Effect of different crosslink densities on the thermomechanical properties of polymer nanocomposites

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ABSTRACT

The effects of crosslink densities on thermo-mechanical properties of thermoset polymeric nanocomposites are investigated via molecular dynamics (MD) simulations. In this study, crosslinked epoxy structures composed of epoxy resin EPON 862 and curing agent TETA with various crosslink densities are considered and the spherical shape of silica (SiO_2) nanoparticulates having different radii are used as a filler material. The changes of the elastic modulus and coefficient of linear thermal expansion (CLTE) with varying crosslink densities and particle sizes are studied with the aid of MD simulations. The results illustrate that the particle inclusion effect on thermo-mechanical properties is observed; enhanced modulus and reduced CLTE. Moreover, in highly crosslinked systems the degree of particle inclusion effect is diminished compared to the lower crosslinked systems. In order to investigate interphase characteristics regarding different crosslink densities, interfacial adhesion is compared. The result indicates that the interphase behaviors are notably hindered by the presence of more crosslinks in nanocomposite structures.

1. INTRODUCTION

With the development of manufacturing technology in nanomaterials, polymer nanocomposites reinforced by nano-sized fillers have drawn huge attention in both scientific and industrial fields due to their enhanced properties. When it comes to dealing with nanocomposites, the understanding of interphase is of primary interest, since the interphase regions play very important roles to characterize the properties of composite structures. Due to the attraction between the particle and matrix, interphase region, which is the densified layers near the particle, can be formed. Interphase has a predisposed characteristic to alter the bulk properties of nanocomposite. For example, with the presence of well-estabilished interphase, elastic property can be increased due to the improved load transfer (Odegard 2005 and Yu 2009), and polymer dynamics can

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be limited because of the confinement effect (Starr 2001). Therefore, many endeavors have been carrying out to manipulate those characteristics when designing nanocomposite.

As far as the contribution of interphase on the bulk property is concerned, particle size dependency can be observed. As the size of particle decreases to a nanometer scale, the ratio of surface area to volume is increased drastically. Consequently, contribution of interphase is significantly increased. In other words, interphase characteristics become dominant in the nanoscale world, which is called particle size effect (Odegard 2005 and Yu 2009).

In thermoset polymer, the interaction between polymers is also important since it has distinct structure called crosslinks. In highly crosslinked structure, the interaction between polymers is enhanced by the formation of more crosslinks, resulting in the limited mobility and the increased stiffness (Bandyopadhyay 2011 and Putz 2008).

Therefore, in order to understand the interphase characteristics of thermoset polymer nanocomposites, both the interfacial interaction and the formation of crosslinks need to be considered. It is difficult, however, to quantify the behavior of interphase regions with experiments. From this point of view computational simulation approaches need to be adopted. In this study, the influence of varying crosslink densities and nanoparticle sizes is investigated by MD simulation methods.

2. SIMULATION METHOD

The procedures for establishing the equilibrated molecular models and implementing ensemble simulations are described in this section, and all of procedures are conducted with the aid of the Material Studio, a commercial MD package, and COMPASS (ab initio Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) forcefield (Sun 1998) is employed.

2.1. Crosslinked Epoxy Unit
Diglycidyl Ether of Bisphenol F (EPON 862) is used as the epoxy monomer and Triethylenetetramine (TETA) is used as the curing agent. Crosslink density is defined as the ratio of the total number of crosslinked sites to the maximum possible number that could be reacted. Crosslinked epoxy networks with different degrees of crosslinking, 16.66%, 33.33%, 50% and 62.5% are constructed while keeping the stoichiometric constant between EPON 862 and TETA.

2.2. Epoxy/Silica Unit Cell
In total, 12 different unit cells are constructed. Firstly, pure epoxy unit cells are prepared, having different crosslink densities as shown in Figure 1 (a). Each cell consists of a number of representative crosslinked epoxy units to meet a proper cell size.

