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Modeling of Nanocomposites

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4.1
Introduction – The Need For Modeling

Polymer- as well as ceramic-based composites filled with nanofillers are a novel class of materials. These systems are compositionally similar to conventional composites. In both nanocomposites and regular composites (referred to here as microcomposites), the matrix is the same. For example, polymer forming a matrix may be essentially any thermoplastic or thermosetting polymer. The feature that distinguishes the two classes of composites is the size and nature of the filler. Nanocomposites are filled with nanoparticles or with carbon nanotubes. The characteristic dimensions of the filler are <100 nm and often in the range of 100 nm. The fillers may be spheroid, such as ceramic nanoparticles or carbon black; plate-like, such as layered silicates; or fiber-like, such as nanotubes.

Nanocomposite materials exhibit properties that are significantly different from those of the corresponding microcomposite. Examples are discussed at length in other chapters of this book. Polymers filled with nanoparticles have significantly enhanced stiffness and strength compared to similar materials filled with regular micrometer-size ceramic particles. Most importantly, a gain in these properties does not compromise ductility, as typically occurs with conventional materials. In other systems a significant ductility enhancement was measured with no decrease in strength [1, 2]. Also, ceramic nanocomposites exhibit increased fracture toughness. Other examples involve fluids such as water or glycol which, when filled with metal nanoparticles, exhibit thermal conductivity enhancement [3] that cannot be explained by classical approaches valid for standard composites [4]. This clearly indicates that, whereas a body of knowledge derived from standard continuum-level modeling approaches provides a good description of microcomposites, it is inadequate in its current form to describe properties and behaviors of nanocomposites.

The development of these new materials, and particularly an understanding of their properties, is still in its infancy. Consequently, to date, proofs of concept have been repeatedly and consistently made, but material optimization is still an elusive goal. For example, good filler dispersion has been demonstrated to be critical for achieving

properties superior to those of microcomposites, but it is still unclear how other parameters such as filler distribution and filler surface functionalization influence the overall properties. Optimization of these materials will be possible only when the physics controlling the enhanced properties is properly understood, and when the processing routes leading to the desired nano- and microstructures are established. The current approach to investigating these issues is experimental and based on trial and error. Hence, modeling the material response would provide valuable information on the underlying physics and the desired structure – property linkages. Furthermore, once the desired structure is established, modeling has the capability to assist the development of material processing.

4.2
Current Conceptual Frameworks

The properties of the matrix, the distribution and properties of the filler, and the nature of their interface control the behavior of a typical microcomposite. The interface plays an important role in controlling several microcomposite properties such as its thermal conductivity, load-carrying capacity, toughness, and transport properties. However, for a characteristic filler particle sizes on the micrometer scale and larger, the main parameter controlling the macroscopic properties is still the filler volume fraction. In these materials, the interface may be viewed in the standard way, as a 2D surface separating the constituents. By contrast, when the matrix is filled with nanosized particles, a significant fraction of the material is either at the interface or within its immediate vicinity. For ceramic composites, one can argue that the interface width is still small relative to the filler size or the filler-to-filler distance; thus extension or modification of standard composite theory or modeling approaches may be sufficient. For polymer nanocomposites, the modification of the matrix may extend over several radii of gyration from the particle surface. In turn, this situation results in novel macroscopic properties that are dictated qualitatively, as a trend, and quantitatively, by the behavior of the confined polymer that forms the modified matrix.

Several attempts have been made to provide a conceptual framework for justifying the observed enhanced properties of polymer nanocomposites. One such theory, alluded to above, the 'bonded polymer layer' [5], is based on the observation that, at the same volume fraction, the total interfacial area in a nanocomposite is much larger than in a microcomposite. The total volume of 'bonded polymer' (confined polymer next to the filler wall) is conjectured to represent a large fraction of the volume of the nanocomposite, and therefore, the properties of this confined material determine the macroscopic properties of the system. However, the available experimental results on the existence of a bonded polymer layer are contradictory [6, 7]. It is also unclear how thick the layer surrounding each particle is and, most importantly, what the properties of the polymer in the interfacial region are.

