MULTISCALE MODELING OF HYGROTHERMAL BEHAVIOR OF EPOXY BASED NANOCOMPOSITES

M. Cho[1*], S. Yu[1], S. Yang[1]

[1] *Multiscale Mechanical Design Division, School of Mechanical and Aerospace Engineering, Seoul National University, Gwan-ak, Seoul, Republic of Korea*
**mhcho@snu.ac.kr*

Keywords: Hygrothermal property, Polymer, Multiscale

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 are investigated. Structural change induced by moisture absorption is also investigated.

1 Introduction

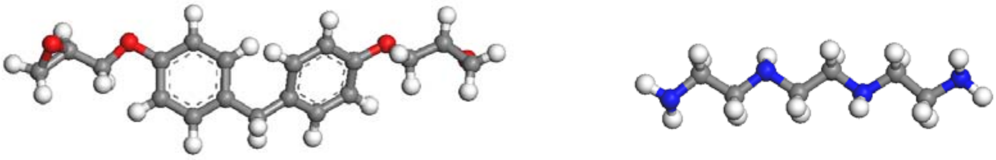
Epoxy and epoxy-based composites have been used as the structural materials in various industrial areas due to their advanced properties and multifunctionality such as high stiffness, low thermal expansion coefficient, and light weight. The lifetime of epoxy composites is even longer than several decades and it can be exposed to severe operation environment such as thermally elevated, cryogenic and humid conditions. Thus, epoxy materials naturally suffer from enduring physical, chemical, and hygrothermal aging which cause the change of cross-linked structure, densification, and moisture adsorption. Aging phenomenon of epoxy 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[1]. Also, it has been found that the elastic moduli decrease with increasing moisture content and decreasing conversion ratio[2]. In addition, the glass transition temperature of epoxy system becomes higher as the exposed time becomes longer and the exposure temperature increase [3].

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

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 cross linker as shown in Fig. 1. To investigate the filler effect on hygrothermal properties, nanocomposites unit cell was constructed as well using the same epoxy material and silica nanoparticle. Its radius is 10 Å and the volume fraction is 8.5 %. Initial configuration of epoxy in the unit cells was uncured state and amorphous state to assume isotropic properties. The constructed unit cells were minimized through conjugation gradient method to obtain the stable configuration at zero temperature conditions. And isothermal (NVT) ensemble simulation was applied at 300K for 100 ps to stabilize the thermal condition. Then, isothermal-isobaric (NPT) ensemble simulation was performed at 300 K and 1atm for 1 ns to achieve the equilibrated configurations at room temperature conditions. The resultant density and cell length of the epoxy cell after equilibrium simulation was 1.1 g/cm^3 and 35.9Å. That of epoxy composites cell was 1.2 g/cm^3 and 36.6Å.



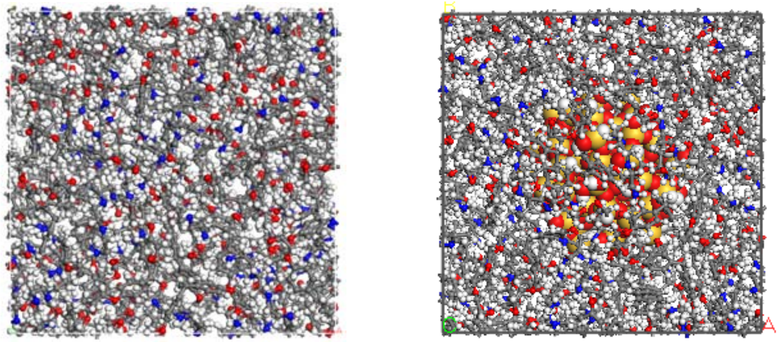
(a) EPON862 (diglycidyl ether of bisphenol F) (b) TETA (triethylenetetramine)

Figure 1. Molecular structure of the epoxy and curing agent used in simulation.

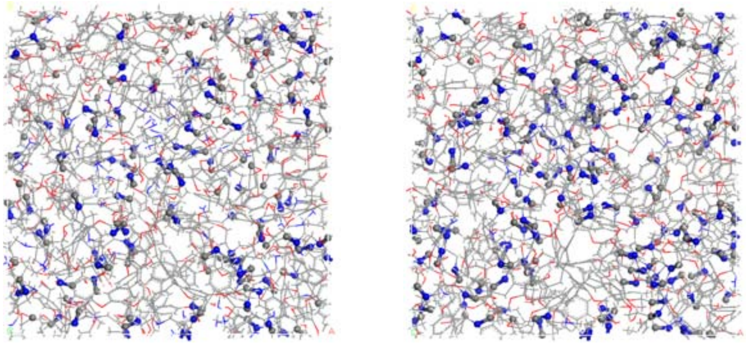
2.2 Curing simulation

After building the equilibrated non-cured epoxy and composites unit cell, 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 [4]. 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. The atomistic configurations of cross-linked epoxy are shown in Fig. 2(b) and 2(c). In this figure, the ball and stick view represents cross-linked atoms.



