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Utilizing real and statistically reconstructed microstructures for the viscoelastic modeling of polymer nanocomposites

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In this paper, we present a new approach to finite element modeling of a nanoparticle filled polymer system that utilizes the actual and statistically reconstructed microstructures of the material. Typically, description of polymer nanocomposites for microstructure generation is difficult given the high degrees of freedom inherent in the location of each nanoparticle. The lack of true microstructure utilization hinders our ability to understand the interaction between the nanoparticle and polymer, which cannot easily be deconvoluted from experiments alone. We consider here a material system of carbon black particle fillers dispersed in synthetic natural rubber. Scanning Electron Microscope (SEM) images are first taken of these carbon black-rubber composites samples and then transformed into binary images. The binary images from either a microscope image of original specimens or microstructure reconstruction according to the material statistical description are used as geometric inputs for the finite element model along with experimentally determined viscoelastic properties of pure rubber. Simulations on the viscoelastic properties of the rubber composites are performed through ABAQUS. The simulated results are then compared with composite viscoelastic data in both frequency and temperature domains. The comparison shows that for the specific rubber/CB composite discussed in this paper, the thickness being 25 nm and relaxation time being 32 times that of matrix polymer provide the best approximations for the properties of interfacial polymer.

1. Introduction

Polymer nanocomposites are materials composed of polymeric matrix in which inclusions (spheres, nanotubes, platelets) of nanoscale dimensions are incorporated. Polymer nanocomposites have been investigated for the past decade because of their outstanding material properties and great potential. The addition of nanosize inclusions into polymer matrix combines the advantage of polymer itself and the excellent properties of nanoparticles. Additionally, interactions between the nanofillers and the surrounding polymer chains alter the mobility of these polymer chains, resulting in a regime of "interphase" polymer, in which the material properties differ from the bulk matrix. Due to the high surface-to-volume ratio of nanofillers, the effects of this special region play an important role in the overall properties of nanocomposites, especially viscoelastic responses [1–4]. The composite material composition and properties are highly tunable, and performance improvements are currently demonstrated for a wide range of properties including stiffness, strength, heat resistance, optical properties, electric conductivity and barrier properties [5–11], leading to a wide range of applications in vehicle, aerospace, medical device industries [12–15].

At the same time, the sensitivity of final nanocomposite properties to small changes in processing, functionalization, additives, and volume fraction has made development of these materials difficult. Much of the property sensitivity can be linked to two factors: (1) changes in dispersion/distribution of nanoparticles and (2) chemical interaction differences between particle surfaces and matrix polymer. Both of these factors affect the properties, extent, and connectivity of interphase domains in the composite system. Therefore, development of methods which can directly link nanoparticle morphology to properties are valuable toward fundamental understanding of the underlying physics, as well as for facilitating material design. This paper deals directly with this needed research.

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Many modeling frameworks have been developed to explain the material properties of polymer composites with nanofillers. These include methods at both nanoscale (molecular dynamics [16–21]) and micros/macro scale (continuum theories [22–24]). Although MD simulations are able to capture the configurations of polymer chains and particles embedded at nanoscale, they could only account for structures with small number of particles and limited polymer chains due to the computational constraints. To study the mechanical responses of polymer nanocomposites at micro/macro scale level, many continuum models have been developed, including rule-of-mixture, self-consistent scheme [25–27], Mori–Tanaka method [28], etc. However, these methods do not explicitly consider spatial distribution of nanoparticles.

The finite element method is another continuum model that has been widely used to predict the viscoelastic properties of polymer nanocomposite systems [29–31]. Recently Qiao and Brinson [32,33] developed a 2D plain strain finite element model to study the impact of interphase on the viscoelastic properties as well as thermal response of polymeric nanocomposites. In this model, finite element analysis is performed on a representative volume element (RVE) with periodic structure (inhomogeneous distribution of particles inside a unit square). Their results show that the distribution of particles has a significant impact on the interphase percolation and further influence on the viscoelastic properties of the bulk composites.

Among the various kinds of polymer nanocomposites, carbon-black/rubber composites is one of the most commonly used materials worldwide in communication, transportation, architecture industries [34]. The creep and relaxation behaviors of carbon black filled rubber systems have been received increasing attention recently [35–38]. Constitutive models [39,40] attempting to characterize their viscoelastic behaviors are also developed for large deformations. Montes and White [41] presented a rheological model to distinct composites with low interaction (viscoelastic) and high interaction ('thixotropic-plastic-viscoelastic') between rubber and carbon black particles. The morphology of carbon black dispersed in rubber is a challenge in predicting the mechanical behaviors of the composites.

