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Multiscale modeling of damage progression in nylon 6/clay nanocomposites

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ABSTRACT

A hierarchical multiscale model for nylon 6/clay nanocomposites is adopted to study its damage and post-damage behavior. The 3D representative volume element (RVE) of the nanocomposites at the macroscale comprises a nylon 6 matrix with embedded silicate layers. Taking into consideration the interactions between nylon 6 and the clay particulates, a gallery inter-layer was inserted between the intercalated silicate layers and an interphase layer was added around the silicate. Both gallery and interphase layers were treated as interfaces in this study. Molecular dynamics (MD) simulations were performed to obtain the material behavior of the interfaces. Results from the MD simulations were used to parameterize a traction–separation law which was incorporated into the RVE to model interfacial degradation. The damage of bulk nylon 6, on the other hand, was governed by the Gurson–Tvergaard–Needleman (GTN) model. The finite element method (FEM) was used to simulate the RVE model under quasi-static uniaxial stress loading. The constitutive relationship and fracture patterns of the nylon 6/clay model with 2.5% weight fraction of clay were studied. The apparent yield stress is found to increase while the ductility decreases when the clay particle size increases or the number of silicate layers decreases. The effect of interfacial strength on the properties of the nanocomposites is also presented. When the interfacial strength was relatively low, debonding of the interphase layer is the cause for damage initiation; a higher cohesive strength of the interfaces will lead to damage initiation from the polymer matrix around the interphase layer. This is due to inherent weak adhesion strength of the polymer chains, which was also observed through experimental results.

1. Introduction

Polymer/clay nanocomposites (PCNs) are a novel class of materials where nanometer-sized layered silicates are introduced into a distinct polymer matrix. These nanocomposites exhibit significant improvements in mechanical, thermal and barrier properties from the dispersion of low weight fractions (<5%) of nanometer-sized layered silicates with high aspect ratios and high strengths in the polymer matrix [1–3].

Clay reinforced nylon 6 nanocomposites were first prepared by Toyota research group [4,5]. Since then, the preparation and mechanical behaviors of these nanocomposites have been extensively studied. It is well documented that the Young's modulus and the yield stress of nylon 6 can be improved with the incorporation of layered silicates. However, the damage and post-damage behavior of the nylon 6/clay nanocomposites are not well characterized. A good understanding of the damage properties of nanocomposites is particularly important for structural design and practical applications. A few experimental works were carried out to study the damage and fracture mechanisms of nylon 6/clay nanocomposites [6,7]. However, it is difficult to analyze the micromechanics of the polymer nanocomposites through experiments alone due to the nanometer-sized reinforcements. Few laboratories have the experimental set-ups to record processes at the nanometer and nanosecond length and time scales. For the same reasons, it is also difficult to obtain experimental repeatability. In most analytical approaches, effective clay models are usually considered to study the effects of the structural parameters of clay particles, such as the number of silicate layers, particle size and interlayer spacing on the mechanical behavior of polymer/clay nanocomposites [8,9]. The analytical models usually give rise to empirical equations that are curve fitted to experimental data. They cannot be used to study damage progression of PCNs with complex microstructures. For damage analyses, the interaction between the layers of minerals which make up the clay particles need be taken into account.

Computational micromechanics is emerging as a powerful tool to study the mechanical behavior of heterogeneous materials

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including nanocomposites. Computational techniques are dependent on the length scale of interest, ranging from the atomic, e.g., Molecular Dynamics (MD), to continuum length scales, e.g., finite element method (FEM). In practice, multiscale modeling methods, which cover both the molecular scale and continuum scale, are often adopted to study polymer nanocomposites with hierarchical structures. There are two typical multiscale modeling methods. They are the hierarchical multiscale modeling method and the concurrent multiscale modeling method. In the hierarchical multiscale modeling method, a series of sequential computational methods are linked in such a way that the calculated quantities from a computational simulation at one scale are used as inputs to determine the properties of the materials considered at a larger scale. For the concurrent multiscale modeling method, several computational methods are linked together in a combined model where different scales of material behavior are considered concurrently. The parameters from different scales could be exchanged by using a handshaking procedure [10]. The applications of the concurrent multiscale modeling method are limited because the computational cost can be unreasonably high for damage problems with complex microstructures. In this study, the hierarchical multiscale modeling strategy is adopted. In the hierarchical multiscale model, a representative volume element (RVE) model is usually established to obtain the macroscopic behavior of nanocomposites. The materials properties of some constituents can be calculated from lower scale simulations. The main advantage of RVE modeling is that heterogeneities of the material, such as shape, size and orientation of reinforcements as well as voids and flaws can be explicitly represented. A numerical example employing RVE model to study the mechanical properties of nano-clay reinforced brittle polymer, namely the epoxy, can be found in [11].

