# Multiscale Modeling Approach to Hygroelastic Aging of Epoxy and Epoxy Nanocomposites

Seunghwa Yang [a*], Inseok Jeon [a], Sunyong Kwon [b]
[a]*Mechanical Energy Division, School of Energy Systems Engineering, Chung-Ang University, Seoul 06974*
[b]*Green Solution Program, Chemical Research Center, Samyang Corp. Daejeon 34055*
[*]*Corresponding author: fafala@cau.ac.kr*

## 1. Introduction

Epoxy has been widely used in aerospace structures, electronics, and power plant for its excellent mechanical durability with highly dielectric characteristics [1,2]. In nuclear power plant systems, the use of epoxy and epoxy-based composites is mainly divided into insulation and sealing, each of which utilizes hard epoxy (HE) and soft epoxy(SE), respectively. In order to secure multifunctional durability of hermetic epoxy for long-term operation of nuclear power plants, aging of epoxy should be considered. For the Service Level 1 epoxy applied to the coating of water bath in emergency core cooling systems (ECCS), leaching and delamination of epoxy result in blockage of sump screen by debris during the loss-of-coolant accident. Therefore, a systematic approach to the evaluation and mitigation of long-time hygroscopic aging of epoxy and epoxy composites is required. In this study, a novel multiscale modeling approach based on molecular dynamic (MD) simulations to the hygroelastic aging of epoxy is demonstrated

## 2. Molecular Modeling and Simulation

In this section preparation of cross-linked epoxy unit cell structure, moisture uptake, and the details on ensemble simulation of the model epoxy to evaluate the swelling and degradation of mechanical properties are demonstrated.

### *2.1 Epoxy molecular model*

As a soft epoxy, EPON862® (diglycidyl ethers of bisphenol F) and TETA (triethylenetetramine) were chosen as resin and curing agent, respectively. According to the number of epoxide groups in resin and amine groups in curing agent, an amorphous unit cell with a 3:1 of mixing ratio is prepared, as shown in Fig. 1. In order to construct the cross linked network structure in epoxy, an *in-situ* cross linking algorithm was applied. Even if this method does not involve electron exchange between carbon atoms and nitrogen atoms in cross linking, the resultant network structure can effectively reflect the conformation and configuration of engineering epoxy and provide cross linking ration dependent properties. In order to describe all the inter- and intra-molecular interactions in epoxy system, the polymer consistent force field (PCFF) was used. The final cross linking ratio of the model epoxy after the *in-situ* cross linking process was 80% representing a stiff thermoset epoxy.

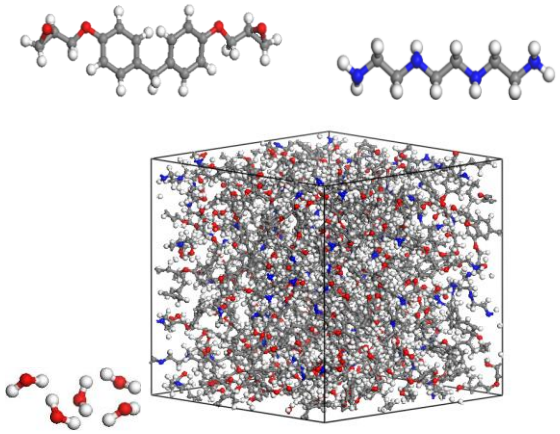


Fig. 1 Molecular model of EPON862®, TETA and amorphous epoxy

### *2.2 Moisture uptake and production runs*

After preparing cross linked epoxy molecular model, all periodic boundary condition was applied to prevent finite size effect and to represent bulk amorphous epoxy. In order to equilibrate the epoxy at ambient condition, and isothermal-isobaric (NPT) ensemble simulation was performed for 3ns under the descript of PCFF force field. To describe the hygroscopicaly aged structure, water molecules were directly inserted into the epoxy unit cell according at various vapor pressure followed by an additional equilibration process to measure the swelling of epoxy.

Upon different epoxy unit cell structures containing different weight percent wt(%) of water, uniaxial tension test was implemented to draw the stress-strain relationship. The strain rate applied to each epoxy is $10^8$/sec. At each loading step, one end of the unit was elongated and the result stress was calculated from the Virial theorem after a short relaxation of stress. From the stress-strain curves, the elastic modulus of epoxy was determined within 2% of elastic strain range. For the computational efficiency, all the stress-strain curves were averaged over 9 different simulation results.

