

## Characterization of interphase for cross-linked epoxy nanocomposites with a multiscale approach

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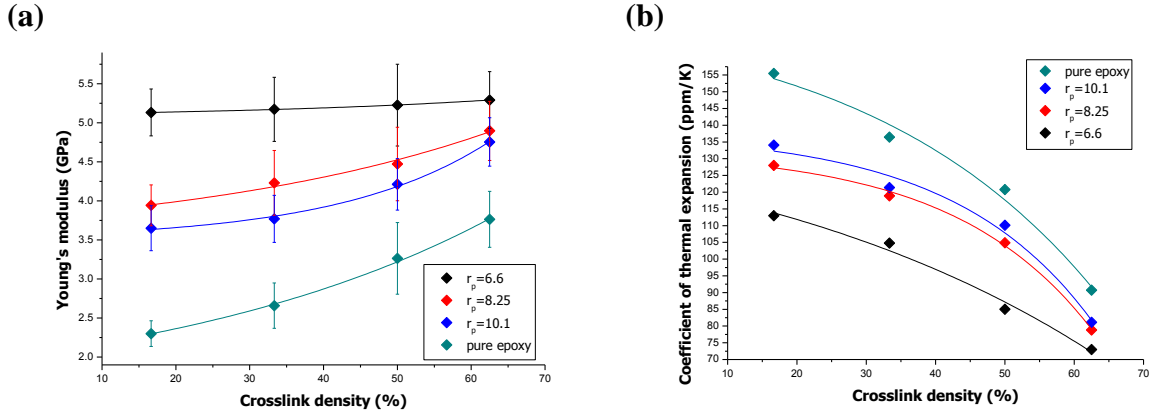
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Recent development in measurement and fabrication techniques for nano-scale materials, epoxy filled with reinforcing nanofillers has received great interests that stem from their enhanced properties. This favorable phenomenon, arising from the embedded fillers, is attributed to the presence of interphase, typically terms the region where the interfacial interactions in the vicinity of filler surface significantly alter polymer chain dynamics. Unlike the conventional composites with micron-sized fillers, in nanocomposite systems, the contribution of interphase region on the bulk properties is dominant due to substantially high surface area to volume ratio. Thus, the understanding of interphase behavior is of critical importance when designing nanocomposite structures. The fundamental mechanism behind interphase formation is directly related to the retarded chain mobility near the filler surface, which is caused by the interfacial interactions. Furthermore, the chain mobility of bulk epoxy is characterized by the conversion of cross-linking. As the cross-linking process proceeds, spatial constraints are imposed on the segmental dynamics, resulting in slowing down of chain mobility. Therefore, the limitation of chain dynamics in epoxy matrix can affect the formation and behavior of interphase [1, 2].

The primary purpose of this study is to determine the influence of the degree of cross-linking on the thermo-mechanical behavior of interphase region using a multiscale approach, which is combined with molecular dynamics (MD) simulations and a micromechanics-based analytical model. For establishing molecular models, cross-linked epoxy composed of EPON 862 and TETA with multiple cross-link densities is considered. The spherical silica (SiO<sub>2</sub>) nanoparticles having different radii are prepared as reinforcing fillers. The thermomechanical responses, elastic modulus and thermal expansion coefficient, are investigated using MD simulations. The result, shown in **Figure 1**, indicates that the degree of bulk property changes of nanocomposites with increasing cross-link density is lower than the cases of pure epoxy systems. Moreover, as the radius of particle inclusions decreases, this tendency becomes obvious.

For the further quantification of interphase behavior, the interfacial interaction energy densities are calculated using molecular mechanics (MM). The adhesive interaction between the filler and matrix is weakened with the presence of more cross-links. The interphase characteristics, generally governed by the interfacial interactions, are likely to be diminished



**Figure 1. Thermomechanical responses of epoxy and epoxy/silica nanocomposites with cross-link density; (a) Young's modulus and (b) coefficient of thermal expansion.**

in highly cross-linked matrix. In this study, a micromechanics-based analytical model, reflecting the interphase behavior with cross-link density, is proposed. The unit cells of nanocomposites are considered as a three-phase structure, consisting of the filler particle, interphase, and matrix: the subscript,  $r$ ,  $i$ , and  $m$ . The elastic stiffness and thermal expansion coefficient of composites are given by **Eq. (1)** and **Eq. (2)**, respectively.

$$\mathbf{C} = \mathbf{C}_{inf} \left[ \mathbf{I} + (\mathbf{S} - \mathbf{I}) \left( \sum_{r=1} f_r \Phi_r \right) \right] \left[ \mathbf{I} + \mathbf{S} \left( \sum_{r=1} f_r \Phi_r \right) \right]^{-1} \quad (1)$$

$$\alpha = \left[ \mathbf{I} + \left( \sum_{r=1} f_r \Phi_r \right) \mathbf{S} \right]^{-1} \sum_{r=1} f_r [\Phi_r (\mathbf{S} - \mathbf{I}) + \mathbf{I}] \alpha_r \quad (2)$$

where  $\mathbf{C}_{inf}$  is the stiffness of the infinite medium,  $f_r$  is the volume fraction of the  $r$ th phase,  $\mathbf{S}$  and  $\mathbf{I}$  are the Eshelby tensor and identity tensor, and  $\Phi_r$  is the fourth-order eigenstrain concentration tensor of the  $r$ th phase. Then, interphase properties are characterized in terms of particle radius, cross-link density and particle volume fraction, as given by **Eq. (3)**.

$$\begin{aligned} C_{interphase} &= f(r_p, \xi, f_r) \\ \alpha_{interphase} &= f(r_p, \xi, f_r) \end{aligned} \quad (3) \quad , \text{where} \quad \begin{aligned} C_{interphase} & \text{ elastic stiffness tensor of interphase} \\ \alpha_{interphase} & \text{ linear thermal expansion coefficient of interphase} \\ r_p & \text{ radius of particle inclusion} \\ \xi & \text{ cross-link density} \\ f_r & \text{ particle volume fraction} \end{aligned}$$

The proposed analytical model, based on the micromechanics regime, represent the hindered interphase behavior that is attributed to the weakened interfacial interactions with increasing cross-link density. The accuracy and applicability of the model is verified by comparing with MD results.

## REFERENCES

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