MULTISCALE MODELING TO CHARACTERIZE THE THERMOMECHANICAL PROPERTIES OF POLYMER NANOCOMPOSITES FOR VARYING CROSSLINK RATIO

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Abstract
In this study, the effect of varying crosslink ratios on the thermal and mechanical properties of thermoset epoxy-based nanocomposites are determined with the aid of molecular dynamics (MD) simulations and scale bridging method. For establishing molecular models, the spherical silica nanofillers having different radii are embedded into the EPON 862-TETA epoxy matrix. Elastic modulus and thermal expansion coefficient are calculated from the equilibrated molecular structures. The thermo-mechanical responses are characterized in terms of crosslink ratio and filler size. The interphase properties are further investigated using a micromechanics-based continuum model.

1. Introduction

Epoxy resins are widely used as matrix materials for the fiber reinforced composites due to their high specific stiffness, high strength, thermal stability, chemical resistance property, and ease of processing. Epoxy is a typical example of thermoset resins, having a distinct structure called “crosslink” that is strong covalent bond between the reactive site of resin and curing agent **[1]**. In experimental circumstances, curing conversions are determined by curing temperature, amount of curing agents, and curing time. Additionally, the fundamental characteristics of thermosets are strongly influenced by crosslink ratios. It is well known that bulk epoxy systems become stiffer and show more retarded polymer chain dynamics with increasing crosslinking conversions **[3]**.

In nanocomposite systems, the interfacial interactions at the nano-sized filler surface substantially confine polymer chains, forming the interphase region, highly densified layers surrounding the reinforcing fillers which exhibit altered behavior compared to the bulk polymers. Owing to the high surface area to the filler volume in a nanoscale, the interphase characteristics become dominant over the bulk properties of nanocomposites, generally resulting in the improved properties. Thus, the understanding of interphase behavior is one of essential issues when designing nanocomposite structures. Considering the newly introduced strong covalent bonds in thermoset resins, the interfacial communication between the filler and matrix can be influenced by the degree of crosslinking. Several literatures are available regarding the interphase characteristics of nanocomposites consisting of thermoset resins **[2]**. However, the understanding of interphase is still limited.

The primary purpose of this study is to investigate the effect of crosslinking on the thermo-mechanical properties of epoxy-based nanocomposites using MD simulations. The interphase behavior is further examined with a scale bridging method that is combined with an atomistic scale and a continuum scale.

2. Molecular dynamics simulation

2.1. Molecular model construction

Molecular models for crosslinked epoxy consisting of EPON 862 and TETA were established using Material Studio® 5.5, a commercial software program. COMPASS forcefield was applied to describe inter- and intra-molecular interactions. A number of crosslinking ratios from 16.67% to 62.50% were considered and the representative molecule method **[1]** was used to model a crosslinked epoxy structures. For reinforcing filler materials, the spherical silica (SiO_2) nanoparticles were introduced having the radius from 6.6 Å to 10.1 Å without any surface treatment.
For epoxy/silica nanocomposites and neat epoxy systems, various unit cells were constructed as shown in **Figure 1**. The target densities were set to be 1.2 g/cm^3 and the filler volume fractions for composite systems were fixed to 5.6%. The periodic boundary conditions for all directions were applied to remove surface effects. The initial molecular structures were minimized using the conjugate gradient method. Then unit cells were equilibrated using NVT ensemble at 300 K for 200 ps, which was followed by 2000 ps of NPT ensemble at 300 K and the atmospheric pressure condition.

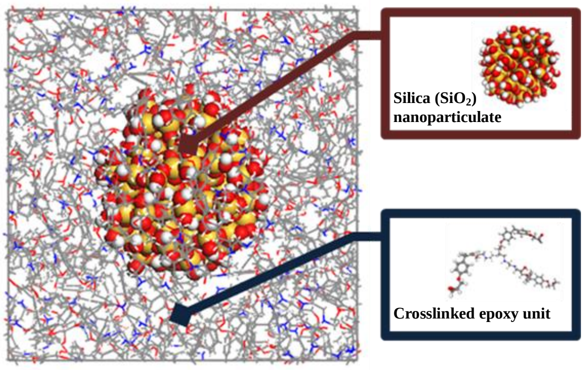

Figure 1. Molecular model for epoxy/silica nanocomposite unit cell.

2.2. Thermo-mechanical property

Once the unit cells were equilibrated, the thermo-mechanical properties were calculated. The elastic modulus was obtained using the Parrinello-Rahman fluctuation method. The stiffness tensor, C_{ijkl}, is given as

$$C_{ijkl} = \frac{kT}{\langle V \rangle} \left\langle \delta\varepsilon_{ij} \delta\varepsilon_{kl} \right\rangle^{-1} \tag{1}$$

where ε_{ij} and V are the strain and volume of the unit cell, respectively, k is the Boltzmann constant, and T is the temperature during the ensemble.

