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Multiscale modeling to characterize interfacial behavior and interphase of crosslinked epoxy nanocomposites

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ABSTRACT

Multiscale modeling approach is proposed to characterize interfacial behavior of crosslinked epoxy nanocomposites. In this study, crosslinked epoxy composed of epoxy resin EPON 862 and curing agent TETA with varying crosslink densities are considered and silica (SiO_2) nanoparticulates having different radii are used as a filler material. The variations of interfacial characteristics are investigated using molecular dynamics (MD) and molecular mechanics (MM) simulations. The reduction of interfacial adhesion with increasing crosslinking is observed which is attributed to the changes of nonbond interaction characteristics between the filler and epoxy chains. The continuum model based on micromechanics regime is introduced to reflect the interfacial behavior depending on crosslinking densities and embedded filler sizes.

1. INTRODUCTION

Polymer nanocomposites have provided various applications for many industrial fields due to their extraordinary enhanced properties. The specific stiffness, specific strength, thermal stability, and chemical resistance property of original polymer are significantly reinforced with addition of well-dispersed nano-particles. These beneficial behaviors are generally attributed to the formation of interphase zone at the surface of imbedded fillers. It is well known that the densified and crystallized regions are formed since the presence of interfacial adhesion between the nanofillers and polymer matrix (Starr 2001 and Yu 2009). Moreover, with substantially high surface area to filler volume in nanocomposites, the thermos-mechanical properties of polymers can be tailored by small fraction of various nanofillers, which provide lightweight and multifunctional reinforced composite materials.

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Epoxy resins are one of typical polymers used as a matrix phase material for filler reinforced composites. Epoxy exhibits relatively high stiffness and better thermal property compared to other polymeric resins due to its distinct structure called crosslink that is strong covalent bond between epoxy resins and curing agents. In experimental circumstance, the degree of crosslinking is determined by curing temperature, time, and amount of curing agents. The fundamental characteristics of epoxy are influenced by curing conversions. Epoxy systems become stiffer and their chain dynamics are restricted with increasing crosslinking. (Yu 2009 and Bandyopadhyay 2011)

When it comes to dealing with epoxy nanocomposites systems, chain dynamics change of bulk epoxy with crosslinking needs to be considered. Interfacial characteristics are varied by crosslinking conversions as reported by experiment (Putz 2008) and simulation (Kim 2015). In the present work, to provide an effect way of understanding interphase characteristics and as well as designing epoxy nanocomposites, multiscale modeling approach is proposed taking into account the variations of interfacial behavior with crosslinking and filler sizes.

2. MOLECULAR DYNAMICS SIMULATION

Molecular models for crosslinked epoxy consisting of EPON 862 and TETA were modeled. For reinforcing filler, spherical silica (SiO_2) nanoparticles were used having the radius from 6.6 Å to 10.1 Å. Detailed MD simulation procedures were described in the previous work (Kim 2015).

Kim (2015) reported that nonbond interfacial characteristics at the silica surface are changed as crosslinking proceeds. MM simulation results indicate that the equilibrium distance between the silica and epoxy molecules increased with the formation of more crosslinks. Moreover, interfacial adhesions between the filler and epoxy matrix were substantially retarded with crosslinking.

3. MULTISCALE MODELING

3.1 Analytical model

To transfer the interfacial characteristics obtained in an atomistic scale to a continuum scale, the mechanical properties of nanocomposites were characterized with respect to crosslink conversions and filler sizes. Firstly, the elastic modulus of pure epoxy systems, $y|_{pure}$, were assumed to be a linear function of crosslink density, ξ. Then Mori-Tanaka solution, $y|_{M-T}$, also defined as a linear function of crosslinking.

$$\begin{aligned} y|_{pure} &= f(\xi) \\ y|_{M-T} &= g(\xi) \end{aligned} \tag{1}$$

