Development of a Reaction Simulation Method for the Generation Process of Crosslinked Network Structure of Epoxy Resins

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[Introduction] In this study, we use a curing reaction simulation model combining quantum chemical (QC) and molecular dynamics (MD) calculations to obtain a comprehensive mechanism with predictive capabilities and accurate kinetic models. The chemical reaction between diglycidyl ether of bisphenol A (DGEBA) and 4,4'-diamino-2,2'-dimethylbiphenyl (2,2'-CH_3-BP) was computed as a base resin and curing agent, respectively. Figure 1 depicts illustrations of DGEBA and 2,2'-CH_3-BP molecules. Ehlers et al. theoretically investigated epoxy-amine reactions using simplified molecular models and found that additional alcohol or amine molecules play a role as a catalyst and assist the reactions [1]. We also investigated catalytic effects using non-simplified molecules and incorporated the effects with the cross-linking MD simulation.

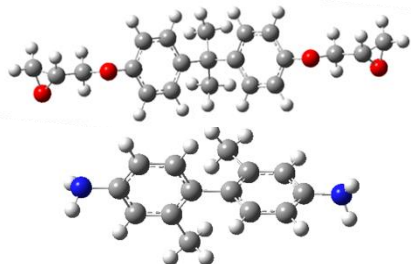

Fig. 1 Illustrations of DGEBA (top) and 2,2'-CH_3-BP (bottom) molecules. Here gray is C atom, white is H, red is O, blue is N.

[Method] When calculating the reaction routes, we employed QC calculations using the global reaction route mapping (GRRM) algorithm [2]. Reaction routes producing one secondary-amine molecule from one DGEBA and one 2,2'-CH_3-BP (1st step) and one tertiary-amine molecule from one DGEBA and one secondary amine (2nd step) were calculated. When simulating the cross-link reactions, we improved the reaction model in the MD simulation proposed by Okabe et al. [3,4]. The simulation consists of two parts: the molecular dynamics simulation part to simulate the motions of atoms in the system and the reaction part to judge whether the reaction occurs and produces the new chemical bonds.

[Results and Discussion] Transition state (TS) structures in the reaction pathways are obtained using GRRM. We found that impurities (water or alcohol) and amine curing agents could function as catalysts to affect the stability of the TS structure. Furthermore, TS states become more stable when a 6-membered ring is formed at the reaction site. When water is the catalyst, the ΔG of the 1st-step reaction decreases considerably. To evaluate the effect of water on MD simulations, two initial models were built. Model 1 consists of 160 DGEBA molecules and 80 2,2'-CH_3-BP molecules, while model 2 includes 8 water molecules as well. With increasing curing rates, the size of the largest molecule grows progressively. When the curing rate reaches 80% in both model 1 and model 2, the weight percent of the largest molecule accounts for approximately 90%, suggesting that the cross-linking reaction occurred and monomers of DGEBA and 2,2'-CH_3-BP are successfully cross-linked. Comparing models 1 and 2, we found the catalytic effect of water can accelerate the crosslinking process with small crosslinking cycles.

[Acknowledgement] This work was supported by Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), "Materials Integration" for Revolutionary Design System of Structural Materials (Funding Agency: JST). Y.X. acknowledges supports from IQCE Research Fellow and Tohoku University Advanced Graduate School Doctoral Fellowship.

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