoprene) BCP material. In particular, small angle X-ray scattering data indicated that a small amount (1 mass %) of C_{60} caused the BCP to remain disordered over a wide temperature range so that a BCP ordering phase transition no longer existed. This phenomenon offers both technological problems and opportunities.

Why might particle clustering influence the BCP ordering so profoundly? Theoretical studies on quenched disorder effects on first-order phase transitions in three dimensions predict the existence of a critical concentration at which the phase transition *either* transforms to second-order phase transition or disappears altogether and evidence for this effect has been observed in various inorganic materials [123–127]. An infinitesimal amount of disorder can destabilize the first-order phase transition by transforming into some “glass-like” state where ordering is so frustrated that only a highly rounded remnant of the original phase transition then exists. A similar effect has been observed in adding a crystallizing species (succinonitrile mixed with $LiClO_4$) to another crystallizing species (polyethylene oxide) where a glass material (as defined by the phenomenological temperature dependence of the rate of structural relaxation) is apparently obtained at intermediate mixture compositions [128]. In this context, the suppression of the ordering process of both the succinolnitrile/$LiClO_4$ component and PEO, a beneficial effect for battery applications using this type of blend since crystallization leads to a drop of conductivity and battery function.

The effect of nanoparticle clustering on the ordering process can be demonstrated by functionalizing the surface of the nanoparticle to inhibit this process and to control the nanoparticle segregation to the different polymer microphases. For example, Schmaltz et al. [129] functionalized C_{60} with PS and found that these nanocomposites order similarly to the neat BCP, although the NPs segregate as one might expect to the PS rich domains in the ordered state. Li et al. have observed that the self-assembly nanoparticles into extended structures can also serve as a template for the directed BCP assembly when the extended nanoparticle superstructures remain localized to the BCP microdomains, implying a synergistic interaction between the nanoparticle assembly and BCP ordering processes [130]. These observations together suggest that the capacity of the clustered nanoparticles to span different BCP domains is important for disrupting the BCP ordering process.

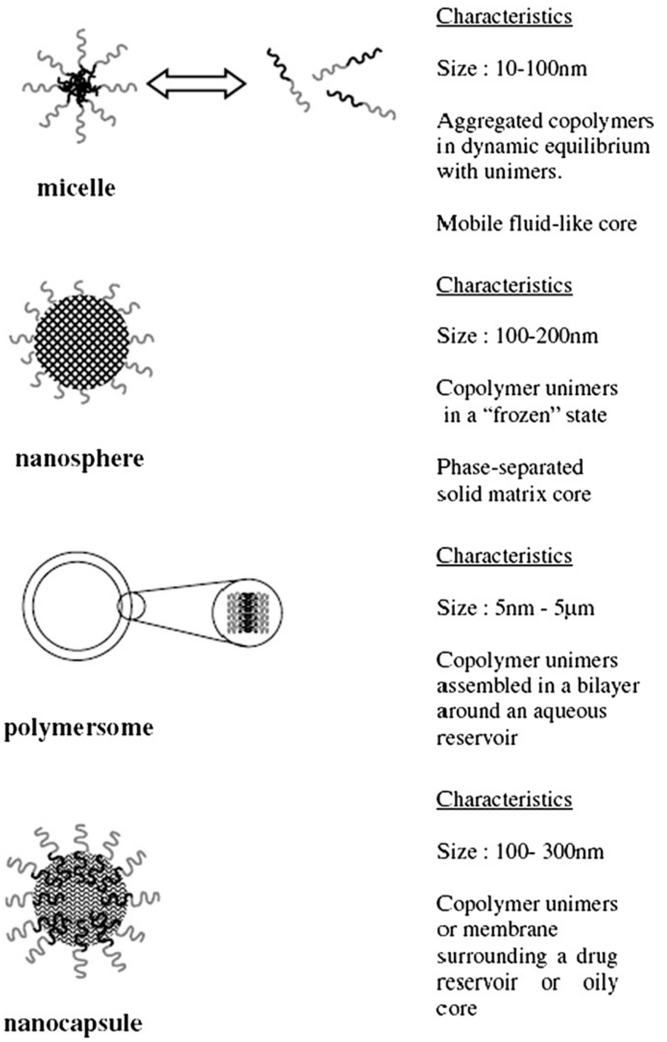
Although the propensity of nanoparticles to associate into clusters in BCP nanocomposites can have a disruptive effect on the ordering process, the promise of these blends can realized by surface functionalization of the particles to control this clustering process or the particle clustering can be exploited by engineering the nanoparticle directional interactions (magnetic, and electric dipolar are prevalent in these particles) to engineer the template morphology for the BCP organization. It should also be possible to use field-directed particle assembly to direct the nanoparticle organization in a similar manner to control BCP morphology [131]. The effective manipulation of this type of BCP organization can be expected to have application in the organic photovoltaic field, fuel cells and bottom-up self-assembly based fabrication processes utilizing BCP materials as templates.