More recently, the 'double network' theory was proposed. This idea is based on the observation that the reduction in particle size entails a similar reduction in the inter-

particle spacing and that special macroscopic properties are obtained when the average distance between particles becomes comparable to the bulk radius of gyration of the polymer chains. These events create conditions for a chain to connect two or more particles, hence forming a network that provides additional strength by increasing the number of effective entanglements in the system [8]. The intuitive appeal of this theory is high, but quantitative predictions that may be compared with experimental results require a thorough understanding of the structure of chains confined between spherical fillers.

4.3
Multiscale Modeling

Considering the multiple time and length scales characterizing nanocomposites, and polymer nanocomposites in particular, a comprehensive approach to modeling these systems requires multiscale modeling. Whereas multiscale modeling across all length scales, from electronic level to bulk-matter sizes, and all time scales is a future challenge, the various components of composites have however undergone extensive independent study. The dynamics of polymers, which control the mechanical and dielectric responses of these materials, have been studied for many years. Much literature exists on both molecular and continuum aspects of this problem. Several classical models of stress production and chain dynamics dominate current thinking. Following an idea introduced by Guth and Mark [9], the chains are regarded as entropic springs in tension. This concept is rooted in the observation that, as the material deforms, the chains are stretched and their entropy decreases. The change in entropy entails a free energy variation, leading to a retractive force. The force required to stretch the chain proves proportional to the change in the end-to-end distance, which suggests that the chain may be compared with a linear spring. The force is always retractive, and in vacuum, the chain should collapse into itself. The corollary is that all chains are in tension. Furthermore, the force is proportional to the absolute temperature, which is the signature of its entropic nature. The energetic component of the free energy is usually neglected in this theory. This view gained support from early experimental observations that established unequivocally that the nature of stress in rubbers is indeed entropic.

Two main models describe chain dynamics, and hence stress and dielectric relaxation. The Rouse model represents the dynamics of chains shorter than the average distance between entanglements, but long enough to behave as entropic springs [10]. This model is in agreement with the entropic spring description of a chain. The principal interactions accounted for are those along the chain, and the surrounding medium is represented in a homogenized way, by means of a frictional force acting on the representative chain. Chains longer than the entanglement length exhibit slower dynamics, which is described by the reptation model [11]. In this model, the effect of nonbonded interactions between monomers not directly connected by backbone covalent bonds is conjectured to lead to constraints that force the chain

to diffuse primarily along its contour. Several other representations have been proposed [12 – 14].

A rich literature exists on the development of continuum constitutive models of polymer behavior. These models are mostly phenomenological and are developed based on macroscopic mechanical testing of both neat and filled polymeric materials. Several excellent treatises exist on this topic; [15] is a general overview.

Polymer interfaces and, in particular, the polymer chain behavior close to flat interfaces, have been studied by simulations and have a long history of theoretical treatment. The study of the conformations and dynamics of linear polymeric chains in the vicinity of flat walls or free surfaces [16 – 29] is motivated by the many applications in which the behavior of confined chains is important. Such applications include, but are not limited to, coatings, flow of molecular solutions in capillaries, and their interaction with filters and membranes.

In nanocomposites, the chain – filler interactions control to a large extent the matrix and macroscopic properties. Therefore, understanding chain conformations and dynamics of the confined chains next to filler surfaces is crucial. The physical picture that emerges from the cited studies is summarized below.

The conformations of a macromolecule located close to an impenetrable interface are restricted. They are determined by the configurational entropy of the chain, by the energetic interactions between polymers (cohesive interactions in bulk), by the nature and strength of the interaction between polymers and the confining wall, and by global system parameters such as temperature and density. When the chain approaches the wall, the configurational entropy decreases due to the reduced number of accessible chain configurations. This generates an entropic driving force that retracts the chain from the interface, with the force increasing linearly with temperature. This effect generates a low-density polymer layer in the immediate vicinity of the interface [30 – 32]. The variation in density has a significant effect on chain mobility as well as on the diffusion of small molecules. The retraction is balanced by packing in the bulk polymer. An attractive energetic interaction between polymers and the wall also promotes chain adsorption. The interplay of these forces determines the actual configuration.