Regarding the thermal behavior, the coefficient of thermal expansion (CTE) was calculated for the glassy region. The equilibrated unit cells were heated to 350 K, and then cooled to 260 K at a rate of 20 K/1000 ps using NPT ensemble. The CTEs were calculated from the temperature-volume relation:

$$\alpha \cong \frac{\beta}{3} = \frac{1}{3V_0}\left(\frac{\partial V}{\partial T}\right)_P \tag{2}$$

The simulation results of elastic moduli and CTEs, shown in **Figure 2**, indicate three major points. First, with increasing crosslinking conversions, the elastic moduli increase and the CTEs decrease, these tendencies being consistent with the literature. Second, the epoxy/silica nanocomposites exhibit substantially enhanced thermomechanical properties in terms of the stiffness and the thermal stability (increased elastic moduli and lowered CTEs), showing the particle size effect. Lastly, as far as the degree of reinforcing effects in nanocomposites is concerned, the degree of reinforcement due to the filler inclusions tends to decrease with increasing crosslink ratio. Recalling that the reinforcing effect is strongly attributed to the interphase region, the reduced enhancement effects with increasing crosslink ratio demonstrate that the interphase characteristics are hindered by the formation of more crosslinks.

(a) **(b)**

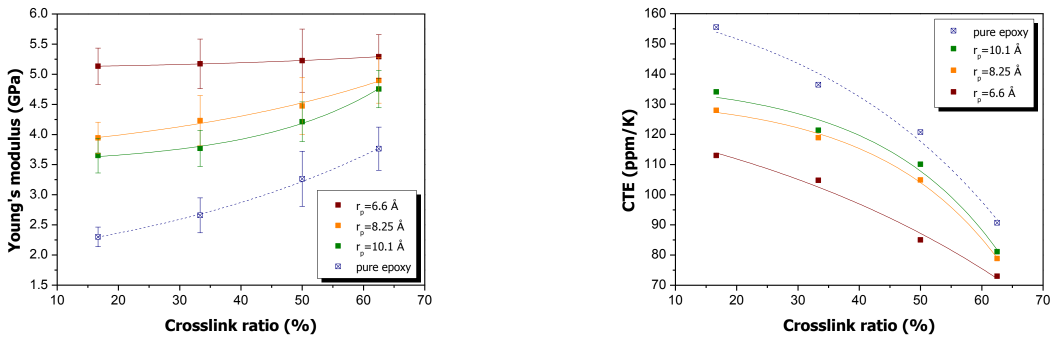

Figure 2. (a) Young's modulus and (b) CTE of nanocomposites and pure epoxy systems.

3. Scale bridging method

3.1. Analytical model for nanocomposites

The main purpose of the scale bridging method is to transfer the information which is obtained in an atomistic scale (MD simulations) to a continuum scale. The first step is that the thermo-mechanical properties of nanocomposites need to be characterized with respect to crosslink ratio and filler size, based on the observations from MD simulation results.

The properties of crosslinked neat epoxy systems $y|_{pure}$ are assumed to be a linear function of crosslink ratio (ξ). Then Mori-Tanaka solution $y|_{M-T}$ also can be regarded as a linear function of crosslinking conversion.

$$\begin{aligned} y|_{pure} &= f(\xi) \\ y|_{M-T} &= g(\xi) \end{aligned} \tag{3}$$

The properties of epoxy/silica nanocomposites are functionalized in terms of crosslink ratio and filler radius. The filler radius (r_p^*) is normalized by the thickness of interphase 6.9 Å . To reflect the effect of crosslink ratio and filler size, the degradation faction (D) is introduced which is defined as the ratio of the properties of nanocomposites to Mori-Tanaka solution, given in **Eq. 4** and **Eq. 5**. The coefficients are obtained using the least-square fitting method, and then the properties of nanocomposites can be expressed as **Eq. 6**.

$$D = D(\xi, r_p^*) = y|_{comp} \big/ y|_{M-T} \tag{4}$$

$$D = D(\xi, r_p^*) = 1 + A\exp\left[-\alpha\xi - \beta r_p^*\right] \tag{5}$$

$$y|_{comp} = D\left(\xi, r_p^*\right) g(\xi) \tag{6}$$

3.2. Multi-inclusion model

In order to characterize the interphase behavior, the continuum-based model consisting of three-homogeneous and isotropic phase (particle, interphase, and matrix) is adopted **[4, 5]**. In the micromechanics regime, the overall stiffness of the three-phase multi-inclusion model is given as

$$\mathbf{C} = \mathbf{C}_\infty \left[\mathbf{I} + (\mathbf{S}-\mathbf{I})\left(f_p\mathbf{\Phi}_p + f_i\mathbf{\Phi}_i + f_m\mathbf{\Phi}_m\right)\right]\left[\mathbf{I} + \mathbf{S}\left(f_p\mathbf{\Phi}_p + f_i\mathbf{\Phi}_i + f_m\mathbf{\Phi}_m\right)\right]^{-1} \tag{7}$$

where $\mathbf{C}_\infty$ is the stiffness of the infinite domain, $\mathbf{S}$ and $\mathbf{I}$ are the Eshelby tensor for the spherical shape of particle and identity tensor, respectively, and $\mathbf{\Phi}$ is the fourth-order eigenstrain concentration tensor of each phase. f is the volume fraction of each phase.