Recently, a novel strategy [132,133] has been developed in order to organize functionalized inorganic nanoparticles in polymer matrices by exploiting microphase separation. This technique is based on self-assembly on nanoparticles in one microdomain of the block copolymer followed by its nanophase-separation and can be expected to be useful in the preparation of nanocomposite films having novel optical and mechanical properties for coating applications [134,135]. The structure of composites formed from block copolymers and nanoparticles has been found to depend on the shapes of the particles, their inter-particle interaction, the interfacial interactions of the BCP material and the ordered morphology that the BCP material forms in the bulk. The morphology of BCP films can also depend on the method of film formation (flow coating *vs.* spin casting [136] and the presence of nanoparticles that span the polymer film [136]. Non-equilibrium effects associated with the physics of block copolymer ordering and polymer glass-formation and the solvent evaporation process can all contribute to the structure of these cast BCP films.

The fabrication of BCP-based nanostructures applicable to nano floating gate memory was investigated by using a block copolymer system composed of Polystyrene (PS) and Polymethylmethacrylate (PMMA). Nanoporous thin film from PS-*b*-PMMA diblock copolymer thin film with selective removal of PMMA domains was used to fabricate needle-like nanostructures. It was demonstrated that by combining these self-assembled BCPs with regular semiconductor processing, a non-volatile memory device with increased charge storage capacity over planar structures can be realized.

9. Nanoparticles formed from block copolymers

Self-assembled amphiphilic BCPs have been shown to greatly improve toughness without sacrificing other mechanical properties. The BCP nanoparticles appear to be more effective than other



Characteristics

Size : 10-100nm

Aggregated copolymers in dynamic equilibrium with unimers.

Mobile fluid-like core

Characteristics

Size : 100-200nm

Copolymer unimers in a “frozen” state

Phase-separated solid matrix core

Characteristics

Size : 5nm - 5μm

Copolymer unimers assembled in a bilayer around an aqueous reservoir

Characteristics

Size : 100- 300nm

Copolymer unimers or membrane surrounding a drug reservoir or oily core

Fig. 22. Nanoparticulate drug delivery systems formed by amphiphilic block copolymers and their general characteristics (Ref. [138]).

conventional rubber particles, probably due to its much smaller sizes and unique morphology [134]. Model diglycidyl ether of bisphenol – An epoxy resins containing well-dispersed 15 nm block copolymer (BCP) nanoparticles were prepared to study the effect of matrix crosslink density on their fracture behavior. The toughening effect from BCP nanoparticles was also compared with core–shell rubber-toughened epoxies having different levels of crosslink density [137].

