

THE THERMOELASTIC BEHAVIOR OF POLYMERIC BASED NANOCOMPOSITES IN GLASSY AND RUBBERY STATES

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1 Introduction

Today, the polymeric based nanocomposites have been widely investigated for their outstanding applicability. When the size of embedded filler comes into nanoscale, the interfacial region which exists between the particle and matrix plays a dominant role in the characteristics of mechanical and thermal properties of overall composites because of their extremely high surface area to volume ratio. Various studies therefore have been performed to characterize the filler size dependent thermomechanical properties of the nanocomposites by experimental [1] and/or computational [2-4] methods.

Recent studies have focused on the numerical simulation to obtain thermomechanical behavior of polymeric nanocomposites[4,5]. Especially, molecular dynamics (MD) simulations are extensively utilized in this study to investigate the particle size effect of nanocomposites quantitatively [5,6]. In the present study, epoxy-based nanocomposites are considered and the thermomechanical properties are investigated in wide range of temperature conditions. Epoxy is one of the representative thermosetting materials for electronic packaging and thus it can be frequently exposed in the wide range of temperature, from 300K to 450K or more. Therefore, the understanding of thermomechanical properties of epoxy-based composites and characterization of the degradation effect by glass transition of both epoxy and epoxy based nanocomposites is one of the most critical issues in the composite material characterization.

Although the fundamentals of the size effect of amorphous polymeric-based nanocomposites are well-known nowadays through a large amount of literatures have been published, most of the previous

studies have been only considered at glassy states so far. For the first time, we characterize the change of the thermoelastic properties considering different size of the nanoparticle under same volume fraction in rubbery state. In this study, we consider the glass transition behavior of each unit cell system and confirm the thermoelastic properties of cross-linked epoxy nanocomposites containing spherical silica particle in both the glassy and rubbery states.

2 Simulation methodologies

2.1 RVEs modeling

To confirm the reinforcing effect of nanoparticles, two kinds of unit cells were constructed. One is the pure cross-linked epoxy representative volume element (RVE) which is made up with nine chains of EPON862® (diglycidyl ether of bisphenol F) cured with three chains of TETA®(triethylenetetramine). The other unit cells are the epoxy based nanocomposites including a spherical silicon carbide (SiC) nanoparticle. To characterize the particle size effect of the nanocomposite, in total of five different sized nanoparticles are embedded into each representative unit cells under the same volume fraction condition of 5.8% at room temperature as depicted in figure 1. The details of unit cell composition are listed in table 1.

The COMPASS forcefield was adopted to describe all the inter- and intra-molecular interactions. The methodologies to make an individual cross-linked matrix molecules and nanocomposites unit cells followed the process demonstrated in the previous work [4, 5]. To reflect the bulk effect to obtain macroscopic properties, periodic boundary conditions are applied to x, y, and z direction. After constructing the RVEs, the total potential energy of each cell are minimized using the conjugate gradient

Table 1. Composition of epoxy and epoxy/SiC nanocomposite RVEs

System	Radius (Å)	Initial volume fraction (%)	No. of cross-linked epoxy	Unit cell length (Å)
Epoxy	-	-	6	36.28
E06	5.18	5.80	2	21.66
E18	7.54	5.80	6	31.14
E30	9.00	5.87	10	36.89
E42	10.00	5.76	14	41.26
E54	10.90	5.80	18	44.84

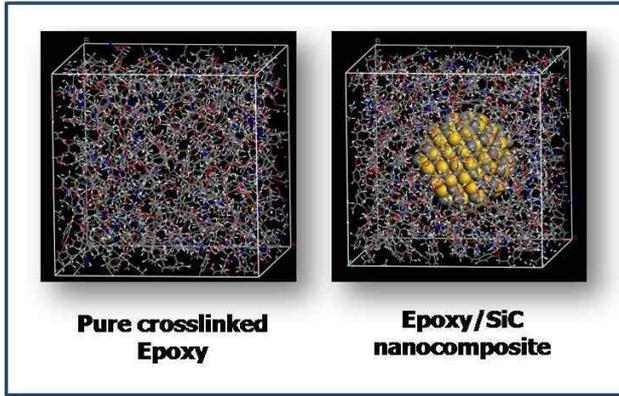


Fig.1. The snapshot of modeled RVEs (nanocomposites was depicted only E30 case)

method followed by an isothermal-isobaric ensemble equilibrium process. The overall simulations are performed using a commercial MD software, Materials studio 5.0 (Accelrys Inc.) [9].

