DETERMINING THE MECHANICAL INTERPHASE THICKNESS OF POLYMERIC NANOCOMPOSITES USING MULTISCALE APPROACH

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1 Introduction
In the past few decades, the development of design skill for polymeric composites has been highly attended in various fields due to its multifunctionality and applicability in industry. Especially, as the size of filler decreases to nanoscale, the overall composites system shows extra high thermomechanical stability comparing with the conventional composites under same loading condition because the extremely high surface to volume ratio of nanocomposites interface generates nanoparticle size effect [1-14]. Both computational [1-6] and experimental [7-14] surveys, therefore, have been dedicated to the investigation of characterization of the filler-matrix interaction effect and its contribution to the theromomechanical stability of the polymer nanocomposites. Many researches has introduced the effective interphase concept which signifies that the finite volume and single independent phase exists near the embedded nanofiller surface to explain the exceptional physical properties of the nanocomposites, and use its quantitative properties as design parameters for the composites system. In this regard, the development of interphase characterization model which reflects both the accurate geometry and effective mechanical properties is important. However, to the best of the authors’ knowledge, most of recent surveys rarely pay attention to the accurate thickness of the effective interphase but set it as a constant based on simple assumption [1-4,5-7,10-12]. In the present study, we propose a logical approach which determines the thickness and stiffness of the effective interphase by adapting a multiscale approach - molecular dynamics (MD) simulation and finite element analysis (FEA) gearing technique. On the strength of the rapid progress of recent computational resource, the full-scale atomistic model of polymer nanocomposites can be considered by MD simulation and their intrinsic nanophysics such as nanoparticle size effect or interface strengthened effect can be verified and quantitatively reproduced in an atomic viewpoint. Furthermore, FEA model can efficiently provide numerical values of the mechanical properties. In addition, FEA can predict not only the global stiffness but also the local sub-domain strain energy and its internal stress for the heterogeneous system. The MD-FEA bridged multiscale model, therefore, can be a guidepost to design polymer nanocomposites with reliability and efficiency considering with their intrinsic nature.

2 Construction of molecular dynamics models
2.1 Atomic structure modeling procedure
MD simulation including amorphous state polymer and polymer nanocomposites unit cell construction, potential energy minimization, and ensemble applying procedures was executed by commercial software package - Materials Studio 5.5 (Accelrys Inc.) and open source code - LAMMPS (Sandia Lab.). The polymer consistent forcefield (PCFF) was applied to describe all the inter- and intra-potential energy of individual atoms in the unit cell. The amorphous state cross-linked thermostet epoxy which consists of EPON862 (Diglycidyl Ether of Bisphenol F) resin and TETA (Triethylenetetramine) crosslinker at a curing ratio of 45% was selected as polymer, and nano-sized spherical SiC (silicon carbide) was inserted to the center of the polymer unit cell as filler. Total three different filler sizes
were considered, sustaining its volume fraction under dilute condition (5.8 vol.-%) to neglect the interaction among particles and their agglomeration effect. An example of the modeled unit cell is depicted in Fig. 1, and the detailed information of their compositions is presented in Table 1. The total potential energy of the constructed unit cell is minimized by conjugate gradient method, followed by the NVT (300K for 1ns) and NPT (0.1MPa, 300K for 2.5ns) ensembles to reach its equilibrium state under room temperature and atmosphere condition.

### 2.2 Local strain energy distribution of nanocomposites in MD simulations

To tailor the potential energy change of the interface between the particle and polymer networks vicinity of the particle during mechanical test simulation which will be introduced in the following section, the sphere-shaped arbitrary energy groups which concentric but have different radius each other was initially set for the models depicted as Fig. 2. Here we can consider two kinds of local potential energy group for the matrix domain; (1) ‘accumulated group’ which includes the overall sphere domain except the particle-matrix interaction and (2) ‘hollowed sphere group’ which has shell-shaped region with one angstrom radial thickness. During the static tensile loading simulation in MD, the potential energy density increase profiles of the accumulated group \(W_A\) and the hollowed sphere group \(W_L\) with respect to the radius of designated sphere domain can be expressed as Eq. (1) and Eq. (2), respectively.