Another entropic force promotes movement of chain-end monomers to the interface [21, 32]. This force is due to the fact that the reduction in the number of accessible chain configurations induced by confinement is less dramatic if the chain comes in contact with the wall with only one of its ends. Hence, chains having their center of mass within two radii of gyration of the wall adjust so as to replace chain-inner-monomer contacts with chain-end contacts.

In the immediate vicinity of a flat impenetrable wall, the polymer chains are preferentially aligned on multiple scales in a direction parallel to the interface. This leads to changes in the glass transition temperature and to a broader relaxation spectrum. The degree of alignment depends on the details of the energetic interaction with the wall. It is generally considered that a chain may adopt a 'docking' type configuration at high temperatures and relatively weak attractive interactions and may completely adsorb if the attraction is strong [33]. Chain collapse in the interface leads to pronounced alignment on the bond and larger scales.

These details are important for understanding the physics of polymer-filler interactions in systems filled with layered silicates, in which interfaces are mostly planar [34]. Another issue in these composites regards the dynamics of polymer intercalation between silicate layers. In polymers filled with nanoparticles and nanotubes, the interface is curved, and it is necessary to ask to what extent the curvature modifies the physical picture described above. This issue was studied [35, 36], resulting in the conclusion that, for realistic curvatures, the polymer structure next to a wall is close to that next to a flat surface in the presence of similar energetic interactions. Interestingly, these models showed that, even in the presence of strong hydrogen bonding of polymers to the curved wall, the shape and size of polymer coils having their center of mass close to the wall remains essentially similar to that in the bulk. However, the ellipsoidal coils undergo a 'docking transition', rotating with their long semiaxis in the direction tangential to the curved wall.

The connection between the physics on the atomic and molecular scales and the meso and macroscopic material behavior requires the development of continuum models. These models must incorporate the smaller-scale physics. Steps along this line have been taken for neat polymer and are reviewed in [37]. In nanocomposites, additional difficulty resides in the fact that the mesoscale continuum model needs to describe deformation on the scale of the inter-filler spacing. Because the fillers have dimensions comparable to those of the polymeric chains, and because the fields vary on the same scale, the homogeneity assumption for the representative volume element is no longer mandated. Under these conditions of high structural and field gradients, nonlocal constitutive laws are required. The development of such laws that incorporate molecular and atomistic information is an emerging field.

On a larger scale, nanoparticles tend to cluster before and during processing of the composite. Currently, it is generally accepted that good dispersion is required for enhanced macroscopic properties. Obtaining the appropriate dispersion in practice is largely a matter of experimental ability. Modeling may be used in this connection to elucidate two issues. On the one hand it is necessary to understand the lower limit of dispersion required for imposed macroscopic properties, and on the other, process modeling that would guide the routes for achieving the desired dispersion is highly desirable. Developing these types of models requires reliable constitutive equations.

On the scale of filler agglomerates and larger, the material may be described in the continuum sense by using the methodologies developed for classical microcomposites. Homogenization theory and asymptotic expansion techniques are useful tools in this endeavor. The standard homogenization theory leads to poor approximations of local fields in the presence of high-gradient regions. In fact, the use of this technique is possible only within the assumption of homogeneous fields over the representative volume considered. In practice, the adequacy (or lack of it) of the homogenization theory can be assessed on the basis of the uniform validity of the double-scale asymptotic expansion [38].

These techniques may be used to study the effect of filler distribution. Good dispersion of fillers, but nonuniform distribution, improved wear properties and scratch resistance of the composite. Most properties depend on filler distribution, and mate-

rial optimization would require the development of models that may provide the gross behavior while accounting for nonuniform distributions of fillers.

4.4
Multiphysics Aspects

One of the principal advantages of polymer nanocomposites is multifunctionality. Through multifunctionality, the material exhibits enhanced properties with regard to several physical phenomena. The composite may be transparent to the visible spectrum and opaque to ultraviolet while being wear- and scratch-resistant; it may simultaneously provide good strength and diffusion barrier properties. All models predicting the macrosopic behavior should capture the relevant multiple physical processes with respect to which the material is being optimized.