2.2 Estimation of glass transition temperature

The glass transition temperature (T_g) of epoxy and epoxy nanocomposites is obtained from two different method - the specific volume-temperature relation and the variation of the mean squared displacement (MSD) curves which were derived from the cooling down simulation from 550K to 280K. The MSD is closely related with the relative diffusivity of molecular structure which undergoes temperature change. When polymeric materials are cooled or heated, the relative diffusivity of each RVE changes drastically near the glass transition temperature. Thus, the T_g can be confirmed from the temperature region where a sudden distinguishable

jump is observed in the MSD curves at each temperature. Referring the candidate glass transition region obtained from the MSD curves, the specific volume-temperature relation was divided into two parts and each of them are linearly regressed respectively. Then, the T_g was obtained from the intersection point of the two regression lines.

2.3 Thermoelastic behavior of systems

Together with the T_g , the thermal expansion coefficient (CTE) can be calculated from the specific volume-temperature relation. Using the initial density of the unit cell, ρ_0 and the slope of the linear regression of specific volume-temperature relation, $\Delta v / \Delta T$ the linear CTE, α and volumetric CTE, γ can be approximated as follows:

$$3\alpha \cong \gamma = \frac{1}{V_0} \frac{\partial V}{\partial T} \cong \frac{1}{V_0} \frac{\Delta V}{\Delta T} = \rho_0 \frac{\Delta v}{\Delta T} \quad (1)$$

Here, it is worth to notice that the basis of initial density and linear regression domain may affect the CTE analysis. In this study, the CTE is calculated from 280K to 320K for glassy state and from 430K to 470K for rubbery state. To minimize the error caused by lack of data points, the cooling-down procedure is simulated three times repetitively in suggested temperature domain and the CTE is obtained from the averaged specific volume-temperature relation.

After the cooling down procedure, the elastic moduli of pure epoxy and nanocomposites were calculated at every 50K using the Parrinello-Rahman fluctuation method [7, 8]. The fluctuation formula for stiffness matrix C_{ijkl} can be expressed as follows:

$$C_{ijkl} = \frac{kT}{\langle V \rangle} \langle \Delta \epsilon_{ij} \Delta \epsilon_{kl} \rangle^{-1} \quad (2)$$

where k is Boltzmann constant, T is the temperature and V is the volume of unit cell. All the elastic constants were averaged over six different simulation results in order to guarantee the computational accuracy.

3 Simulation results

3.1 Glass transition temperature

Table 2. Analysis results of the T_g of pure epoxy and nanocomposites

System	Radius (Å)	T_g by Regression (K)	T_g by MSD (K)
Epoxy	-	390.12	380~390
E06	5.18	418.02	410~420
E18	7.54	404.79	400~410
E30	9.00	400.66	400~410
E42	10.00	413.37	400~410
E54	10.90	400.03	400~410

The predicted T_g of epoxy and nanocomposites by MSD and intersection of linear regressions of specific volume-temperature are listed in table 2. The T_g of the pure cross-linked epoxy predicted from the present study is about 390K which is very closed to the value of preceding research [4] on the same material and at the same conversion ratio condition. In addition, compared with the pure cross-linked epoxy, the T_g is increased by 15K by embedding SiC nanoparticle. From the size effect point of view, however, there is no clear particle size effect in glass transition temperature.

3.2 Thermoelastic properties

The linear CTEs and elastic moduli of the systems are depicted in figures 2 and 3. From the results of CTEs of nanocomposites, it can be found that the CTE of pure epoxy matrix decreases more than 20% at glassy state. Although all the CTEs from the current MD simulations in glassy state are slightly smaller than those in reference [5], this gap is not significant issue because of the specific volume-temperature convexity of polymeric based composite. Therefore, the CTE of the polymeric material may vary according to the measured domain of the temperature. From the results shown in figure 2, it can be noticed that the CTE of the nanocomposites decreases as the radius of the nanoparticle decreases indicating that smaller nanoparticle is superior to larger ones to decrease the CTE of pure epoxy matrix. Finally, one major finding obtained from the present study is that the size effect of the nanoparticle still appears event after the nanocomposites unit cells undergo glassy-to-rubbery phase transition.

The elastic moduli of nanocomposites also shows similar tendency of CTEs. The elastic stiffness of nanocomposites increases as the embedded particle radius decreases. Also, these size effect holds out even the nanocomposite undergoes glass transition and becomes rubbery state as shown in figure 3.