\[
W_A = \frac{U_{par+1+2+3} - U_{par} - U_3}{(4/3)\pi \left( (R + d)^3 - R_{par}^3 \right)}
\]

\[
W_L = \frac{U_{par+1+2+3} - U_{par} - U_1 - U_5}{(4/3)\pi \left( (R + d)^3 - R_3^3 \right)}
\]

where \(U\) is total potential energy increase during tensile simulation, \(d\) is the thickness of local energy measuring gap (the value was set as one angstrom in the current study) subscript ‘par’ means particle domain, subscript 1, 2, and 3 is the local matrix domain which is depicted in Fig. 2. Not only the polymer phase contained domain, but the total strain energy density of the ‘particle-participated sphere group’ \(W_T\) also can be considered as Eq. (3)

<table>
<thead>
<tr>
<th>Model label</th>
<th>Particle diameter (Å)</th>
<th>Particle vol. (%)</th>
<th>Unit cell length (Å)</th>
<th>Crosslinking ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>-</td>
<td>-</td>
<td>36.21</td>
<td></td>
</tr>
<tr>
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<td>10.36</td>
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<tr>
<td>0900</td>
<td>18.00</td>
<td>5.8</td>
<td>37.07</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>20.00</td>
<td></td>
<td>41.29</td>
<td></td>
</tr>
</tbody>
</table>

Table 1
Compositions of representative volume elements
Eq. (3) directly denotes the local load transfer characteristics of the nanoparticle and its vicinity polymer. By using those three different types of arbitrary energy group, the local strain energy distribution as well as the global stiffness of the nanocomposites can be observed in the atomistic models.

2.3 Static tensile loading simulation in MD

For each constructed molecular model, simple uniaxial tensile test was carried out under static loading condition. Fully equilibrated unit cells minimized their total potential energy under 0.1K NVT ensemble for 500ps, and then the unit cell lattice in x-direction was gradually increased while the other lattice parameters sustained their original length until the strain of each unit cell was reached to 0.3%. The strain rate was set as $10^6$/sec. Because the modeled nanocomposites show elastic response under 0.3% strain condition, the polymer strain energy vicinity of the nanoparticle ($E_{\text{int}}$) could be simply derived in terms of the strain in axial direction ($\varepsilon_{11}$) as Eq. (4).

$$W_A\left(\varepsilon_{11}, R_i\right) = E_{\text{int}}\left(\varepsilon_{11}, R_i\right) = \frac{1}{2} C_{11} \varepsilon_{11}^2$$ (4)

The models were constructed to target fully amorphous state and therefore have isotropic properties in ideal condition. However, discrete morphology of the crosslinked polymer generates small anisotropies in the system so the uniaxial tensile tests were carried out not only in x-direction but also y- and z-direction and averaged all the elastic constants to remove their anisotropy effect.

3 Finite element analysis of multi-inclusion model

3.1 Deriving nanocomposites stiffness by homogenization method

Three-dimensional finite element model which consists of 3-phase (particle-interphase-matrix) inclusions was prepared for the analysis of elasticity of the nanocomposites (See Fig. 3). Here, we adopt an asymptotic homogenization–molecular dynamics sequential bridging method which was proposed by Cho et al. [3]. The effective mechanical properties of interphase domain of the nanocomposites model can be solely characterized by using an inverse iterative algorithm with rigorous mathematical formulation and its numerical discretization by finite element equations. Homogenized elasticity $C^{I\!I}$ of the multi-inclusion nanostructure model can be obtained by following equation:

$$C^{II} = \frac{1}{Y} \int_V \left(\left[C\right] - \left[C\right][B][\chi]\right) dV$$ (5)

where $\chi$ is characteristic function tensor, $Y$ is the homogenized unit cell domain, $C$ is the fourth-order stiffness tensor of the element, and $B$ is the strain-displacement tensor corresponding to the 10-node tetrahedral element.
3.2 Strain energy density profile of the interphase

Similar to the MD tensile simulation, uniaxial tensile tests were executed for a three phase multi inclusion FEM model. The strain energy of the effective interphase, $E_{\text{int}}$, is calculated by Eq. (6):

$$E_{\text{int}} = \frac{1}{2} \int_{\text{int}} \sigma \varepsilon \, dV$$

with respect to the effective thickness of interphase. From the intersection point of the two energy density profiles of the polymer phase vicinity of the nanoparticle which are derived from Eq. (4) and Eq. (6) respectively, the effective thickness of the interphase and its stiffness can be numerically obtained. The remeshed structure with preserving its multi inclusion shape and applied the interphase thickness and mechanical properties as the solution of this energy method can describe not only the global mechanical behavior of the nanocomposites but the quantitative contribution of local load transferring on the interface between the particle and matrix.