Various physical phenomena are intimately coupled at the atomic and molecular scales and, as such, are captured by discrete models. In continuum representations, the physics is traditionally decoupled. Nanocomposite models should overcome this limitation. Hence, when going from discrete to continuum models, one has to ensure that discretely represented processes can be described by conventional partial differential equations, that the constitutive law selected for the 'smallest-scale continuum' is able to represent the (mean) 'fields', and that the time scale cutoff, which is associated with this transition, does not alter the essential physics studied. Accurate modeling of discrete-continuum transition hinges on an affirmative answer to all these questions.

Multiphysics coupling in the continuum sense may be performed either by adding additional terms in the continuum balance equations ('equation coupling') or by requiring the phenomenological coefficients entering the constitutive laws to depend on the fields to be coupled ('constitutive law coupling'). The coupling of fields (stress/strain, temperature, solute/reactants concentration) occurs through diverse phenomena, some of which are shown in the interaction matrix of Table 4.1. The interaction matrix is 'nonsymmetric', with cell (i, j) representing the phenomenon induced by the

Tab. 4.1 Coupling of physical phenomena in continuum models.

Deformation (displacements)	Deformation-induced heat production	Strain-controlled diffusion	Strain-controlled chemical activity
Thermal expansion	**Heat transfer (temperature)**	Temperature-controlled diffusion	Temperature-controlled chemical activity
Clustering, precipitation (eigenstrains)	Diffusant concentration-controlled heat transfer	**Diffusion (diffusant concentration)**	Transport of reactants
Reaction products accommodation (eigenstrains)	Heat production during chemical reactions	Transport of reaction products	**Chemical reactions**

process corresponding to field *i* and which influences field *j*. For instance, cell (1, 2) represents heating due to deformation, and cell (2, 1) corresponds to thermal expansion and thermal stresses. A fully coupled continuum analysis would consider all processes shown in the matrix, but an uncoupled approach would only consider the diagonal entries. As mentioned, the coupling of various physical processes in the mathematical model can be carried out either by considering additional terms in the field equations or by allowing the constitutive law to depend on the interacting field. An example from the first category is the effect of the temperature gradient on the stress field, which can be captured by adding a thermal stress term to equilibrium equations. A less familiar example within the same class of problems is the effect of diffusion (clustering of diffusants) and chemical reactions (reaction products) on the stress field, which can be accounted for by the eigenstrain formulation [39]. An example from the second category is the influence of temperature upon diffusion, which can be captured by simply considering the diffusion coefficients to be temperature dependent.

4.5
Validation

Development of faithful predictive multiscale models of nanocomposites will require a systematic validation effort. The multiscale multiphysics models must be calibrated and validated *at multiple scales* against experiments that resolve the finer scales. For polymer nanocomposites, the experimental data obtained by nuclear magnetic resonance (NMR), dielectric spectroscopy (DS) and quantitative dynamic mechanical analysis (QDMA) can be used to verify the ability of the developed models to predict the conformation and kinetics of polymer chains. NMR measurements probe segmental motions of the main chain and side chain movement over a frequency domain from several Hz to several MHz. Longer-time and larger-scale dynamic effects, which can be modeled by coarse-grained discrete and continuum approaches, would be validated against DS and QDMA measurements. By these techniques, short- and long-time relaxation modes are probed by mechanical or electric excitations.

The challenge to the experimental work will be to perform measurements on well characterized systems, such as those with well defined particle size and shape distribution and particle dispersion. Ideally, one would like to control and vary individual parameters so as to asses their roles. Some successes in this area involve the ability to change surface chemistry, thus controlling the strength of the particle-matrix interactions. However, in experiment, it is often very difficult or even impossible to control various parameters and characteristics independently of one another. The hope is that the combined experimental–modeling effort will allow the acquisition of better and deeper understanding of the structure–property–processing relationships in the quest for guided design of nanocomposites with desired, optimized properties.

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