3.3 Effect of interphase

The thermoelastic properties and their size dependency obtained from the present study can be explained by adopting an interphase which is formed near the nanoparticle. The molecules that form an interphase is adsorbed onto the particle and then immobilized, thus, this structural change appears in the decrease of the CTE and the increase of the elastic moduli in macroscopic properties. As has been confirmed from the present results, it can be concluded that the spherical SiC can significantly improve the thermomechanical properties of pure cross-linked epoxy remarkably regardless of their phase - glassy and rubbery and both the elastic stiffness and the linear CTE prominently show particle size dependency. Thus, the existence of the interphase is still an important structure-property relationship to enable particle size dependent thermoelastic properties at rubbery state.

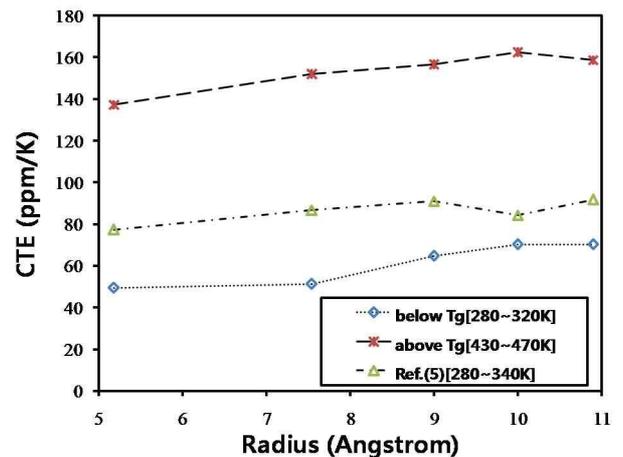


Fig. 2. The CTEs of nanocomposite below and above glass transition region

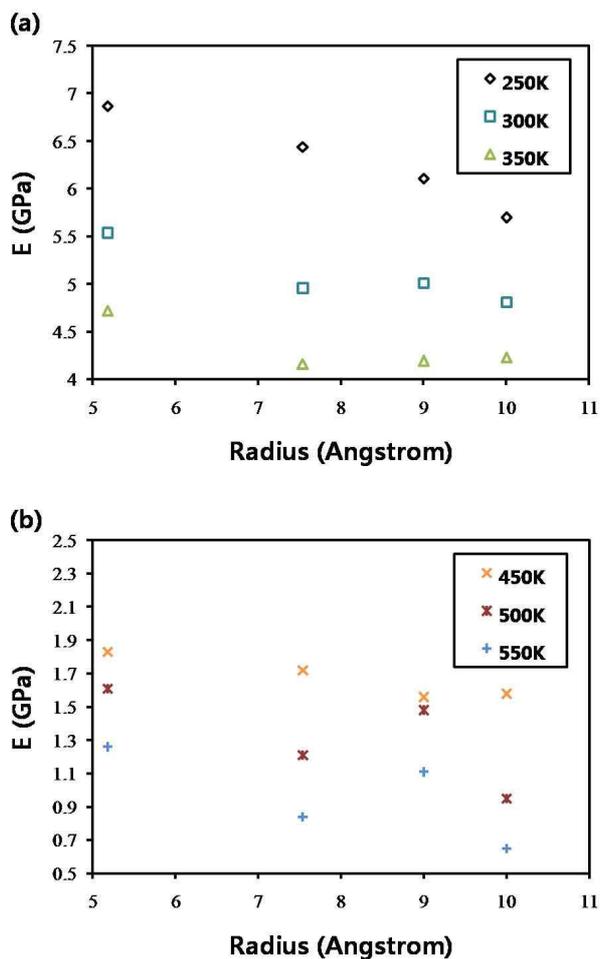


Fig. 3. The elastic moduli of nanocomposites in below (a) and above (b) T_g

4 Conclusion

In this study, the glass transition and thermoelastic behavior of polymeric and polymer-based nanocomposite systems had been investigated by MD simulation. Using the cooling down procedure under isobaric ensemble condition and fluctuation analysis through Parrinello and Rahman's method, we verified the size dependency of CTE and stiffness of nanocomposites below and above the glass transition temperature. As a result, the glass transition and thermoelastic properties of pure epoxy are found to be improved by embedding the SiC nanoparticle. Especially in thermoelastic properties of nanocomposites, the particle size-dependency is clearly observed both below and above the glass transition temperature. It can be concluded that the

size of the embedded filler are critical design parameter for tailoring the thermoelastic properties of underfilled materials, even in case that the material may laid on rubbery state under high temperature condition.

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