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Thermomechanical characteristics of Epoxy Vitrimers Using Molecular Simulations

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Abstract - In this study, a self-healing mechanism of vitrimers containing disulfide bonds is explored and verified by combining quantum chemical (QC) calculations and molecular dynamics (MD) simulations. QC calculations are performed using the Global Reaction Route Mapping (GRRM) algorithm to explore a reaction pathway. As a result, it was found that, the sulfur atom created by disulfide bond breaking forms stable bonds to carbon atoms at the ortho and para positions of a benzene ring in addition to disulfide bond recombination. The activation energies are calculated and compared with the bond exchange reactions, which are previously proposed reaction pathway, to reveal that the reaction we found could predominantly occur. MD simulations show that the structure with the covalent bond repair mechanism we found repairs more disulfide bonds and exhibits higher stress in tensile simulations than the structure with the direct recombination-only repair mechanism.

***Keywords*:** polymer materials, thermosetting resins, vitrimer, molecular dynamics, quantum chemical calculations

1. Introduction

Carbon Fiber Reinforced Plastics (CFRPs) are composite materials that combine a base resin and carbon fibers, and has attracted attention in many industrial fields such as aerospace due to its excellent mechanical properties [1]. Thermosetting resins, which are mainly used as base materials for CFRP, have a three-dimensional crosslinked structure between the constituent atoms, and thus have high mechanical properties and thermal stability. However, it has the disadvantage of being unsuitable for reprocessing or recycling. Therefore, from the viewpoint of environmental preservation, etc., vitrimer was developed as a resin that combines the reprocessability and recyclability of thermoplastic resin with the excellent mechanical properties of thermosetting resin [2]. Unlike conventional thermosetting resins with irreversible crosslinking structures, vitrimers have covalent adaptive networks. This allows the topology of the crosslinked structure to change when stimuli such as heat, light, or pH changes are applied [3]. By introducing covalent adaptive networks, it is expected to provide excellent thermo-mechanical properties when used as a structural material, and to allow for easy disassembly and remolding, like thermoplastics, when reprocessing. The self-healing property of vitrimers is also a factor attracting attention for polymer materials, which are prone to safety and material life degradation if damaged during use. This self-healing property, as well as reprocessability and recyclability, is thought to result from topology modification through covalent adaptive networks, and many experimental results have been reported [4, 5].

Although various epoxy-based vitrimers have been reported, in this study, a disulfide-based vitrimer with diglycidyl ether of bisphenol A (DGEBA) as the base resin and 4-aminophenyl disulfide (AFD) as the curing agent, as shown in Fig. 1. This structure is very similar to the crosslinked polymer of DGEBA and 44DDS, which has already been shown to have high mechanical properties [6], and contains a disulfide bond that expresses its function as a vitrimer.

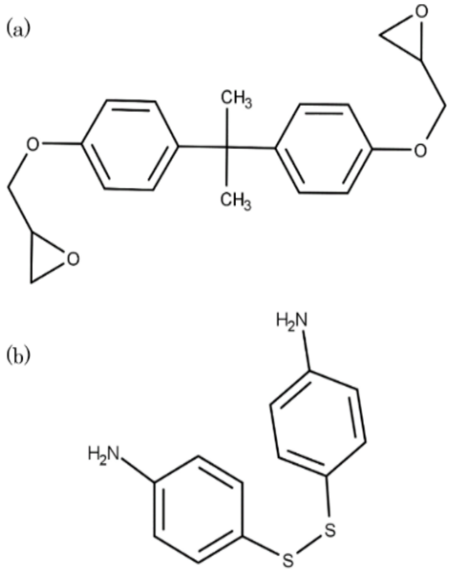

Fig. 1: Structure formula of (a) DGEBA and (b)AFD

Epoxy vitrimers containing such disulfide bonds have attracted much attention because they show many advantages such as easy implementation and relatively easy access to precursors. According to previous studies, these epoxy vitrimers are thought to exhibit self-healing property through bond exchange reactions of the disulfide bonds (S-S) [7]. However, since the average distance between disulfide bonds is long and these bonds are geometrically constrained by the crosslinked structure, bond exchange reactions do not occur frequently enough to affect the macroscopic properties. Therefore, the bond exchange reaction of disulfide bonds alone is not sufficient to explain the self-healing properties observed in the experiments, and other reaction pathways are considered to contribute to the self-healing property.