(a) Uncured epoxy (left hand side) and uncured epoxy/silica nanocomposites (right had side)

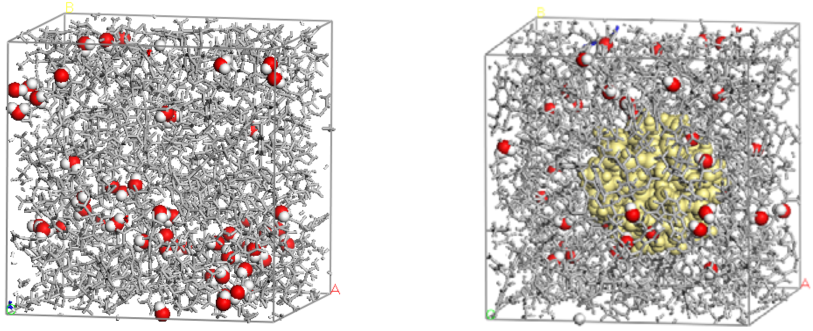


(b) 60% cured epoxy (c) Fully(89%) cured epoxy

Figure 2. Molecular structure of epoxy unit cell at different conversion ratio.

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. Three different water absorption ratio, 1, 2 and 3 wt% were considered to investigate the variation of mechanical properties according to the absorption ratio. The including water molecules were positioned randomly but kept from aggregating each other. The initial configurations of wet epoxy and nanocomposites unit cells are shown as Fig. 3. 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.



(a) Water molecules inserted epoxy (b) Water molecules inserted nanocomposites

Figure 3. Molecular structure of wet unit cells (Epoxy is non-cured state).

3 Results

3.1 Calculation method for 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

$$C_{ijkl} = \frac{kT}{\langle V \rangle} \left\langle \delta\varepsilon_{ij} \delta\varepsilon_{kl} \right\rangle^{-1} \tag{1}$$

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

3.2 Modulus change according to the variation of cross-linking ratio

During the cross-linking simulation, the cross-linking radius changed from 4 to 10 Å. After finishing the cross-linking simulation when the cross-linking radius reached 10 Å, cross-linking ratio of EPON862 and TETA was not 100%. At the convergence condition, 142 cross-links were formed from 160 candidate cross-links, thus, the final cross-linking ratio was only 0.9. Perfect cross-linked epoxy can be constructed through additional cross-linking procedure. But, to mimic the actual reaction of cross-linking in experiments, the cross-linking radius was restricted within 10 Å.

Elastic moduli according to the cross-linking ratio were calculated through Parrinello-Rahman method. Young`s modulus and shear modulus of non-cured epoxy was 1.06 GPa and 0.37GPa respectively. The moduli increased to 3.39GPa and 1.23 GPa as the cross-linking was proceeds. Young`s modulus and shear modulus of non-cured epoxy/silica nanocomposites was 1.26 GPa and 0.44GPa respectively. Moduli of composites also increased with increased cross-linking ratio, the values became 3.98 GPa and 1.69 GPa. The moduli according to cross-linking ratio are listed in Tables 1 and 2. The reinforcing effect of silica nanoparticle on epoxy materials was 20~35% for the various cross-linking ratio.

Water absorption ratio	Young`s modulus of epoxy [GPa]			Shear modulus of epoxy [GPa]		
	uncured	60% cured	90% cured	uncured	60% cured	90% cured
0	1.06	2.60	3.40	0.37	0.93	1.23
1	0.99	2.48	3.20	0.35	0.89	1.22
2	0.71	2.50	3.45	0.25	0.90	0.25
3	0.88	1.14	3.10	0.31	0.40	0.13

Table 1. Elastic moduli of epoxy according to the water absorption ratio and cross-linking ratio

Water absorption ratio	Young`s modulus of nanocomposites [GPa]			Shear modulus of nanocomposites [GPa]		
	Non-cured	60% cured	90% cured	Non-cured	60% cured	90% cured
0	1.26	3.34	3.98	0.44	1.22	1.69
1	1.24	3.40	3.90	0.44	1.24	1.42
2	0.95	3.30	3.95	0.33	1.20	1.45
3	1.04	3.27	3.72	0.36	1.19	1.36

