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A study on the multiscale strategy of polymer nanocomposites consisting of agglomerated fillers

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ABSTRACT

The degradation mechanism of the mechanical properties of a polymer nanocomposite consisting of agglomerating fillers is elucidated. The interfacial characteristics (filler–matrix interaction) and filler–filler interaction are identified on the molecular level through full-atom molecular-dynamics simulations. The simulation results show that the vacancy zone inside the agglomeration plays the role of a defect in a nanocomposite's mechanical behavior. Sequential multiscale modeling to predict the mechanical properties is thus proposed. In this study, a percolation-related interphase model is characterized as a function of the overlapping density zone. The proposed multiscale model should be applied to a more complex multiparticulate system with an agglomerate filler distribution as well as a composite system with a uniform filler distribution.

1. INTRODUCTION

Polymer nanocomposites can exhibit unique material properties which come from size effect of reinforcements. The main reason is that well-dispersed nanoparticles enhance an extensive degree of immobilized chains along the particle-polymer interface, which makes efficient stress transfer from filler to matrix assuming perfect interfacial contact. Recognizing this nanoscale physics, extensive research has been reported for development of dispersion technologies, however, which is still open and

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wayward issue. There are several numerical studies to elucidate dispersion/aggregation mechanism, compute effective elastic modulus for non-uniform distributed reinforcements, and construct multiscale modeling considering dispersion mechanism. However, among the numerical studies, none of these studies involves fundamental understandings for the origin of mechanical properties degradation in molecular simulations.

In this paper, authors will provide the origin of mechanical properties degradation through molecular dynamics (MD) simulations. Due to limitation of computation, authors take unit cell including only two reinforcements in order to investigate nanoscale physics in the vicinity of agglomerates. Unit cell models are employed for various inter-particulate distances. In order to provide more physical insights for this complex phenomenon, interfacial characteristics (filler-matrix interaction) and filler-filler interaction are investigated, respectively. In order to generalize interfacial characteristics for various dispersion states, percolated effective interphase are characterized by function of overlapped density ($\delta_{\mathbf{overlap}}$). It is applied to the continuum-based homogenization model and validated to molecular models with multi-nanoparticles.

2. Molecular modeling and simulation

Our model structure consists of two silicon carbide spherical shape nanoparticle and polypropylene matrix composed of 50 repeating unit monomers. The entire system (approximately 20,000 atoms) is contained within 46.6908×46.6908 Å^2 and a length of 93.3817 Å, as shown in Fig. 1. Periodic boundary conditions are used in all directions. For investigation of correlation between distance of reinforced fillers and overall elastic property of nanocomposites, we studied six types of different unit cells with different inter-particulate gap (d) as shown in Table 1. Filler radius (r_p) and volume fraction (V_f) are fixed as 9 Å and 3% for every system. Targeted density of the employed systems is 0.8 g/cm^3 same with reference data. Detail computation procedure of longitudinal elastic property of nanocomposites, thickness and elastic property of interphase, and overlapped density listed in Table 1 is described in following paragraphs.

Table 1. Longitudinal elastic properties of molecular system and corresponding interphase characteristics for various inter-particulate distances.

Model	d (Å)	E_L^{comp} (GPa)	E^{int} (GPa)	V_f^{int} (%)	$\delta_{overlap}$ (%)	t_{int} (Å)
Comp. I	2.7 (=20.7-18)	2.27	3.6	43.01	17.31	10.0
Comp. II	4.7 (=22.7-18)	2.15	2.9	44.51	13.35	
Comp. III	10.7 (=28.7-18)	2.50	4.3	48.12	4.84	
Comp. IV	16.7 (=34.7-18)	2.55	4.6	50.14	0.62	
Comp. V	22.7 (=40.7-18)	2.52	4.6	50.45	0	
Comp. VI	28.7 (=46.7-18)	2.61	5.1	50.45	0	
PP	-	1.68	-	-	-	-
M-T	28.7 (=46.7-18)	1.80	-	-	-	-

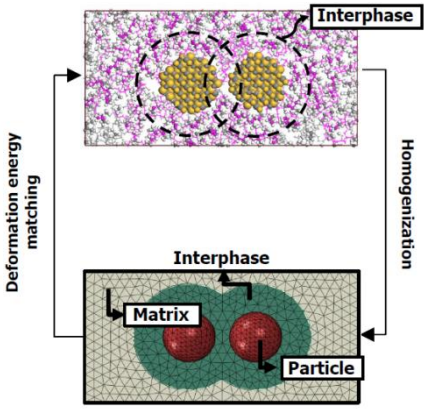

Fig. 1. Multiscale strategy to characterize interphase zone through molecular dynamics simulation and two-scale homogenization.