Numerical calculations are extremely useful in investigating such microscopic self-healing mechanisms. In this study, we investigate the molecular-scale self-healing mechanism of epoxy vitrimers containing disulfide bonds by coupling quantum chemistry (QC) calculations and molecular dynamics (MD) calculations.

Vitrimers are multiscale materials in which quantum chemical phenomena such as covalent adaptive networks affect the macroscopic thermo-mechanical properties of the condensed system. Therefore, approaches that focus only on QC and MD cannot provide a fundamental understanding of the phenomena. By incorporating the information on reaction pathways obtained by QC into MD calculations, it is expected that the condensed system will accurately reproduce the self-healing of crosslinked structures.

In this study, we search for reaction pathways and calculate their activation energies using QC calculations. Compare their reactivity with that of bond exchange reactions that are previously proposed reaction pathway. The reaction pathways obtained by QC calculations will then be introduced into MD simulations to reproduce self-healing properties in condensed matter systems.

2. Methods

First, the reaction pathways are explored and identified by QC calculations, and then MD simulations are performed introducing these pathways. In the MD simulation, a crosslinked structure is created by chemical reaction calculation, and the disulfide bonds in this structure are broken by uniaxial tensile calculation. Then, the covalent bond repair reaction pathway identified in the QC calculation is introduced and the uniaxial tensile calculation is performed again to obtain the stress-strain curve. These series of calculation conditions are described below in each section.

2.1. Quantum Chemistry (QC) Calculations

The Global Reaction Route Mapping (GRRM) algorithm [8] was used to search reaction pathways by QC calculations in this study. The GRRM algorithm explores multidimensional potential energy surfaces controlling the quantum chemical calculation package program Gaussian [9] at a higher level and can determine the transition state and equilibrium structures of reactions in polyatomic systems.

In the search for reaction pathways, we investigate how the disulfide bonds return to its original state after dissociation. Using a model of dissociated vitrimer fragment shown in Fig. 2, the structures and energies of the reaction intermediates and transition states were obtained using density functional theory (B3LYP).

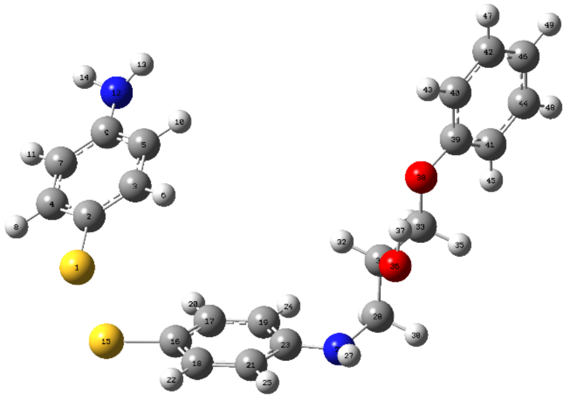

Fig. 2: Structure of vitrimer fragment model

2.2. Molecular Modeling and Curing Simulation

The MD simulations in this study were performed by Large-scale Atomic/ Molecular Massively Parallel Simulator (LAMMPS), a general-purpose MD software, on a supercomputer [10] at the Institute for Solid State Physics, the University of Tokyo. We utilized the Optimized Potential for Liquid Simulation (OPLS-AA) force field for molecular structure and assigned ESP charges to each atom through density functional theory calculations based on the B3LYP/6-31G (Hamiltonian/based set).

Epoxy resins form crosslinked structures through chemical reactions between epoxy groups in the base resin and Amine groups in the curing agent [11]. First, the molecules shown in Fig. 1 were placed in a simulation box with a total particle number of about 27,000 at a functional group equivalence ratio (AFD : DGEBA = 1 : 2). A stepwise relaxation was then performed to create an equilibrium structure at a constant temperature of $T = 300$ K and atomospheric pressure ($P = 1$ atm) before the cross-linking reaction.