In recent decades, there has been increased interest in the use of polymer nanostructures for drug delivery applications. Drugs may be encapsulated, adsorbed or dispersed in them (Fig. 22). The nano-size range of these delivery systems allows them to be injected directly into the systemic circulation without the risk of blocking blood vessels. Researchers have demonstrated that opsonization and subsequent recognition and phagocytosis by macrophages is strongly correlated with the size of the particle. Amphiphilic BCPs are able to form a range of different nanoparticulate structures. These include micelles, nanospheres, nanocapsules, and polymersomes [138]. A recent advance is the development of multi-functional polymersomes that carry pharmaceuticals and imaging agents simultaneously. The ability to conjugate biologically active ligands to the brush surface provides a further means for targeted therapy and imaging. Hence, polymersomes hold enormous potential as nanostructured biomaterials for future *in vivo* drug delivery and diagnostic imaging applications [139,140]. Simulation suggests that novel porous nanocontainers can be formed by the coating of a sacrificial nano-bead by a block copolymer layer with a well-controlled nanostructure [141] (Fig. 22).

10. Polymer brushes on nanoparticles

The surface functionalization of nanoparticles by grafting of a polymer is expected to play important role in the designing of novel organic/inorganic nanocomposite materials [142,143]. In recent years, much attention has been paid to the use of atom-transfer radical polymerization (ATRP) from nanosurfaces (Fig. 23) [144–148], because this allows better control over the molecular weight and molecular weight distribution of the target grafted polymers [149]. The surface-initiated ATRP technique had been successfully used for the grafting of well-defined homopolymers [144,150], diblock copolymers [151], graft copolymer [152], star polymers [153], and hyperbranched polymers [154] from the nanoparticles, nanotubes, nanowires, and clays. A versatile method was developed for the chain-end functionalization of the grafted polymer chains for surface modification of nanoparticles with functionalized groups through a combination of surface-initiated atom-transfer radical polymerization (ATRP) and Huisgen [3 + 2] cycloaddition [143]. Novel (inorganic nanoparticles/polymer) nanocomposites were prepared through a direct polymer grafting reaction from the surfaces of magnetite (Fe_3O_4) ($d = 10$ and 25 nm) and titanium oxide (TiO_2) ($d = 15$ nm) nanoparticles. The initiator was chemisorbed onto the nanoparticles and gave controlled polystyrene (PS) and poly(3-vinylpyridine) (P3VP) graft layers on their surfaces [155].

The fabrication of responsive/adaptive colloidal systems possessing quasi-stable organization, which can be tuned by an external signal, is a strong stimulus for research of polymer brushes [156]. These systems are capable of switching their interfacial interactions in response to external signals due to a reversible change in their surface chemical composition (Fig. 24). Recently, synthesis and characterization techniques for nanoparticles have rapidly developed, indicating the importance of organizing these particles into various assemblies to obtain novel properties that may arise from their 2D and 3D arrangements [157]. Thus, there is a strong need to build an appropriate level of interaction between neighboring nanoparticles, as well as between nanoparticles and their host environment. Here we address one of the important applications of nanoparticle suspensions with tunable interactions, for the fabrication of functional coatings.

11. Polymer nanostructures for electronic and photovoltaic applications

Carbon nanotubes (CNTs) have shown high potential in improving electrical conductivity at low CNT content [158–161]. Recently, double wall carbon nanotubes (DWCNT) were found to be useful in field electron emitters as they have longer lifetime than SWCNT [162,163]. The inner tube in DWCNT is shielded by the outer tube. The shielding of inner tube is also an argument for preferable use of DWCNTs in nanotube composites, since the interaction between the polymer and the outer tube would not apparently change the electronic structure of the inner tube. Thus it is challenging to investigate the embedding of DWCNTs into a polymer matrix. In situ polymerization is considered as a very efficient method to significantly improve the CNT dispersion and the interaction between CNTs and polymer matrix [164].