MD simulations are employed to obtain elastic properties of unit cell systems. Modeling the complex atomic structures listed in Table 1 is conducted using the commercial MD simulation package, Materials Studio 5.5 (Accerlys® Inc.). In every simulation, the polymer-consistent force field (PCFF) is employed. After initial construction of unit cell system, potential energy is minimized using the conjugate gradient method with energy deviation convergence cutoff of 0.1 kcal/mol·Å. In order to obtain elastic properties of unit cell systems, typical relaxation procedures (NVT ensemble at 200K for 700 ps, and NPT ensemble at 200K and 1atm for 5 ns) and Parrinello-Rahman fluctuation analysis are carried out.

Because the glass transition temperature of the PP is below room temperature, the elastic constants are obtained at 200K. For more realistic calculation of the non-bonded interaction energy (=van der Waals + electrostatic), the distance-dependent dielectric constant is applied as 2.5. To avoid statistical noise of inherent MD model uncertainty, 6 times average of longitudinal elastic properties are employed.

3. Multiscale modeling of polymer nanocomposites and simulation results

To identify elastic properties of interphase zone, we conducted multiscale homogenization about three-phase continuum model as shown in Fig. 1. Cho *et al*. (2011) developed multiscale framework for characterization of effective interphase though multiscale homogenization and molecular information. A three-phase continuum model includes nanoparticle, matrix, and homogeneous and isotropic interphase. The homogenized elastic stiffness tensor is determined by following equation.

$$\mathbf{C}^H = \frac{1}{|Y|}\int_Y \left(\mathbf{C} - \mathbf{C} : \nabla_y \boldsymbol{\chi}\right) dV_y \tag{1}$$

where Y is homogenized unit cell domain, and microscopic deformation field under unit macroscopic strain $\boldsymbol{\chi}$ can be computed by following equation.

$$\int_Y \nabla_y \mathbf{v} : \mathbf{C} : \nabla_y \boldsymbol{\chi} dV_y = \int_Y \nabla_y \mathbf{v} : \mathbf{C} dV_y \tag{2}$$

where $\mathbf{v}$ is virtual displacement field. Eqs. (1) and (2) are computed by finite element method, and periodic boundary condition is imposed.

In order to construct percolated interphase model including weakened interfacial characteristics, overlapped density ($\delta_{\mathbf{overlap}}$) is introduced as following form:

$$\delta_{overlap} = \frac{V_{overlapped}^{\text{int}}}{V_{total}^{\text{int}}} \tag{3}$$

Percolated interphase model could be constructed through linear fitting of interphase Young's modulus data listed in Table 1 as shown in Fig. 2 (a). Note that linear fitting of interphase Young's modulus about overlapped density is appropriate for predicting elastic properties of nanocomposites as shown in Fig. 2 (b).

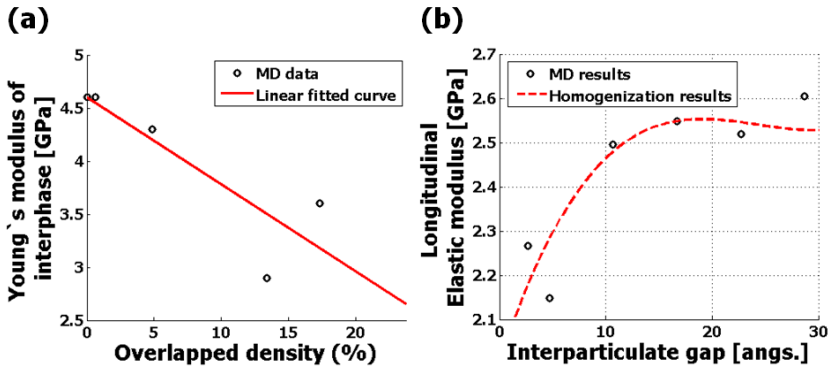

Fig. 2. Linearity of correlation between interphase Young's modulus and overlapped density: (a) interphase Young's modulus, and (b) corresponding longitudinal elastic modulus using two-scale homogenization.

4. Conclusion

To summarize, we evaluate longitudinal elastic properties of nanocomposites including two reinforcements for various inter-particulate gap through MD simulation. Longitudinal elastic properties of nanocomposites are declined up to 20% as inter-particulate gap is less than 1nm. For longitudinal elastic properties degradation of nanocomposites, filler-matrix interaction is more dominant than filler-filler interaction. Through percolated interphase model, elastic properties of nanocomposites including multi-particles are predicted and validated through MD simulation. This suggests the future development of a stochastic multi-scale design framework that includes uncertainties of filler size and filler location.

REFERENCES

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