The spherical silica (SiO_2) particle, having the radius of 6.6 Å and 10.1 Å, is embedded at the center of an amorphous polymer matrix that has 4 different crosslink densities, as illustrated in Figure 1 (b). Each matrix of epoxy/silica unit cell is also consists of the number of crosslinked epoxy units, which is set to satisfy the same volume fraction, 5.6% approximately.
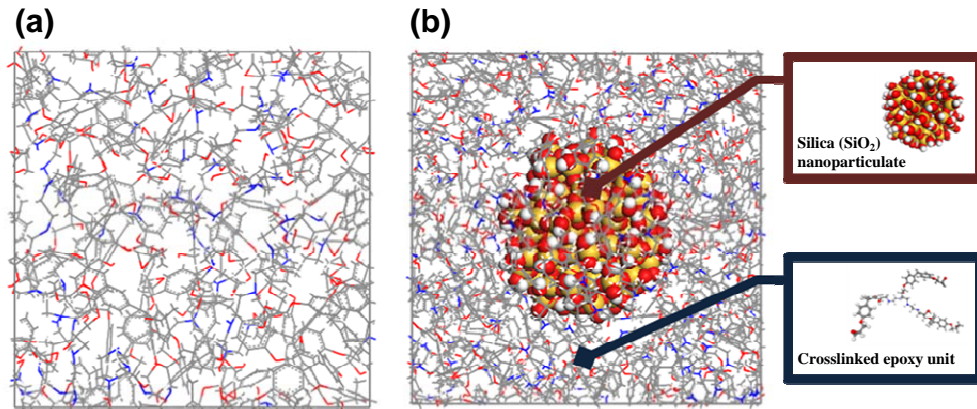
Figure 1. (a) epoxy unit cell and (b) epoxy/silica nanocomposite unit cell

The target density for pure epoxy and epoxy/silica composite unit cells is set to be 1.2 g/cm^3 and periodic boundary conditions are applied to remove surface effects.

The initial molecular structures are minimized using the conjugate gradient method. Then unit cells are equilibrated as follows. NVT ensemble at 300 K during 200 ps is followed by 2000 ps of NPT ensemble simulation at 300 K and 1 atm.

2.3. Thermomechanical properties

In order to quantify the change of thermo-mechanical behavior due to varying crosslink densities and particle sizes, the elastic modulus and the coefficient of linear thermal expansion (CLTE) are calculated for each unit cell.

The elastic modulus of each unit cell is obtained with the Parrinello-Rahman fluctuation method (Parrinello 1980). The results of 8 different simulations for each cell are averaged for computational accuracy.

The CLTE values are calculated for the glassy region. The unit cells are heated to 350 K using the NPT ensemble simulation for 2000 ps and a stepwise cooling-down procedure is applied with the cooling rate of 20 K/1000 ps. The volumetric changes during the cooling-down, where the temperature range is from 260 K to 350 K, are calculated and CLTE, α, is given by

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

where β is the coefficient of volumetric thermal expansion (CVTE) and V_0 is the initial volume of the unit cell.

3. RESULTS

### 3.1. Influence of crosslink density and particle inclusion

The elastic modulus and CLTE of each unit cell, having different crosslink densities and particle sizes, are shown in Figure 2 (a) and (b) respectively.

First of all, as illustrated in Figure 2 (a), the elastic moduli of pure epoxy and composite structures show an increasing trend with increasing crosslink densities. Meanwhile, CLTE values, Figure 2 (b), show a decreasing tendency with crosslink

density. This result indicates that with the formation of more crosslinks, the crosslinked epoxy structures become stiffer and the polymer chain mobility is limited.

Moreover, as the particle size decreases, the particle inclusion effects become dominant; elastic modulus is enhanced and CLTE value is decreased due to the formation of interphase regions near the surface of particle inclusions. The interphase leads to the improved load transfer and the limited polymer dynamics.

As far as the particle inclusion effects on thermo-mechanical properties are concerned, the degree of particle inclusion effects is different with crosslink density. In lower crosslink density, it is observed that the particle inclusion effect is apparent. The degree of modulus increment and CLTE reduction in lower crosslinked systems is relatively larger than that of highly crosslinked system. In order words, interphase behaviors on the bulk properties of nanocomposites are likely to be hindered by the presence of more crosslinks.