Semiconducting polymers are widely used as electronically active materials, e.g., as emitters in organic (materials based) light emitting diodes (OLEDs), or polymer lasers [165, 166]. In this

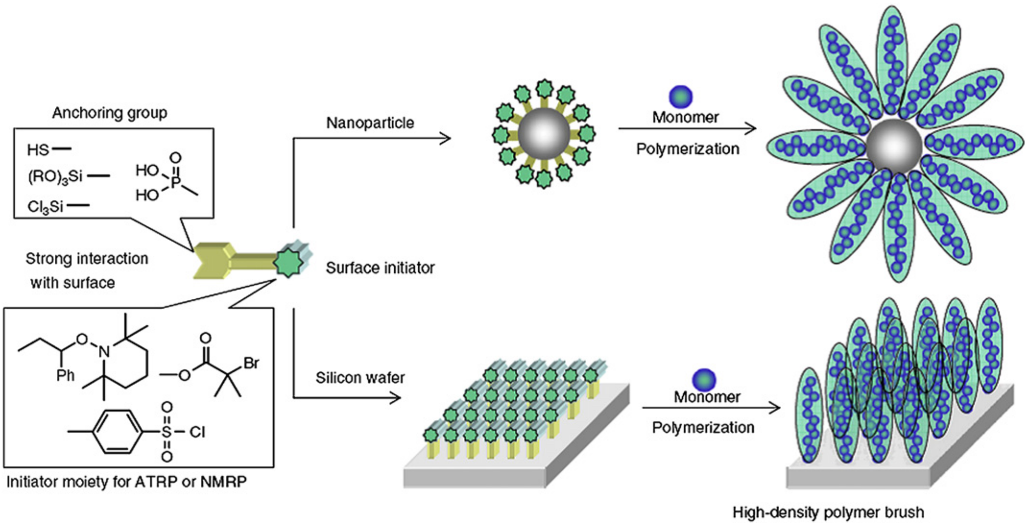


Fig. 23. Design of initiator for surface-initiated radical polymerization on the surface of metal oxide nanoparticles and Si–wafer surfaces (Ref. [155]).

cases, the active polymers are single component layers of uniform morphology. For other applications, especially in photovoltaic devices (photodiodes or solar cells) more complex materials have been favoured [167,168]. The efficiency of such photovoltaic devices is often limited by the short diffusion range of photogenerated charge carriers. Structures in which a heterojunction is distributed throughout the film have been described (Fig. 25). Among them, conjugated donor polymers doped with fullerene acceptors or fullerene/polymer multilayer systems attracted most attention [169,170]. However, only light absorbed close to the heterojunction results in charge generation. The size of the active region corresponds to the diffusion range of photogenerated charge carriers, in conjugated polymers typically 10–20 nm [171,172]. Novel systems, which are able to undergo a controlled nanophase-separation, came in the focus of interest, since such systems should allow for a more efficient generation of electron/hole pairs. Different approaches towards such structures are possible. Blends of two immiscible polymers can lead to the formation of complex phase-separated structures [173]. Here, the scale length for phase separation is relatively less controlled. In di- or tri-block copolymers the scale length of phase separation is directly related to the chemical structure and the various blocks lengths. Especially semiconducting block copolymers which are composed of electron-rich and electron-poor conjugated blocks are very attractive targets [174].

Photovoltaics comprised layers and blends of a hole-transporting derivative of poly(p-phenylene-vinylene) with a variety of electron-transporters such as TiO_2, a cyano-substituted PPV, and a fullerene derivative (PCBM) were prepared [175]. Photovoltaic device characterization was combined with time-resolved and steady-state photoluminescence to understand the nature of the excited state and its effect upon device performance. It was found that morphological differences, such as chain conformation or domain size, often overshadow the effect of charge transfer, so that device performance is not necessarily correlated with rapid decay times. Exciton generation was found to be a similarly important factor in most devices.

It was found, that the photoinduced electron transfer from semiconducting polymers onto C_{60} is reversible, ultrafast with a quantum efficiency approaching unity, and metastable. This photoinduced electron transfer leads to a number of potentially interesting applications, including photodetectors and photovoltaic cells [176]. In order to meet realistic specifications for practical applications in the near future, more detailed researches are required to resolve several fundamental issues limiting the device performance of the polymer-based photovoltaic cells, such as stability of the active materials, device lifetime issue, and still low power conversion efficiency, etc., [177].

