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Hygrothermal effect on mechanical and thermal transport properties of epoxy based nanocomposites

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ABSTRACT

In this study, by analyzing structural change and property degradation which are induced by the cross-linking and moisture absorption, hygrothermal effect on epoxy materials is investigated through molecular dynamics simulation. To verify the effect of cross-linking ratio on mechanical properties, three different cross-linked epoxy and three different cross-linked epoxy/silica nanocomposites are constructed and analyzed. Then, by adding water molecules to the dried unit cells, the moisture effects on mechanical properties and thermal transport properties are investigated. Structural change induced by moisture absorption is also investigated.

1. INTRODUCTION

Polymeric nanocomposites have been used in various industrial areas due to their advanced properties and multifunctionality. Nanocomposites are exposed to severe operation environment such as thermally elevated, cryogenic and humid conditions. Thus, they naturally suffer from enduring physical, chemical, and hygrothermal aging which cause the change of cross-linked structure, densification, and moisture adsorption. Aging phenomenon of polymeric materials has been investigated actively and many researchers have reported the hygrothermal effects on the physical properties of polymeric materials through various experiments and simulations. Using a molecular dynamics simulation, the diffusion coefficient of water molecules absorbed into the polymeric materials according to the moisture concentration and temperature has been investigated(Wu 2007). Also, it has been found that the elastic moduli decrease with increasing moisture content and decreasing conversion ratio(Clancy 2009). In addition, the glass transition temperature of polymeric system becomes higher as the exposed time becomes longer and the exposure temperature increase (Zhou 1999).

In this study, the hygrothermal effects on mechanical properties and thermal conductivities of epoxy and epoxy-based nanocomposites are investigated through molecular dynamics simulation. To verify the relation between plasticization and

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hygrothermal effect, the cross-linking simulation is applied at first. Then degradation of the mechanical property and swelling behavior according to the moisture absorption at various cured state are also investigated. And change of thermal conductivity induced by the moisture absorption is also investigated.

2. ATOMISTIC SIMULATION

2.1 Modeling

To investigate the hygrothermal effects on polymer materials, a dry epoxy unit cell was prepared using epoxy material which was constructed with 80 chains of EPON862 (diglycidyl ether of bisphenol F) as epoxy resin and 40 chains of TETA (triethylenetetramine) as curing agent. To investigate the filler effect on hygrothermal properties, nanocomposites unit cell was constructed as well using the same epoxy material and silica(for mechanical properties) and silicon carbide(for thermal conductivity) nanoparticle as shown in Fig. 1. Their radius are 8~11 Å and the volume fractions are 6~10%. Initial unit cells were amorphous state to assume isotropic properties. After construction, the unit cells were minimized through conjugation gradient method. And isothermal (NVT) and isothermal-isobaric(NPT) ensemble simulation were applied at 300K and 1atm for 100 psec and 1nsec to achieve the equilibrated configurations.

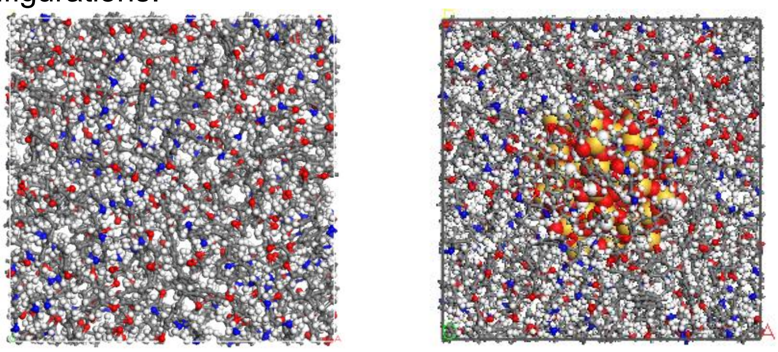

Fig. 1 Epoxy (left hand side) and nanocomposites (right had side) unit cells consist of epoxy and silica nanoparticle.