(a) **(b)**
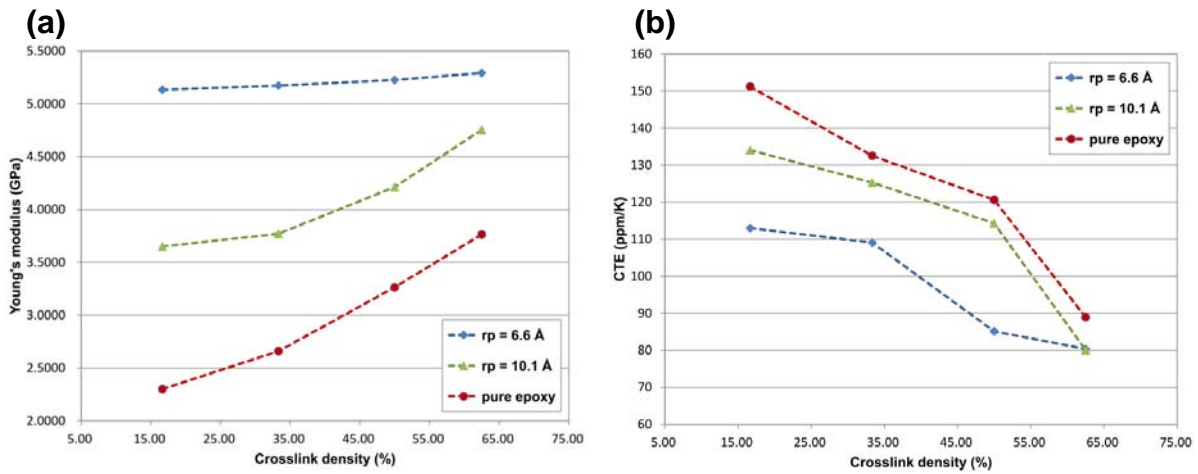
Figure 2. (a) Young's modulus and (b) Coefficient of thermal expansion of pure epoxy and epoxy/silica nanocomposite

Table 1. Interaction energy density of epoxy/silica nanocomposite with respect to crosslink density

Particle radius [Å]	Crosslink density [%]	Interaction energy density [kcal/mol/Å³]
6.6	16.66	-0.1552 ± 0.0045
	33.33	-0.1419 ± 0.0105
	50.00	-0.1410 ± 0.0076
	62.50	-0.1452 ± 0.0066
10.1	16.66	-0.0843 ± 0.0014
	33.33	-0.0842 ± 0.0015
	50.00	-0.0794 ± 0.0010
	62.50	-0.0762 ± 0.0010

3.2. Interfacial interaction

The interfacial attraction between silica particle inclusions and polymer matrix needs to be compared to characterize the interfacial adhesion with respect to crosslink densities and particle sizes. The nonbonding interaction energy (Parathab 2007) between the particle and matrix is given by

$$E_{interaction} = E_{total} - (E_{particle} + E_{matrix}) \qquad (2)$$

where E_{total} is the total nonbonding energy of the composite, $E_{particle}$ is the nonbonding energy of the silica particle, and E_{matrix} is the nonbonding energy of matrix. For qualitative comparison an intensive property is considered, which is obtained by dividing the volume of the silica particle. The calculated interaction energy densities for nanocomposite structures with respect to crosslink densities are listed in Table 1. The negative values of interaction energies represent the interfacial attractive forces. As shown in Table 1, the adhesion between the particle and matrix is decreased with increasing particle sizes. Moreover, the interfacial adhesion is diminished with increasing crosslink densities. Thus, the interphase characteristics can be weakened by the formation of more crosslinks.

4. CONCLUSION

The thermomechanical properties of epoxy/silica nanocomposites are investigated using MD simulations regarding varying crosslink densities and particle sizes.

From the results of elastic moduli and CLTE values, significant particle size dependency can be observed; as the radius of silica particle decreases, the elastic property is enhanced and the CLTE value is reduced with comparison to the pure epoxy structures. Moreover, with increasing crosslink densities, the particle inclusion effect is relatively decreased and the interfacial interaction between the particle and matrix is diminished.

In conclusion, these results indicate that the interphase characteristics in nano-composite structures are weakened by the presence of more crosslinks in polymer matrix.

ACKNOWLEDGEMENT

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