3.3 MD-FEA scale bridging analysis scheme

Fig. 4 is the overall scheme of the current multiscale methodology. Firstly, the stiffness matrix of the pure epoxy and epoxy/SiC nanocomposites model is derived from the atomistic model by using the molecular dynamics and its molecular mechanics testing. The global elastic response derived by the static tensile test of the molecular structures is transferred to the equivalent finite element model which has arbitrary interphase thickness and elastic modulus. By using the asymptotic homogenization technique, the effective interphase modulus which matches with global stiffness of the nanocomposites is numerically obtained. Then the deformation energy of the interphase in FEM model is compared with the strain energy density of the accumulated group in molecular model under same small strain condition (0.3%). If the two deformation energies are not equal, the geometrical condition of the interphase in the FEM model is changed and the asymptotic homogenization and energy matching processes are executed repeatedly.

4 Simulation Results

4.1 Elastic behavior of the considered models

The axial stress profiles of the modeled epoxy/SiC nanocomposites and pure epoxy are depicted in Fig. 5. In Fig. 5, it can be found that the stress-strain curves have a strong linearity in all locally grouped regions within the given range of strain. Also, the hollowed sphere groups which have 12-13 Å and 13-14 Å radial distances show the highest slope among uniaxial stress-strain curves. On the other hand, the local energy distribution of the pure epoxy has nearly consistent stress-strain profile under same local region regardless of its selected area. It alludes that the polymer chain vicinity of the nanoparticle is highly anchored (immobilized) and densified to the surface of the particle due to their strong non-bond interaction. These morphological changes of the polymer chain significantly affect its mechanical stability and become the main cause of the generation of the interphase. The inhomogeneities of the nanoparticle embedded polymer can be observed more clear when we plot the strain energy density as a function of radial distance (Fig. 6). Both the accumulated group energy density ($W_b$) and the local group energy density ($W_i$) have their maximum value around the interface between the particle, and they are quickly dropped down and converged with oscillation as the designated region farther apart from the particle. Meanwhile, it is worth to note that unlike the nanoparticle embedded one, the stress-strain curve profile of pure epoxy is fully dispersed.
Fig. 4. The MD-FEA multiscale scheme to tailor the local load transferring range of the interphase as well as the global elastic response of nanocomposites in mechanical sense into the overall epoxy unit cell under tensile loading, regardless of its grouped region as it can be found on sub-figure of Fig. 5. So it can be confirmed that the heterogeneous behavior of the resin in the nanocomposites model mainly comes from their interaction with the nanoparticle in simulation.

4.2 Particle size effect and the local load transfer characteristics

We consider the local strain energy density distribution of the nanocomposites under three SiC particles of different sizes to characterize the nano-size effect of nanoparticles quantitatively. It has been well known that most of polymer matrix in nanocomposites is located in close vicinity of the filler particles and even the interphase properties is exhibited in macroscopic thermomechanical properties of the overall composites such as stiffness, interfacial strength, thermal expansion coefficient...
and thermal conductivity. In this regard, it is very intuitive that the Young’s and shear modulus of the nanocomposites are superior to microcomposites at the same loading condition if the particle is fully dispersed [1-4], and our current simulation also clearly indicates the strengthen effect (See Table 2). All the considered nanocomposites models show higher stiffness than the one of pure epoxy model, and the strengthened effect can be observed more obviously as the particle size decreases under constant volume fraction condition.