There is also a significant progress in studies of polymeric covalent and noncovalent modifications of fullerenes (mainly C_{60}) and carbon nanotubes (CNTs), and their applications. By using functional polymers to react with fullerenes, or synthesizing polymers in the presence of fullerenes, various kinds of polymeric fullerenes can be prepared: side-chain polymers, main-chain polymers, dendritic fullerenes, star-shaped polymers, fullerene end-capped polymers, etc. 'Living' polymerization methods have also been introduced for preparation of fullerene polymers allowing both the architecture of the fullerene polymers and the grafted polymer chains can be well-controlled. The synthesis of polymeric CNTs is only in its infancy. However, present results show promise that the combination of the unique properties of CNTs with functional polymers will lead to novel materials with unusual mechanical, electrical, magnetic, and optical properties. Doping of polymeric systems with fullerenes in is also a very important research area, especially for preparation of electronic and optical materials. Both conducting and conventional polymers can be used as matrices in the preparation of functional composites. The combination of the unique properties of fullerenes and CNTs with polymers makes these materials potential candidates for many applications, such as data storage media, photovoltaic cells and photodiodes, optical emitting devices, photosensitive drums for printers, and so on [178,179].

The organic nanoparticle–polymer photovoltaic (PV) cells contain fullerene derivatives (e.g., phenyl C61-butyric acid methyl ester, PCBM) or single-walled nanotubes as the nanoparticle phase. The second type is hybrid inorganic nanoparticle–polymer PV cells. These contain semiconducting nanoparticles that include CdSe, ZnO or PbS. An outcome of consideration of the literature in both areas are two sets of assembly conditions that are suggested for constructing PCBM–P3HT (P3HT is poly(3-hexylthiophene)) or CdSe–P3HT PV cells with reasonable power conversion efficiency. The maximum PCE reported for organic nanoparticle PV cells is about twice that for inorganic nanoparticle–polymer PV cells. This appears to be related to morphological differences between the respective photoactive layers. The morphological differences are attributed to differences in the colloidal stability of the

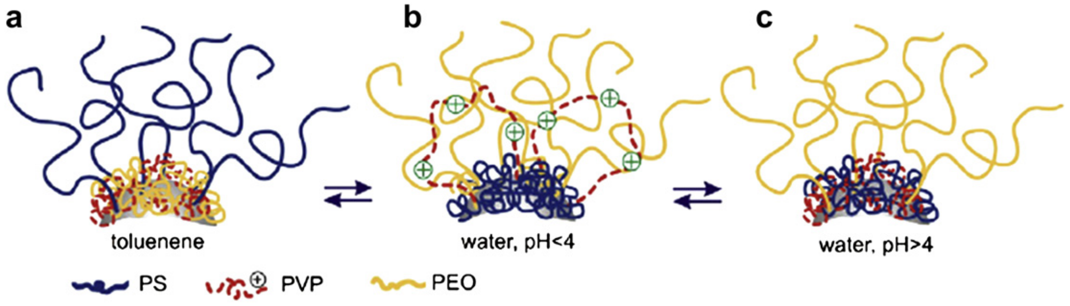


Fig. 24. Schematic representation of different morphologies of particle shells prepared from the PS–2VP–EO brush: collapsed P2VP, and stretched PS chains in toluene, a good solvent for PS, and a poor solvent for P2VP (a); collapsed PS, and stretched P2VP, PEO in water at $\text{pH} < 4$, a good solvent for P2VP and PEO, and a poor solvent for PS (b); collapsed P2VP, PS, and stretched PEO chains in water at $\text{pH} > 4$, a good solvent for PEO, a poor solvent for P2VP and PS (c) (Ref. [156]).

nanoparticle/polymer/solvent mixtures used to prepare the photoactive layers [180,181].