Table 2. Elastic moduli of epoxy/silica nanocomposites according to the water absorption ratio and cross-linking ratio

3.3 Hygrothermal properties

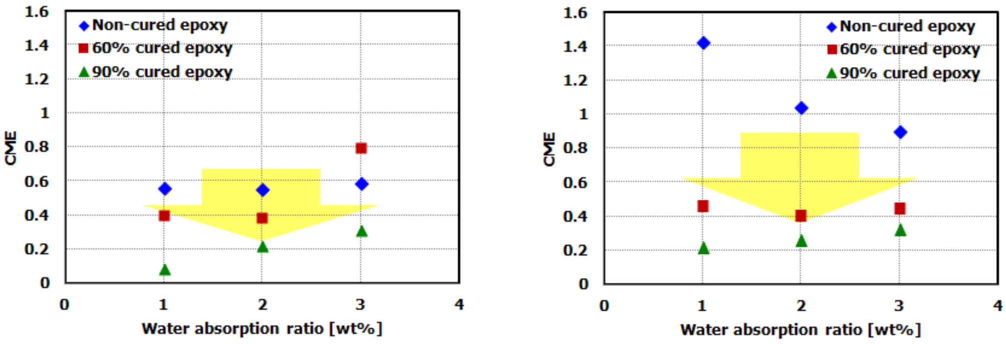
Elastic properties of epoxy at different moisture weight fraction and cross-linking ratio are arranged in Table 1 and those of epoxy/silica nanocomposites are arranged in Table 2. Moisture in epoxy materials degraded both Young`s modulus and shear modulus. In case of uncured epoxy and uncured nanocomposites, both moduli decreased remarkably with moisture absorption. But, in cross-linked epoxy materials, amount of degradation was insignificant. 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.

3.2. Structural analysis

When water molecules are absorbed into a polymer, it undergoes prominent swelling behavior. By quantifying the volumetric expansion after the moisture absorption, the coefficient of moisture expansion (CME) (also referred to as coefficient of hygroscopic expansion or swelling coefficient) can be obtained as below:

$$CME = \left(\frac{\Delta l}{l_0}\right) / \left(\frac{\Delta M}{M_0}\right) \tag{2}$$

where l_0 and M_0 is initial length and mass of the cell respectively. And Δl and ΔM are the variations of length and mass after absorbing water. CME obtained from the fully equilibrated unit cell after the isothermal-isobaric ensemble at 300 K and 1atm are shown in figure 4. The CMEs of epoxy materials became smaller as the cross-linking ratio increased because cross-links between polymer chains kept from swelling due to the water molecules. In uncured state, epoxy and epoxy/silica nanocomposites shows much different value. In cross-linked state, CME decreased with the cross-linking ratio. But CMEs of epoxy and epoxy/silica nanocomposites were almost same regardless of reinforcing filler. The value is about 0.4 at 0.6 cross-linking ratio and 0.2 at 0.9 cross-linking ratio.



(a) Epoxy (b) Nanocomposites

Figure 4. Change of CME(coefficient of moisture expansion) according to the cross-linking ratio and the water absorption ratio

Conclusion

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 were obtained. Then, water molecules were added into the dry epoxy and the mechanical properties and structural change according to the water absorption ratio were estimated. Moisture in polymer materials degraded the mechanical properties. Volume of epoxy material increases linearly and the elastic moduli decreased non-linearly with water absorption ratio.

Acknowledgement

This research was supported by WCU(World Class University) program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R31-2011-000-10083-0) and NLRL(National Leading Research Lab.) program through the National Research Foundation of Korea(NRF) grant funded by the Korea government(MEST) (No. 2011-0020476)

References

[1] Wu, C. and Xu, W. "Atomistic simulation study of absorbed water influence on structure and properties of crosslinked epoxy resin", *Polymer*, 48, 5540-5448 (2007).

[2] Clancy, T.C., Frankland, S.J.V., Hinkley, J.A. and Gates, T.S. "Molecular modeling for calculation of mechanical properties of epoxies with moisture ingress", *Polymer*, 50, 2736-2742 (2009).

[3] Zhou, J. and Lucas, J. P. "Hygrothermal effects of epoxy resin. Part II: variations of glass transition temperature", *Polymer*, **40**, 5513-5522 (1999).

[4] Wu C, Xu W. "Atomistic molecular modelling of crosslinked epoxy resin", *Polymer*, **47**, 6004–6009 (2006).