MULTISCALE MODELLING OF POLYMER-CLAY NANOCOMPOSITES

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Keywords: *multiscale modeling, nanocomposites, representative volume element, periodic boundary conditions, cohesive zone model*

1Introduction

Polymer-clay nanocomposites is a subject of growing interest as they often exhibit markedly improved material properties compared to the pure polymer matrix or traditional micro/macro composites. However, these novel materials also bring about challenges in the prediction of their properties. Simulations using classical molecular dynamics (MD) are normally limited to a few billions of atoms while traditional continuum mechanics and composite theories are unable to include the atomistic characteristics of the nanoscale interfaces; an important feature in nanocomposites because of the high surface-to-volume ratios involved. In this study, a multiscale modeling approach of polymer-clay nanocomposites is presented. The mechanical properties of the matrix, clay particles and interfaces are obtained from MD simulations which are then imported into a representative volume element (RVE) modeled using the finite element method (FEM). Hydrostatic tension is conducted on the RVE cell to investigate the influence of splitting failure within intercalated clays on the mechanical performance of the bulk materials.

2Models and Methodology

2.1 Material System

The computational model is based on an actual nanocomposite system. The polymeric matrix being studied is Nylon6. The clay particles specified in the study is organic modified montmorillonite (OMMT) with cations exchange capacity (CEC) of 90 mequiv/100mg and it closely represents the product from the Southern Clay Company, US.

2.2Molecular Dynamics Model

2.2.1 Polymer Matrix

For the matrix, the thermoplastic Nylon6 is investigated, and the chain length is set to be 20 due to the computational limit of classical molecular simulation. A cubic cell packed with Nylon6 chains is built and loaded in uni-axial tension to explore the elastic-plastic properties of the pure matrix.

Table 1. Elastic constants of Nylon6

Young' modulus	3.3 Gpa
Possion's ratio	0.35

The plastic regime of the stress-strain relationship was also obtained but is not shown here.

2.2.2 Clay and Cohesive Zone Model (CZM)

The intercalated clays have a layered structure, composed of inorganic silicate sheets and organic galleries between them. It has been experimentally observed that the interlayer failure of organic galleries would lead to the formation of the microcracks which are able to propagate along the silicate surface and then into the matrix, leading to final failure of the macroscale samples [1, 2]. In order to understand the influence of the gallery failure on the mechanical performance of the bulk system, the clay particles are modeled as a disc-like sandwich [3], comprising two stiff and isotropic effective layers with a cohesive layer [4] in the middle representing the organic gallery as illustrated in Figure 1. The isotropic layers and cohesive layer are also fully parameterized by MD simulations using the modified PCFF force field [5].

2.3 Finite Element Model

2.3.1 Geometric Features

A RVE cell of polymer-clay nanocomposite at the mesoscale level is introduced to study the failure mechanism of the hybrid system. It is assumed that the intercalated clay particles are randomly distributed throughout the matrix, and they follow the periodic distribution on the boundary surface as illustrated in Figure 2(a).

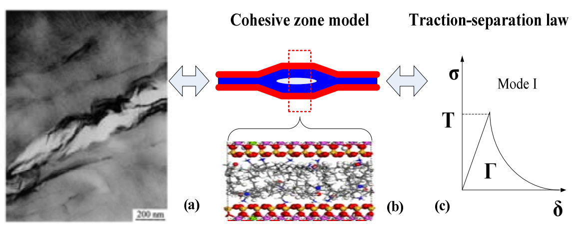

Fig.1. (a) Experimental observation of the formation of microcracks in layered clay particles, (b) Cohesive zone model of layered clays with molecular details, (c) Traction-separation law to describe the splitting failure of the gallery.

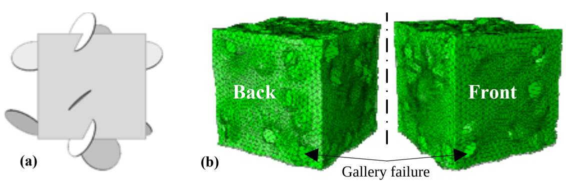

Fig.2. (a) Geometric periodic distribution of clay particles, (b) Periodic boundary condition constrain on the surface nodes of the RVE cell.

2.3.2 Periodic Boundary Condition

Periodic Boundary Conditions (PBC) are imposed on the surface nodes to ensure the continuity of stress contours and synchronous splitting failure on opposite surfaces of RVE, as shown in Figure 2 (b). Figure 3 shows the comparison of stress contours and splitting failure of two opposite surfaces with two different boundary conditions.

2.3.3 Loading condition

Hydrostatic loading is applied on the RVE cell. The mean stress $\sigma_m = (\sigma_1 + \sigma_2 + \sigma_3)/3$, volumetric strain $\varepsilon_v = \varepsilon_1 + \varepsilon_2 + \varepsilon_3$ of the RVE domain and the scalar stiffness degradation (SDEG) of the cohesive elements of the galleries are recorded to study the failure process from the splitting damage of the intercalated clay particles.

