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Mechanical percolation in nanocomposites: Microstructure and micromechanics

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ABSTRACT

Polymer nanocomposites can enable innovative designs of multifunctional materials. Metallic fillers in polymer matrices exhibit improved electrical properties at low volume fractions, often maintaining the low density, transparency and easy processing of polymers. Surprisingly, enhanced mechanical properties have also been observed at uncharacteristically low volume fractions in these nanocomposites. The majority of mathematical models used to describe this novel mechanical behavior are based on percolation models of microstructural connectivity. Changes in mechanical properties, however, are likely to be affected by complex microstructures, beyond simply connected, as well as by the micromechanical mechanisms associated with a composite material. Both microstructural and micromechanical mechanisms are thought to be significantly influenced by the presence and properties of an interface region, between particles and matrix, which functions as a third composite phase. In this work, the relative influence of the competing and compounding effects of the spatial position/distribution of the particles (microstructure) and of the composite constitution (micromechanics) are examined. The results show that models based solely on the inclusion of a third composite phase do not predict the experimentally observed mechanical response. This work continues with a study of the micromechanical effects of microstructure using a probabilistic and statistical characterization of the local strain fields associated with random microstructures. These continuous fields are not only more amenable to statistical characterization than the spatial ternary (matrix, particle and interface) fields that describe the microstructure, but offer a more direct, and potentially more visual, link between microstructure and mechanics. An apparent percolation threshold for a 2D material model is identified based on statistical characterization of the elastic moduli, distributions of local strains and spatial autocorrelation of local strain fields. The statistics of strain fields associated with microstructures producing minimum and maximum moduli are also compared.

1. Introduction

Enhanced mechanical properties have been observed in polymer nanocomposites at uncharacteristically low volume fractions [1–3]. These effects are thought to be due, in part, to the significant scale effect of the matrix–particle interface region in nanocomposites [4–6]. This interface region occurs as a result of a perturbation of the properties of the matrix material due to the presence of the included particles. Factors that may cause this perturbation are, e.g., the quality of bonding between the material phases, confinement of the matrix, or interference in the mobility of the flexible chains of the polymer. These factors can result in an increase in the stiffness of the matrix in a thin layer surrounding the reinforcing particles, effectively creating a third composite phase. These local effects, and the development of this interface region, are present in all composite materials. However, because of the high surface area to volume ratio at the nanoscale, the volume fraction of the interface in nanocomposites can be greater than that of the particles, representing a significant, stiffer than the matrix, composite phase. In addition to contributing to the overall effective stiffness of the composite it has been hypothesized that these interfacial regions contribute to the formation of percolated microstructures by forming connections between particles and interface, a pseudo-percolation [5,7–9], or by percolating themselves.

The majority of application based models used to describe percolation effects depend on prior knowledge of a theoretical percolation threshold. This threshold is the volume fraction at

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which a connected microstructure within a random composite is likely to form. Models based on percolation thresholds are well developed in the study of electrically conducting composites. Because of the resemblance of the mechanical curves to electrical percolation curves, many of the electrical models have been adopted to describe mechanical effects; conductivity terms are replaced by stiffness terms. However, composite electrical conductivity is relatively binary; below the threshold volume fraction the composite has low conductivity and above the threshold its conductivity is greatly enhanced. In contrast, mechanical percolation may have more intermediate stages. Certainly a connected microstructure will enhance mechanical properties, but composite properties are continuously affected by the volume fraction of filler. Additionally, when a compliant matrix is confined between unconnected regions of a stiffer included phase, the ability of the matrix to deform may be reduced, making it effectively stiffer.

A number of researchers have attempted to include more mechanics in modeling mechanical percolation. Early work included the Generalized Effective Media model [10], which interpolated between a mean field model, at low volume fractions, and percolation theory, above the percolation threshold. This model has been used to predict both electrical and mechanical percolation [3]. The series–parallel model [11] included an intermediate parameter that described the volume fraction of material that was active in the transfer of forces. A limitation of both of these models is that a previously identified value for the percolation threshold is required as input. In [12], the authors examined the influence of an interface region, as well as the effects of clustering using the concentric cylinder micromechanics model, but not in the context of percolation thresholds. A hybrid numerical analytic model was used in [13] to investigate polymer nanocomposites with complex microstructural configurations; the model included the effects of an interface as a third, independent phase, i.e., not linked to particle placement.