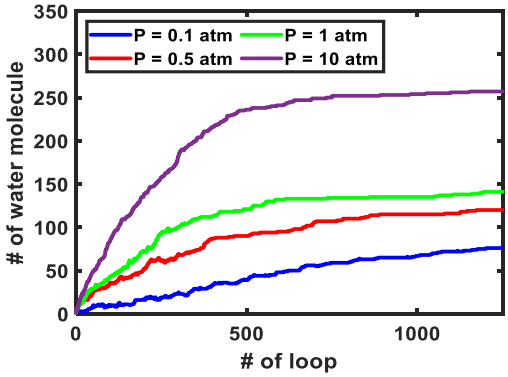
## 2. Results and Discussion

### *2.2 Coefficient of moisture expansion (CME)*

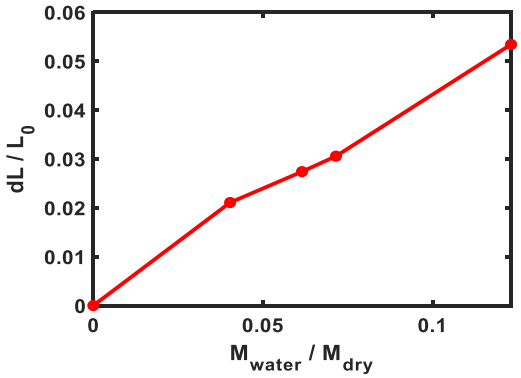
The moisture uptake into the 80% cross linked epoxy molecular unit cell is shown in Fig.3 according to the simulation time and the vapor pressure. As the vapor

pressure increases, water molecules can penetrate into the free volume epoxy more easily. The water bath environment is a critical condition for the moisture uptake. Therefore, the high concentration of water in surface coated epoxy can penetrate into the epoxy-substrate interface and result in critical coating failure of epoxy.

The moisture uptake-eigen strain relationship of epoxy is shown in Fig. 2(b). As the moisture content increase to 10 wt%, 4% of hygroscopic strain is induced. The CME of epoxy determined from the slope of moisture content-eigenstrain relation is 0.4087. This swelling corresponds to 169K of temperature increase in thermal expansion problem. Therefore, the moisture uptake and the resultant swelling can result in a critical distortion and internal stress of coated epoxy in ECCS system.




(a)




(b)

Fig. 2 (a) Moisture uptake into epoxy unit cell (b) Swelling of epoxy under hygroscopic aging

The stress-strain curves of hygroscopically aged epoxy are depicted in Fig. 3. As the vapor pressure increases, the stress of epoxy dramatically decreases as a result of the plasticization by the uptaken moisture. Compared with the dry epoxy, more than 200% of degradation occurred at 1atm of vapor pressure. Such degradation can result in tearing and delamination of coated epoxy after exposure to a long-time service condition in water.

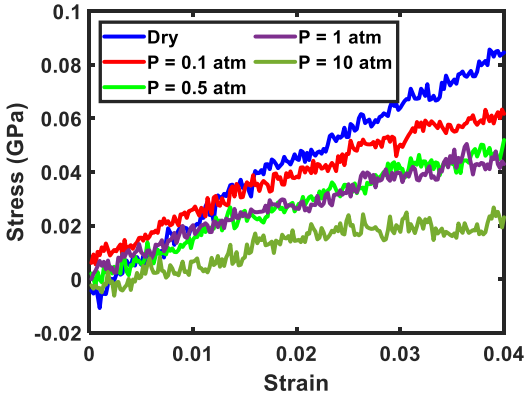



Fig. 3 Mechanical behavior of hygroscopically aged epoxy at different moisture uptake condition.

## 3. Conclusions

An *in-silico* simulation based multiscale modeling approach was proposed in this study. The moisture uptake and the swelling phenomena could be effectively described from classical MD simulations. By the hygroscopic aging, the elastic modulus of epoxy was seriously degraded. In the presentation, micromechanical approach to the degradation of epoxy nanocomposites will be demonstrated

## REFERENCES

[1] S. Yang, S kwon, M. Lee, M. Cho. Molecular dynamics and micromechanics study of hygroelastic behavior in graphene oxide-epoxy nanocomposites. Composites Part B, Vol. 164, 425-436, 2019.

[2] S. Kwon, M. Lee, S. Yang. Molecular dynamics approach on hygroelastic behavior of epoxy/graphene nanocomposites. Journal of Mechanical Seicen and Technology, Vol. 33(2), 741-747, 2019.