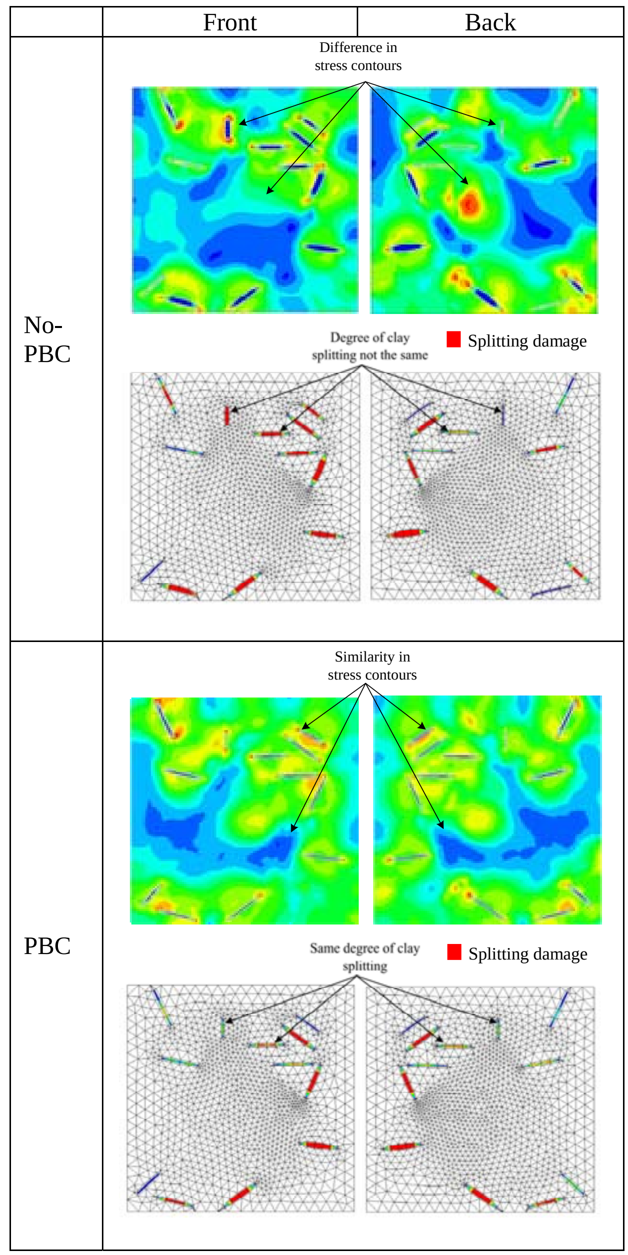

Fig.3. Comparison of stress contours and particle splitting of two opposite surfaces with and without PBC.

3 Results and discussions

3.1 Softening of galleries

Figure 4 shows the comparison of mean stress vs. volumetric strain curves of models with different softening characteristics of the cohesive gallery, including linear, exponential degradation and tabular form from MD results. For all three cases, the mean stresses first increase linearly before any splitting failure of the clay particles.

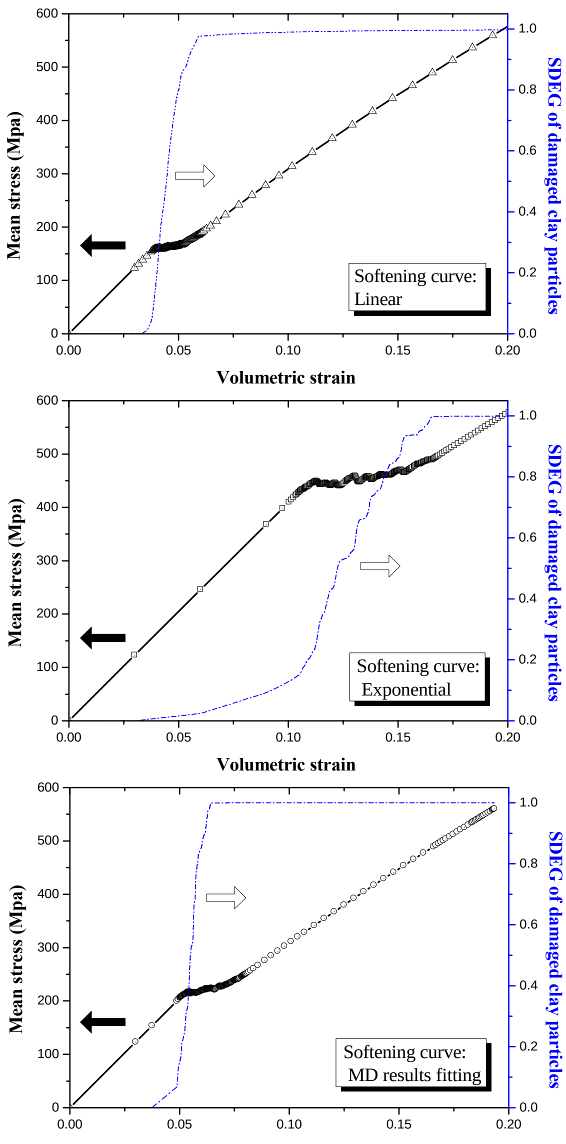

Fig.4. Mean stress of RVE cell and SDEG of damaged clay particles with different traction-separation for the cohesive elements.