2. Microstructure and micromechanics

Fralick et al. [9] studied percolation effects by simulating populations of random microstructures for a three phase nanocomposite; particles, matrix and interface, at discrete volume fractions. Effective properties of each microstructure were calculated and statistical averages of these properties were used to predict composite response. In this approach, composite mechanical response defines the percolation threshold, rather than the reverse. This model also predicted a distribution of properties resulting from the random microstructures; these probabilistic distributions varied with particle volume fraction [14].

The most easily identifiable microstructures, which produced significant increases in stiffness, were those where particle and interface regions formed connected pathways, a pseudo-percolation [8]. However, these microstructures were difficult to associate with the distribution of intermediate stiffnesses observed in the population of simulated microstructures and expected as a result of the random placement of particles. This distribution of properties is likely due to a combination of mechanisms, potentially dominated by *microstructural* effects, spatial arrangements, percolation and/or pseudo-percolation, but are also affected by the *micromechanical* effects of a third composite phase.

To investigate the relative contributions of these effects, the results presented in [9], which used the grid based computational Generalized Method of Cells (GMC) micromechanics model [15,16], are compared to the predictions of an analytic micromechanics model, Mori–Tanaka (MT) [17,18], to provide an illustration of the competing and compounding effects of spatial position and composite constitution. In what follows, a brief overview of both models is presented.

2.1. GMC/Simulation model

In [9], the model nanocomposite was a polymer matrix embedded with metallic nanoparticles. Random microstructures were simulated at volume fractions ranging from 0 to 1 in steps of 0.05; 300 microstructural realizations were generated for each volume fraction. The Generalized Method of Cells micromechanics model was used to calculate effective elastic properties in the simulated microstructures. GMC is a periodic unit cell model that uses a rectangular repeating unit cell (RUC), composed of multiple subcells, as the representative volume element (RVE). The homogenization process in GMC connects the material microstructure to an equivalent homogeneous material through a set of continuum level equations. Periodic boundary conditions are used to enforce continuity of displacements and tractions across subcell boundaries and between RUCs. The nano composite model consisted of a cubic RUC with cubic subcells. Each subcell was assigned the specific properties of one of the phases; matrix, particles or interface.

Each composite phase was assigned isotropic elastic properties. The metal particle subcells were assigned a stiffness of $E_p \sim 10^{10}$ Pa and a Poisson's ratio of 0.33 and the polymer matrix subcells a stiffness of $E_m \sim 10^4$ Pa and a Poisson's ratio of 0.45. There are no accurate measurements of interfacial stiffness, however it is reasonable to expect that the interface will have a stiffness between that of the matrix and the included phase. Here the interface region was assigned a stiffness equal to the geometric mean of the polymer and particles, $\sqrt{E_m E_p}$, and a Poisson's ratio of 0.45. Interface thickness was set at one-half of the particle diameter based on an assumed interface thickness of 15 nm, a value often mentioned in the literature, surrounding a 30 nm diameter particle.

Fig. 1 shows the GMC/Simulation results, plotting the minimum, mean and maximum values of the elastic stiffness. All values are scaled by the matrix stiffness, $E_{composite}/E_m$. The increase in properties on the log-scale plot, between volume fractions of 0.20 and 0.35, characterizes an 'apparent' percolation threshold effect.

In the GMC/Simulation model the interface region was simulated as an effect of particle placement rather than as a distinct third composite phase, i.e., particle subcell positions were established first and interface subcells were inserted around them.

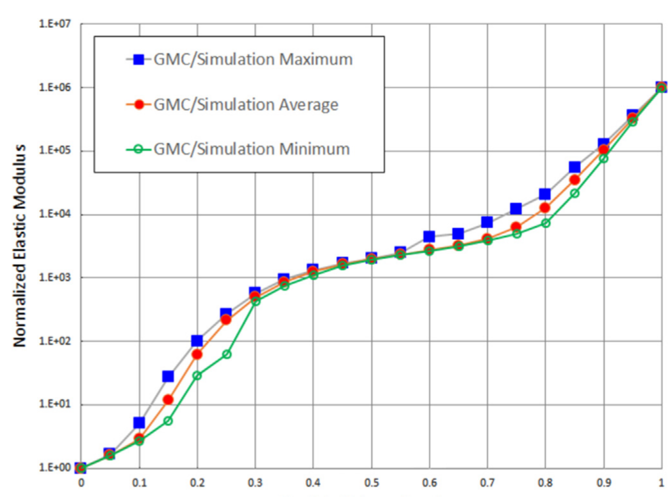

Fig. 1. Scaled elastic moduli for 3-phase nanocomposite based on the GMC/Simulation model results. Minimum, mean and maximum values versus particle volume fraction.