The elastic modulus of epoxy/silica nanocomposites were expressed in terms of normalized variables, crosslink density and filler radius. The filler radius (r_p^*) is normalized by the interphase thickness of 6.9 Å. To quantify the variation of interphase effect with crosslinking and filler size, the degradation factor, D , is introduced as,

$$D = y\big|_{comp} \big/ y\big|_{M-T} \tag{2}$$

According to the previous MD and MM results by Kim (2015), the degradation factor inherently represents the reinforcing effect that is significantly influenced by crosslinking and filler size. Thus, D is regarded as a function of ξ and r_p^* as given in Eq. (3). The coefficients were determined using the least square fitting and the elastic modulus of nanocomposites was expressed by Eq. (4).

$$D = D(\xi, r_p^*) = 1 + A\exp\left[-\alpha\xi - \beta r_p^*\right] \tag{3}$$

$$y\big|_{comp} = D\left(\xi, r_p^*\right) g\left(\xi\right) \tag{4}$$

3.2 Interphase characterization

The analytical model for elastic modulus of epoxy/silica nanocomposites are given in Fig. 1 (a). Interphase property was obtained from this model using 3-phase multi-inclusion micromechanics method. Once the interphase property was determined by continuum approach, those were expressed as follows using the similar manner applied in the previous step, and the fitted result is plotted in Fig. 1 (b).

$$D' = D'(\xi, r_p^*) = y\big|_{int} \big/ y\big|_{pure} \tag{5}$$

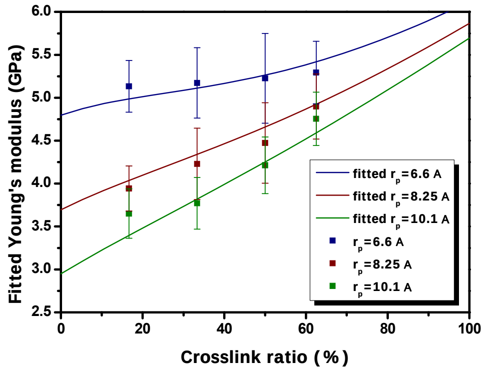
$$D' = D'(\xi, r_p^*) = 1 + A'\exp\left[-\alpha'\xi - \beta' r_p^*\right] \tag{6}$$

$$y\big|_{int} = D'\left(\xi, r_p^*\right) f\left(\xi\right) \tag{7}$$

4. CONCLUSION

The variations of interfacial characteristics in epoxy/silica nanocomposites were investigated with the aid of MD and MM simulations considering the effect of crosslinking and embedded filler size. The results indicate that the interfacial characteristics are changed by crosslinking density and filler size; the inherent nonbond interfacial behavior changed and the adhesions between the filler and epoxy matrix with increasing crosslink density. To understand the interfacial characteristics depending on crosslinking conversion and filler size in a continuum scale, the multiscale modeling approach is proposed. The elastic properties of nanocomposites are characterized as a function of crosslink density and filler size. From the analytical

(a)



(b)

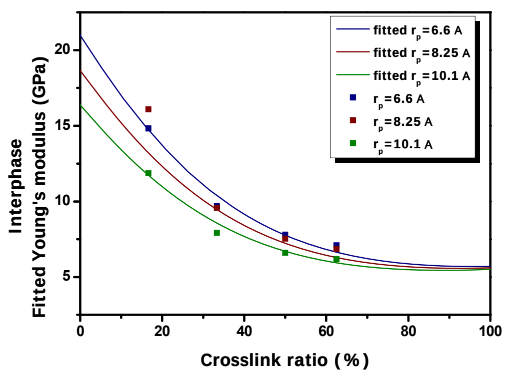


Fig. 1 Multiscale model for (a) Young's modulus and (b) interphase property of epoxy/silica nanocomposites

model, interphase properties are obtained using micromechanics regime and then interphase characteristics are characterized in terms of crosslinking and filler size. The present method provides not only the nanoscale physics of interphase region but also an efficient design guideline of epoxy-based nanocomposites.

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