In this paper, a 3D RVE model was established and a hierarchical multiscale modeling method was adopted to determine the initiation of microcracks and their evolution in nylon 6/clay nanocomposites. MD simulations were performed to obtain the properties of interfaces, including the gallery layer and the interphase layer. Effects of structural parameters of clay particles such as the particle size and the number of silicate layers per particle on the mechanical behavior of nylon 6/clay model were studied. Effects of interfacial strength are also reported. Different constituents of the nanocomposites were governed by different damage criteria. These criteria included the Gurson–Tvergaard–Needleman (GTN) model and traction–separation laws parameterized by MD simulations. The response of the RVE model to uniaxial stress loading was solved by a commercial implicit/explicit FEM code, ABAQUS.

2. Methodologies

2.1. FE clay model and RVE model

Micro-fracture and deformation mechanisms of nylon 6/clay nanocomposites have been experimentally studied by He et al. [6]. It is known that fracture initiation and evolution is strongly influenced by local inhomogeneities in composite materials. Establishing a computational model that reflects the actual microstructure of nylon 6/clay nanocomposites is fundamental to reliable fracture prediction of such new systems. Many of the properties associated with polymer/clay nanocomposites are a function of the extent of exfoliation of the clay platelets. High exfoliation is desirable for enhancing the functional properties of nanocomposites. For intercalated polymer/clay nanocomposites, polymer molecules would penetrate between stacked silicate layers to form a gallery layer during the manufacturing process. The interphase layer is regarded as the layer of polymer formed immediately around the silicate platelet. It has properties distinct from the polymer matrix due to the chemical reaction between silicate layers and polymer matrix. In this study, both the gallery layer and interphase layer are defined as interfaces. Although small in thickness, the aspect ratio of these interfaces is very large as they are adjacent to the clay platelet. It is reasonable to expect that these interfaces can significantly affect the properties of the particles and the polymer as a whole, i.e., weak interfaces will decrease the strength of the nanocomposites [12]. A FE model for the clay particle in nylon 6/clay nanocomposites is shown in Fig. 1b. It should be noted that in actual nanocomposites, the geometric parameters of the nano-clay may vary due to various factors of the synthesis process. Usually experimental techniques, such as wide angle X-ray scatting (WAXS) are used to characterize the geometric properties of the nano-clay particles. In highly exfoliated nylon 6/clay nanocomposites containing intercalated silicates, experimental observation shows that the thickness of the mono silicate layer is around 1 nm, the thickness of the gallery layer is within 1–4 nm, and the in-plane dimensions range from 100 nm to 1000 nm [2,3]. In this study, the nano-clay is modeled as perfectly round and flat particles for simplicity. N is the number of silicate layers per nanoparticle. A unity value of N means completely exfoliated nano-clay particles whereas $N \geqslant 2$ means intercalated layers. The gallery layer, the interphase layer and silicate layers have the same diameter, i.e., $d_g = d_i = d_s$. The thicknesses of the gallery layer, interphase layer and silicate layer are $h_g = 2.82$ nm, $h_i = 6$ nm and $h_s = 0.95$ nm, respectively. These values are determined by measuring the thickness of the molecules within the gallery, the interphase and the single silicate sheet with crystal lattice structure under equilibrium in MD simulations. All these values are also within experimental range. Unless explicitly stated, these values will be used throughout the manuscript.

The RVE model, comprising four constituents – the matrix, the silicate layer, the gallery layer and the interphase layer – was generated using in-house algorithms. In each RVE model, 35 clay particles are randomly and periodically distributed in the cubic matrix. RVE models of nylon 6/clay nanocomposites with 1%, 2.5% and 5% weight fractions of nano-clay were generated for analysis. For each combination of structural parameters, nine models with different resolutions and particle configurations were generated and used in the computations to obtain an average of the predicted properties. An RVE model with 2.5% weight fraction of nano-clay, $N = 2$, and $d_g = d_i = d_s = 208$ nm is shown in Fig. 1c. The finite element mesh is shown in Fig. 1d. Due to the complexity of the local geometry, the matrix and silicate layers were meshed with tetrahedron elements – C3D4 elements and the interface layers were meshed with 3D cohesive elements – COH3D8 elements. Different failure criteria were applied to different material phases. When these criteria were satisfied, the corresponding elements are removed. Quasi-static loading conditions were simulated using explicit FEM. One major difficulty encountered by explicit FEM is the simulation incremental step needs to be small to guarantee a stable solution. This will result in extremely long simulation times for the quasi-static analysis. The computational time for explicit FE simulation can be reduced by mass scaling with minimal influence on the results. In this study, mass scaling was applied for the silicate layer since the elastic stiffness of silicate layer is much higher than that of the gallery layer, the interphase layer and the nylon 6 matrix in the RVE model. For all simulations, the kinetic energy was less than 5% of the total strain energy indicating quasi-static loading processes were simulated.

2.2. GTN model

In this study, the Gurson–Tvergaard–Needleman (GTN) model [13–15] was applied to nylon 6 to mimic its plasticity and damage