2.2 Curing simulation

Cross-linking simulation was applied to investigate the change of hygrothermal properties according to the cross-linking ratio of epoxy materials. The cross-links are produced between the carbon atoms in the epoxide group of EPON862 chain and the nitrogen atoms in TETA chain. As the EPON862 and TETA chains become reactive state, the bond between the carbon and oxygen in the epoxide group breaks and new bond (which is cross-link) generates between the carbon and nitrogen. Such reaction can be occurred generally when two reactive atoms are within from 4 to 10 Å (Wu 2006). Therefore, in this simulation, the radius of cross-linking reaction was restricted from 4 to 10 Å. The methodology for cross-linking simulation is as follows. First, initial cross-linking radius was set as 4 Å. Then, interatomic distances from a carbon atom to all nitrogen atoms within the cross-linking radius were monitored. And the carbon atom and the nitrogen atom which had the shortest distance among all candidate pair atoms were connected covalently. Such cross-linking reactions were applied to all carbons. Then, additional isothermal ensemble simulation was performed at 500 K for 10 ps. The cross-linking radius increased as much as 1 Å and the previous process was repeated until the cross-linking ratio became the target value or the reaction radius became 10 Å. After finishing the cross-linking interaction simulation, cross-linked unit cell was minimizes and equilibrated through the isothermal-isobaric ensemble simulation at 300 K and 1 atm.

2.3 Water absorption

In order to study change of hygrothermal properties according to the moisture in epoxy materials, water molecules were added into the dried epoxy unit cells which had been applied cross-linking simulation. To consider the effect of the cross-linking ratio on hygrothermal properties, three different cross-linking ratios, that is, zero, 0.6 and 0.9 were adopted. Different water absorption ratio, 0~6 wt% were considered. The including water molecules were positioned randomly. The initial configurations of wet epoxy and nanocomposites unit cells are shown as Fig. 2. To obtain the equilibrium state of the moisture unit cells, the minimization and equilibrium processes were carried out in the same condition as the previous simulation. Then, the coefficient of volume expansion(CME) according to the moisture absorption at 300K and 1atm was analyzed.

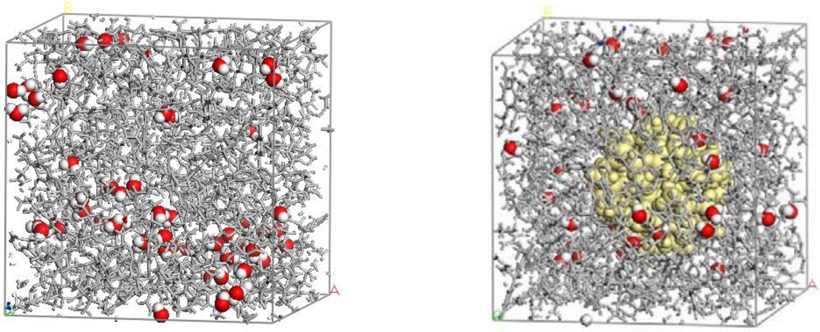

Fig. 2 Molecular structure of unit cells including water molecules

3 RESULTS

3.1 Mechanical properties

The mechanical properties such as Young`s modulus and shear modulus were calculated through Parrinello-Rahman fluctuation method. This method obtains elastic moduli using the ensemble averaged value of cell length and angle change induced by perturbing the cell during constant stress (NσT) ensemble simulation. In this study, the ensemble averaged values of deformation tensor and the metric tensor were obtained from the 10000 data extracted for 200 ps. The stiffness was calculated from the equation as shown below

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

where k is the Boltzmann constant, T is the temperature and $\langle V \rangle$ is the ensemble average of the cell volume.

Elastic properties of epoxy at different moisture weight fraction and cross-linking ratio are shown Fig. 3. Young`s modulus of non-cured epoxy was 1.06 GPa. The moduli increased from 1.06 GPa to 3.39GPa as the cross-linking was proceeds. Moisture in epoxy materials degraded Young`s modulus. In uncured epoxy, Young`s moduli decreased remarkably with moisture absorption. Young`s modulus decreased from 1.06 to 0.88 GPa (-17%). But, in cross-linked epoxy materials, amount of degradation was insignificant. Young`s modulus decreased from 3.4 to 3.1GPa (-9%). Thus, it can be concluded that even small amount of moisture absorption can critically affect the performance of uncured epoxy. But in case of cross-linked polymer, cross-links between polymer chains improve resistance to the degradation of mechanical properties due to moisture.