The overall CTE is given by

$$\begin{aligned} \alpha = &\left[\mathbf{I} + \left(f_p\mathbf{\Phi}_p + f_i\mathbf{\Phi}_i + f_m\mathbf{\Phi}_m\right)\mathbf{S}\right]^{-1} \\ &\times\left[f_p\left(\mathbf{\Phi}_p(\mathbf{S}-\mathbf{I}) + \mathbf{I}\right)\alpha_p + f_i\left(\mathbf{\Phi}_i(\mathbf{S}-\mathbf{I}) + \mathbf{I}\right)\alpha_i + f_m\left(\mathbf{\Phi}_m(\mathbf{S}-\mathbf{I}) + \mathbf{I}\right)\alpha_m\right] \end{aligned} \tag{8}$$

Since the stiffness and CTE of matrix phase are assumed to be identical with those of pure epoxy systems and the properties of silica particle is known values which are same as the material properties, the elastic and thermal properties of interphase region can be obtained using the inverse form of **Eq. 7** and **Eq. 8**.

3.3. Characterization of interphase

The obtained properties of interphase from the multi-inclusion model indicate that with the presence of more crosslinks the improvement effects are weakened. Moreover, as filler size increases, interphase effects become lowered as well. Based on these findings, the properties of interphase can be functionalized in terms of crosslink ratio and filler size with the similar manner applied for nanocomposites. Then, the interphase properties are expressed as follows.

$$D' = D'(\xi, r_p^*) = y|_{int} / y|_{pure} \tag{9}$$

$$D' = D'(\xi, r_p^*) = 1 + A'\exp\left[-\alpha'\xi - \beta' r_p^*\right] \tag{10}$$

$$y|_{int} = D'\left(\xi, r_p^*\right) f\left(\xi\right) \tag{11}$$

4. Results

The analytical models for epoxy/silica nanocomposites are plotted in **Figure 3**. The reproduced overall properties from the interphase properties are also shown in **Figure 3**. From the scale bridging framework, the analytical models for nanocomposite systems are propose, reflecting the observation of MD simulation results. The properties of interphase region can be calculated using the micromechanics-based continuum model. Cleary, the obtained interphase properties can predict the overall properties of composites showing excellent agreement as shown in **Figure 3**.

(a) **(b)**

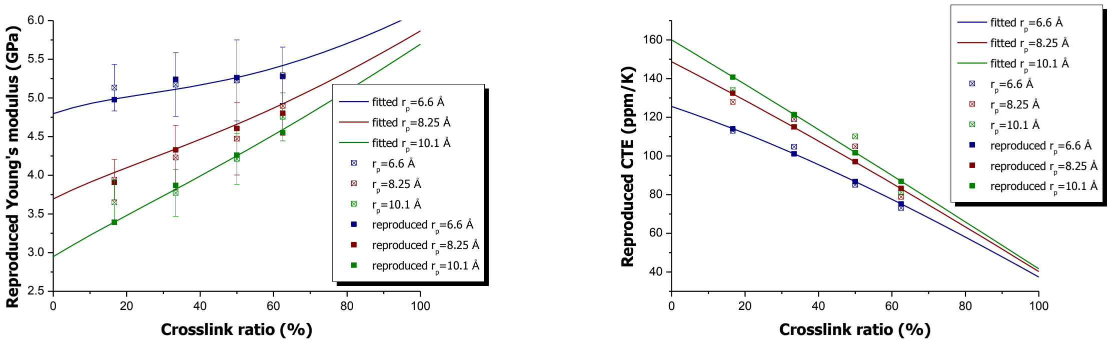

Figure 3. Analytical model and reproduced properties of nanocomposite; (a) Young's modulus and (b) CTE.

5. Conclusions

For thermoset resin-based nanocomposites, the effect of crosslink ratio on the thermo-mechanical response is investigated using MD simulations. As crosslink ratio increases, the reinforcing effect due to filler inclusions tends to be decreased. This result indicates that interphase behavior is likely to be disturbed by crosslinks. In order to understand this behavior in a continuum scale, the scale bridging method is proposed. The properties of nanocomposites are characterized in terms of crosslink ratio and filler size. From the analytical model, the interphase properties can be obtained using the multi-inclusion model. The calculated interphase properties reflect the observations in an atomistic scale with MD simulations. Based on the present method, the nano-scale physics regarding interphase can be understood in a continuum perspective, providing the efficient design guidance to fabricate and optimize the thermoset-based nanocomposite structures.

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