In this work, we built up a microstructural image-based finite element framework to simulate and predict linear viscoelastic mechanical responses of carbon black-rubber composites. We focus on detailed characterization of the microstructure morphology which has twofold benefits. First, it enables a quantitative understanding of the microstructure–property relationship and the sensitivity of various descriptors of microstructure morphology, such as clustering, percolation, dispersion, and orientation of inclusions, with respect to their impacts on the prediction of bulk properties [42,43]. The knowledge gained from this can be further utilized for sophisticated material design through shaping the microstructure morphology via controlling ingredients and manufacturing processes [42,43]. Second, based on the statistical descriptors, a microstructure can be reconstructed from a sample space to reduce the need for difficult and time consuming high resolution imaging techniques like scanning or transmission electron microscopy (SEM, TEM). In the situation where three dimensional (3D) imaging like X-ray microtomography technique is not affordable or unavailable and information about the isotropy of the material is known, the 3D structure of heterogeneous material can be reconstructed using statistical information extracted from 2D planar cuts and extrapolated to the third dimension [42–47]. To predict the material property of a given microstructure, the binary digitized medium from either the real microscopic image of specimens or microstructure reconstruction are imported into ABAQUS input file as the geometries of the finite element model. The predicted tan δ curves of the composites are compared with experimental tan δ curves from DMA (Dynamic Mechanical Analysis) tests. Due to the complexity of retrieving interphase properties from experiments, the unknown interphase properties can be extracted by calibration to best fit the experimental results.

2. Modeling framework

2.1. Data-driven framework for microstructure construction

A data-driven framework was developed to generate binary digitized medium from the grey SEM image [48]. It includes five steps as shown in Fig. 1. The grayscale microstructure images are taken by a high-resolution imaging technique (SEM shown in Fig. 1) in Step 1 and act as the data driving the rest of the process.

For two-phase materials like the carbon black filled rubber composite, Step 2 transforms a high-resolution grayscale image to a binary image that discretely separates the two phases. Two image enhancement algorithms, namely the contrast-adjustment method and the median noise filtering algorithm, are first used to increase the quality and contrast of the grayscale images before transformation [49]. The known volume fraction of the experimental samples are used as the threshold criteria for determining white and black pixel populations.

In step 3 we characterize the microstructure morphology with a set of statistical descriptors based on the binary digitized medium. A variety of descriptors have been proposed to quantify the inherent statistical characteristic of material microstructure [50–54]. Two point correlation function $S_2(r)$ and two-point cluster correlation function $C_2(r)$, defined as the probability of finding a pair of points in the same phase and the probability of finding a pair of point in the same cluster respectively, are chosen to characterize the carbon black filled rubber composite in our study [55,56]. An illustration of the two-point correlation and two-point cluster correlation of a polymer composite with 20% carbon black fillers is shown in Fig. 2.

Given the statistical descriptors from the real micro structural image, i.e., two-point correlation and two-point cluster correlation, the microstructure can be reconstructed in a statistical sense. In Step 4, the microstructure reconstruction is naturally formulated as an optimization problem where the discrepancies between the target statistical descriptors and that of a reconstructed image are minimized [46,47,55,50,57,58]. The simulated annealing algorithm is developed to resolve the resulting optimization problem [46,47,56], and to find the "optimal" material configuration based on thousands of microstructures generated in a stochastic fashion. The detailed procedures of the optimization can be found in [48]. Many such statistically equivalent microstructures can be generated through Step 4. Then in Step 5, the binary digitized medium from either the real microscopic image of specimens or microstructure reconstruction will be imported into ABAQUS as the geometries. An example of the comparison between the original image and reconstructed images is shown in Fig. 3.

2.2. 2D Finite element simulation

We adopted a 2D plain stress finite element model to predict the tan δ curve of carbon black filled rubber composites and compare with experimental data. The discretization of a 2D binary image directly retrieved from either the SEM image of rubber-carbon black composite sample or statistical microstructure reconstruction is used as one input geometry into our FE model (Fig. 4). In this process, the image with its physical size 7.46 μm $\times$ 7.46μm is divided into 300 $\times$ 300 pixels, where each pixel has the initial material properties of either carbon black or the matrix, depending on the color (black or white) of the pixel in the image. Therefore the pixels belonging to particle phase correspond to carbon black