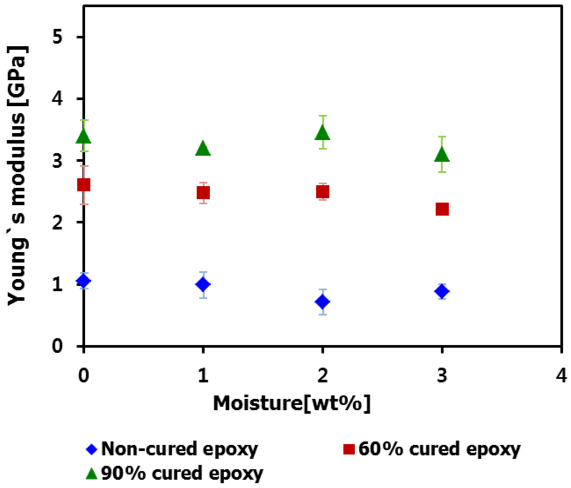

Fig. 3 Young`s modulus of epoxy according to the cross-linking ratio and the water absorption ratio.

3.2 Thermal transport properties

To obtain thermal conductivity, the NEMD(non-equilibrium molecular dynamics) method was performed using the microcanonical (NVE) ensemble. The thermal conductivity was obtained using the heat flux induced the temperature difference inside the unit cell. To make the temperature difference, the heat sink region and source region were defined. Then the same amount heat energy was added and removed from the defined regions. During the microcanonical ensemble, the cell became equilibrium state which the temperature gradient did not change in spite of continuous heat exchange. Then thermal conductivity was calculated using Fourier`s law as follows:

$$\lambda = -\frac{J_q}{dT / dz} \tag{2}$$

where heat flux, J_q is determined from the added or removed heat energy, ΔE and the cross-sectional area of unit cell, A_c as follows:

$$J_q = \frac{\Delta E}{2A_c} \tag{3}$$

dT / dz is the steady-state temperature gradient determined from a least squares approximation of the discrete temperatures inside the cell. The discrete temperatures of each part according to the heat flow direction were obtained using virial theorem.

Thermal conductivities of epoxy at different moisture weight fraction and cross-linking ratio are shown Fig. 4. Cross-linking between EPON862 and TETA improved the thermal conductivity. Thermal conductivity increased from 0.11 to 0.18W/mK (+64%). And Water molecules included in epoxy materials enhanced the thermal transport properties. Thermal conductivity of non-cured epoxy increased from 0.11 to 0.13W/mK (+14%) and that of 90% cured epoxy increased from 0.18 to 0.20W/mK (+12%).

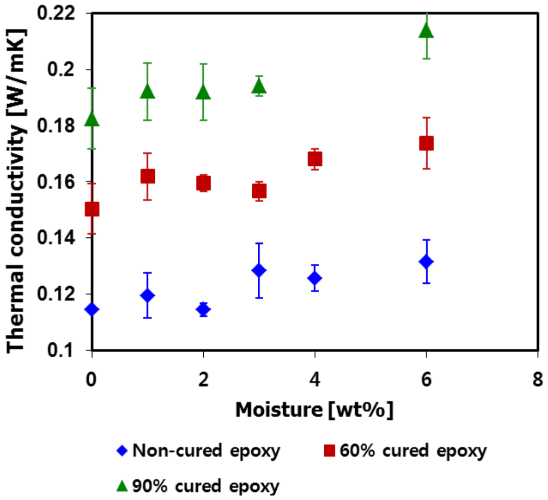

Fig. 4 Thermal conductivity of epoxy according to the cross-linking ratio and the water absorption ratio.

4. CONCLUSIONS

In this study, the variation of epoxy materials due to cross-linking between polymer chains and water absorption were verified through molecular dynamics simulation. Three different cross-linked state, zero, 60% and 90% cross-linked state, were considered and elastic moduli and thermal conductivities were obtained. Then, water molecules were added into the dry epoxy and the mechanical properties and the thermal transport properties according to the water absorption ratio were estimated. Moisture in polymer materials degraded the mechanical properties. On the other hand, moisture enhanced the thermal transport properties.

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