One of the aims of this study is the characterization of the effective geometry and mechanical properties of polymer-adsorbed region in equivalent continuum model. On the intersection points between the potential energy increase density of accumulated group in MD simulation and the strain energy density of homogenized interphase domain in FEA, an equivalent interphase in an MD model can be found. The procedure is performed to the considered models in the current study and the results are described in Fig. 7. Interestingly, the accumulated groups considered in current molecular study keep their independent energy density profiles nearly consistent regardless of its embedded particle radius condition. This result is very meaningful because it directly indicates that the particle size effect is mainly dependent on the non-bond interaction between the vicinity polymer and embedded particle surface while the effect of equilibrated polymer morphology is insignificant. The energy density profiles of the polymer domain derived by MD simulation have almost same load transfer tendency, however, the strain energy density profiles of the homogenized interphase in FEA highly depends on their embedded particle size condition because the mechanical load transferring between the particle and matrix is already considered in the asymptotic homogenization process. Therefore in all the considered nanocomposites models the effective thickness of the interphase is determined uniquely. The final analysis results of the geometry (effective thickness of adsorbed polymer) and elastic modulus of its domain are listed in Table 3. The interphase keeps its effective volume fraction nearly 28% for all considered molecular models so the actual thickness of the interphase is gradually increased as the embedded particle radius is increased. On the other hand, the elastic properties such as Young’s and shear modulus of the interphase are significantly reduced with respect to the embedded particle radius. In other words, the nanoparticle size effect on the elastic properties of the polymer nanocomposites mainly comes from the strengthened interphase stiffness, not from the change of effective volume fraction. It is worth to note that even though the thickness of the interphase which is determined by mechanics based method shows dependency on its

<table>
<thead>
<tr>
<th>Model label</th>
<th>E (GPa)</th>
<th>G (GPa)</th>
<th>v</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>3.65</td>
<td>1.33</td>
<td>0.37</td>
</tr>
<tr>
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</tr>
<tr>
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<td>1000</td>
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<td>1.83</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Fig. 7. Comparing the interphase strain energy density in FEM model under various interphase thickness conditions with the accumulated local energy density of MD models
Table 3
Equivalent geometry and moduli of the interphase

<table>
<thead>
<tr>
<th>Model label</th>
<th>$l_{int}$ (Å)</th>
<th>vof$_{int}$ (%)</th>
<th>$E_{int}$ (GPa)</th>
<th>$G_{int}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>9.40</td>
<td>3.51</td>
</tr>
<tr>
<td>0900</td>
<td>6.9</td>
<td>27.05</td>
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<td>2.90</td>
</tr>
<tr>
<td>1000</td>
<td>8.2</td>
<td>29.70</td>
<td>6.54</td>
<td>2.40</td>
</tr>
</tbody>
</table>

Fig. 8 describes the strain energy density profiles of the particle-participated sphere group in the nanocomposite models which are calculated by Eq. (3). It can be clearly found that the amount of strain energy is significantly decreased as the particle size is decreased because the stiffness of the interphase is higher as the particle radius is smaller and the high stiffness structure has smaller deformation energy stored under constant strain condition comparing to the soft region (matrix domain). Therefore, the MD results described on Fig. 8 are exactly correlated with the effective interphase modulus derived by FEA in Table 3. In conclusion, the effective interphase thickness which explains not only the global composites behavior but also local load transferring mechanism. Its intrinsic physics is verified through FEA in the current multiscale model through the energy density distribution and derived mechanical properties of the overall composites.

5 Conclusion

In this study, the interfacial characteristics between the nanoparticle and vicinity polymer resin in polymer nanocomposites and its effective range is quantitatively characterized by using MD-FEA multiscale bridging model. Unlike the other related previous surveys, the current model is able to tailor not only the global stiffness considering with the nanoparticle size effect but the local load transfer characteristics between the particle and matrix under elastic loading condition. In addition, the proposed methodology does not make any geometry-based assumption to constitute the effective geometry and modulus for an interphase in the composites system because the accurate volume fraction of densified polymer region is derived by mechanics-based MD-FEA energy matching method. Through the current multiscale model, a physical meaning of nanoparticle size effect on the local load transfer of the densified polymer domain is revisited and contributes the generation of the interphase.
analyzed in detail. The obtained results indicate that the interphase thickness dependency on the embedded particle size considerably affects to the effective stiffness of interphase in nanoscale even though the order of its magnitude is in the same range with the polymer adsorption distance assumed in our previous studies. Based on the current bridging model, we can establish micromechanics model or continuum FE model with mechanics-based particle/matrix interphase properties and thickness. This sequential multiscale model is suitable to be applied in the analysis and design of mechanical behavior of nanocomposites.

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