A promising route for photovoltaic conversion has emerged from the combination of electroactive nanomaterials and small bandgap polymers. The formation of bulk heterojunctions resulting from the extended interfaces leads to efficient dissociation of the charge pairs generated under sunlight shown by the rapid extinction of the polymer photoluminescence for increasing contents of fullerenes or TiO_2 nanoparticles in MEH–PPV or PVK. Unconventional elaboration routes of the blends have been developed to increase the nanofiller dispersion and inhibit phase separation at high concentration. The size reduction of the acceptor domains led to a complete quenching of the radiative recombinations, obtained by specific solvent processing of MEH–PPV/C_{60} nanocomposites or sol gel elaboration of TiO_2 nanoparticles in a PVK film. A simultaneous increase of the photocurrents could be achieved by the dispersion and size optimisation of the nanofillers. In situ generation of Ag particles in MEH–PPV provides an example of enhanced charge separation induced by the plasmon resonance at the metal/polymer interface. The strong influence of the molecular morphology on the nanocomposite properties emphasizes the large improvements which can still be gained on the performances of organic solar cells [182].

Conductive carbon nanoparticles were also introduced into PEO/P(VDF–HFP)/SiO_2 nanocomposite polymer electrolyte for dye sensitized solar cells (DSSCs). The dependence of ionic conductivity on nanoparticle content was not monotonous. The energy conversion efficiency of DSSC increased with addition of carbon nanoparticles up to 8wt% and above this threshold, the efficiency sharply decreased [183].

A hydroxyl-coated CdSe nanocrystal (CdSe–OH) and a CdSe–polymer nanocomposite were synthesized and used as the electron acceptors in polymer solar cells (PSCs). The CdSe–polymer nanocomposite was prepared via atom-transfer radical polymerization (ATRP) of N-vinylcarbazole on functionalized CdSe quantum dots [184]. DSC indicated that CdSe–PVK had a lower glass transition temperature (T_g) in comparison with PVK due to the branch effect of the star-shaped polymer hybrid. TEM and SEM micrographs exhibited CdSe nanoparticles were well coated with PVK polymer. Both CdSe–OH and CdSe–PVK were blended with poly(3-hexylthiophene) (P3HT) and used as the active layer in bulk heterojunction solar cells. In comparison with the P3HT:CdSe–OH system, PSC based on P3HT:CdSe–PVK showed an order of magnitude improved power conversion efficiency. Film topography studied by AFM further confirmed the better device performance was due to the enhanced compatibility between P3HT and CdSe–PVK.

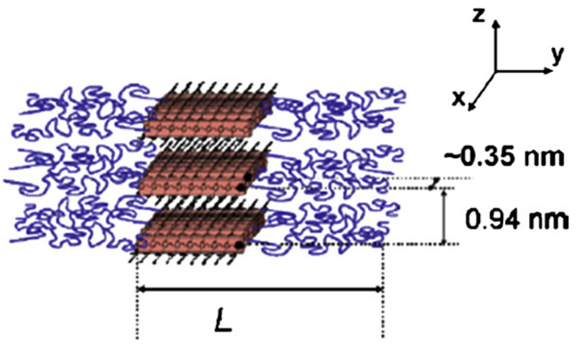


Fig. 25. Proposed model for the nanostructure of (DEH–PPV)-*b*-PBA-s films (Ref. [185]).

12. Conclusions

The nature of the effects caused by adding solid nanoparticles into amorphous polymer matrix has been reviewed. The presence of the attractive or repulsive polymer–NP interaction led to an increase or decrease of the particle relaxation time relative to the pure polymer in a ‘layer’ about the particles, respectively, and these changes were correspondingly reflected in both T_g and fragility increasing. An examination of local force constant fluctuations in these mixtures implicates changes in the elastic constant fluctuations, which are presumably related to fluctuations in the local molecular packing within the polymer matrix. These results indicate that the NP can ‘polarize’ the configurational state of the polymers to alter the nature of the molecular packing about the particles and thereby alter the intrinsic breadth of the glass transition process. Evidence supporting this scenario was discussed, although it is pointed out that the observed trends may be more complicated in polymer matrices involving hydrogen bonding polymers where self-assembly competes with the glass transformation process. Taken together, these results nonetheless indicate that the NP can induce large non-continuum effects on the nanocomposite materials, even in the regime of good dispersion. This effect is quite apart from those involving particle-induced cross-linking and self-assembly.