The splitting of the clay particles coincides with the transition to non-linearity in all curves. It has been reported that during the transition, microcracks caused by the splitting failure will quickly propagate into the matrix, leading to the total failure of the bulk material [1, 2].

It is found that the strain at which the transition occurs is very sensitive to the softening characteristics of the cohesive gallery. Specifically, the exponential degradation would lead to a delay of the transition range and the corresponding failure stress is thus highest, while the linear degradation would result in earlier failure of the cohesive gallery and give a low failure stress threshold. The MD fitted tabular form gave a failure stress that is slightly higher than the linear softening gallery. From the comparison, it is suggests that accurate representation of the softening characteristics of the cohesive gallery is essential for predicting the mechanical behavior of nanocomposite materials, and hence relevant interfaces should be investigated at the molecular scale in order to accurately predict the mechanical performance of the hybrid system.

3.1 Clay particle size

The influence of particle size on the mechanical behavior of the RVE cell is also investigated. Figure 5 shows the stress-strain curves of models with different clay size under the same volume fraction of 4%. It is seen that larger particles would bring about slightly higher reinforcement efficiency in terms of elastic stiffness because of the increase of the aspect ratio (diameter/thickness). However, it is also found the splitting failure occurs earlier for large clay particles and the corresponding failure stress threshold is also slightly decreased.

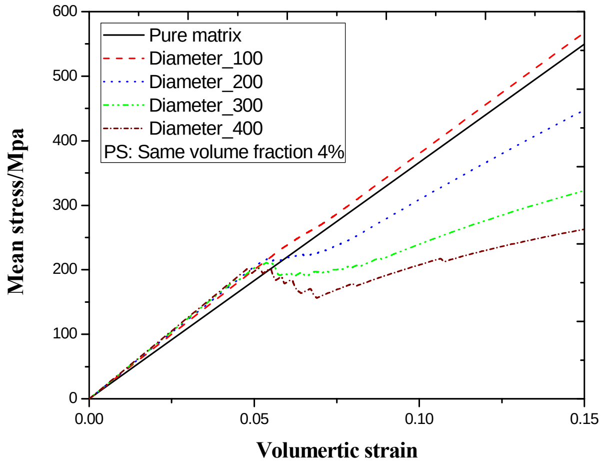

Fig.5. Mean stress vs. volumetric strain curves of RVE cells with different clay particle diameter.

3.3 Volume fraction

RVE cells with different concentrations of clay particles are studied and the influence of the volume fraction is shown in Figure 6. The bulk modulus of the RVE cell increases with the volume fraction due to the stiffening effect of the rigid clay particles; a trend which agrees well with micro-mechanical models, such as the Mori-Tanaka and Halpin-Tsai models [6]. Also, high volume fraction would also slightly advance the splitting failure because of the severe stress concentration arising from the close proximity of clay particles to one another.

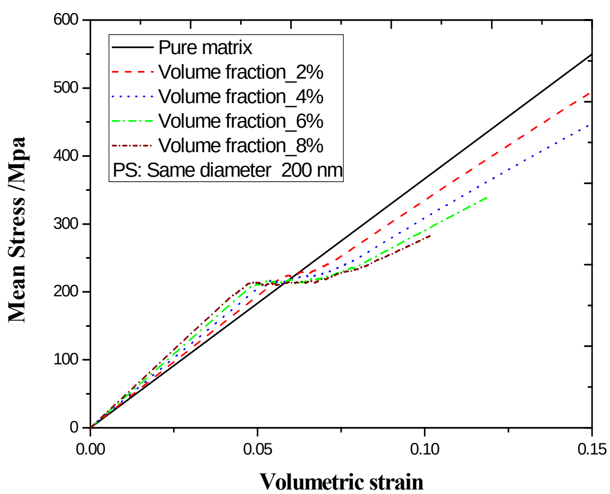

Fig.6. Mean stress vs. volumetric strain curves of RVE cells with different volume fraction of clay.

4 Conclusions

In this paper, a hierarchical multiscale approach has been proposed to study the failure mechanism caused by the splitting failure of intercalated particles. The RVE model of polymer-clay nanocomposites are fully parameterized using the results of molecular dynamics simulation. It is demonstrated that the softening of the cohesive gallery within the clay particles affects the mechanical behavior of the bulk system. The influence of the geometry of clay particles is also investigated. Large diameter and high volume fraction of clay particles would slightly decrease the failure threshold.

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