We have also examined the mechanism of nanoparticle clustering in a simple model polymer nanocomposite above T_g, as well as the interplay between clustering and NP shape effect on nanocomposite viscosity and shear strength. Clearly, there are clustering or assembly mechanisms that differ from phase separation and are equilibrium in nature. We also find differences in the materials viscosity due to clustering or shape that cannot be understood from traditional continuum hydrodynamic effects. Instead, multiparticle interactions, such as chain bridging play a significant role. Tabulating and quantifying the various non-continuum effects in polymer nanocomposites is important, but it is only one step toward a goal of a more comprehensive theoretical framework in which to understand NP clustering and the resulting effects on material properties. Many questions remain unanswered – or even un-asked. As a result, the field will likely be a fertile ground for investigation for many years to come.

Controlling the dispersion of nanoparticles into polymer matrices is a significant challenge in achieving the dramatic property improvements promised by polymer nanocomposites. 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. Thus, optimizing one *vs*. two properties of a composite can require very different morphologies. It suggests that the creation of multifunctional composites requires exquisite control over nanoparticle spatial distribution 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 but transparent polymers which are wear resistant. Making such connections between nanoparticle dispersion and organization with macroscale properties is then a crucial aspect that is only now beginning to be considered.

Systematic investigation of the effects of the manner in which the nanocomposites are prepared/assembled on their mechanical response has been recommended. Rheology of chain near solid surfaces should be used to investigate effects the interfacial interaction on the chain dynamics over several length and time scales. Differences between reactive (thermosetting) and non-reactive (thermoplastics) systems should also be addressed, since in these systems, local structure partitioning obeys different set of natural laws.

Biology utilizes hierarchical structures in an intriguing way to create multi-functional materials. The integration of scales, as well as the mixing of physical, biological and chemical concepts into novel engineering designs could complement the current practice of disease diagnosis and treatment, as well as the design of new materials, and thereby unfold many opportunities for technological innovations. The wide impact of the use of materials science approaches in biology and biomedical sciences in the context of tissue engineering and regenerative medicine, materials science approaches have started to play an important role in the biomedical literature. As for mechanical properties, the study of materials failure could provide an interesting platform to advance our understanding of diseases.

Using block copolymers, the preparation of nanocomposites with nanoparticles in variety of polymer morphologies and consequently with atypical viscoelastic properties for coating applications. The detailed nanostructure of composites formed from BCPs and nanoparticles is known to depend sensitively on the preferred morphology of the block copolymer, on the shapes of the particles, and on interactions between the two components. But it can also depend on the kinetics of self-assembly in the polymer, and there are circumstances under which the kinetics of morphologically selective domain nucleation and growth determine the overall nanostructure of the composite.

The surface functionalization of nanoparticles by grafting of a polymer is expected to play important role in the designing of novel organic/inorganic nanocomposite materials. The fabrication of responsive/adaptive colloidal systems possessing quasi-stable organization, which can be tuned by an external signal, is a strong stimulus for research of polymer brushes. These systems are capable of switching their interfacial interactions in response to external signals due to a reversible change in their surface chemical composition.

The efficiency of photovoltaic devices is often limited by the short diffusion range of photogenerated charge carriers, typically of the order of 10–20 nm. Structures in which a heterojunction is distributed throughout the film have been described, e.g., conjugated donor polymers doped with fullerene acceptors or fullerene/polymer multilayer systems. It was found, that the photoinduced electron transfer from semiconducting polymers onto C_{60} is reversible, ultrafast with a quantum efficiency approaching unity, and metastable. In order to meet realistic specifications for practical applications in the near future, more detailed researches are required to resolve several fundamental issues limiting the device performance of the polymer-based photovoltaic cells, such as stability of the active materials, device lifetime issue, and still low power conversion efficiency, etc.

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