To ensure a uniform crosslinked structure, it is essential that the molecules are uniformly dispersed prior to the cross-linking reaction. Thus, relaxation calculation was performed in the *NVT* ensemble at a constant temperature of $T = 800$ K to randomize the molecular arrangement inside the system. The density was then increased to about 0.75 by repeated relaxation calculations and shrinkage of the system box while gradually lowering the temperature in the *NVT* ensemble. Finally, relaxation calculation for 1 ns was performed in the *NPT* ($T = 300$K, and $P = 1$ atm) ensemble to obtain the equilibrium structure. This equilibrium structure was used as the initial state for chemical reaction calculations.

The chemical reactions between these functional groups were reproduced for molecular pairs with a distance between the epoxy group of the base resin and the amino group of the hardener within 5.0 Å. After that, relaxation calculation for 1 ns was performed in the *NPT* ensemble ($T = 300$K, and $P = 1$ atm) to obtain the equilibrium structure of the epoxy vitrimer. The equilibrium structure of the epoxy vitrimer is shown in Fig. 3.

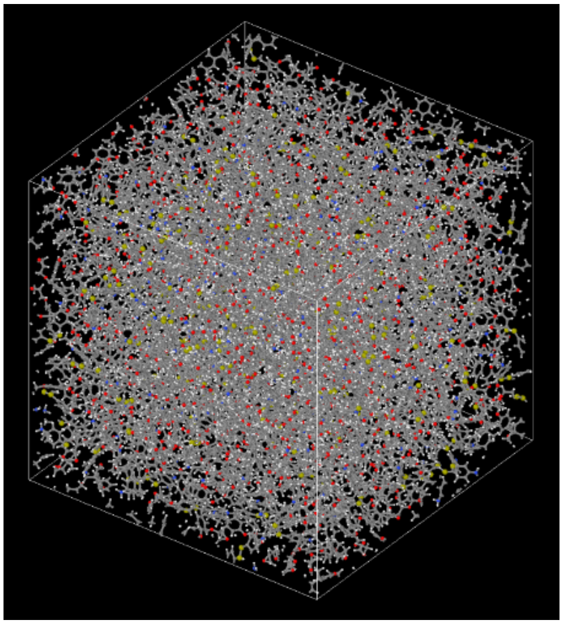

Fig. 3: Equilibrium structure of the epoxy vitrimer

2.3. Uniaxial Tensile Simulation Considering Disulfide Bond Dissociation

A uniaxial tensile calculation is performed on the resin after the chemical reaction described in the previous section to degradate the crosslinked structure. The method of covalent bond dissociation and degrading crosslinked structures by uniaxial tensile simulations is commonly used in previous studies [12]. Here, to generate vitrimer fragments required in the repairing process, a bond dissociation algorithm is applied only to disulfide bonds, and all disulfide bonds are broken. Here, disulfide bonds are dissociated when they are stretched to 1.1 times their natural length (2.07 Å) in this bond dissociation algorithm.

2.4. Covalent Bonds Repairing

First, the structure of the previous section, in which all disulfide bonds have been dissociated, is compressed to restore it to the same box size as the original crosslinked structure. Then, relaxation calculation for 1 ns was performed in the *NPT* ensemble to obtain the equilibrium structure. The following three repair processes were performed to prepare three distinct structures:

(1) A reaction path obtained from quantum chemical (QC) calculations was introduced.
(2) An algorithm in which sulfur atoms directly recombine was applied.
(3) No bond-repairing algorithm was introduced; the structure remains in a damaged crosslinked state.

In processes (1) and (2), the number of repaired disulfide bonds depends on the distance between the reactive atoms. Therefore, in this study, reactions were carried out using molecular pairs whose interatomic distances were within 3.0, 3.1, and 3.2 Å, respectively. The relationship between reaction distance and the number of repaired bonds was also investigated.

2.5. Tensile Simulation

Uniaxial tension calculations are performed on the four structures prepared in the previous section to obtain the stress-strain diagrams. In this tensile simulation, no covalent bond dissociation algorithm is introduced. Also, the strain rate in this simulation is 5×10^{8} s^{-1}, the temperature is 300 K, and 1 atm is applied in the direction perpendicular to the tensile direction.

3. Results and discussion

3.1. Quantum Chemistry (QC) Calculations

QM calculation finds out the following two types of stable bonds in addition to disulfide bond recombination. In these bonding patterns, a sulfur atom is bonded to carbon atoms at the ortho and para positions of a benzene ring. As shown in Fig. 4.

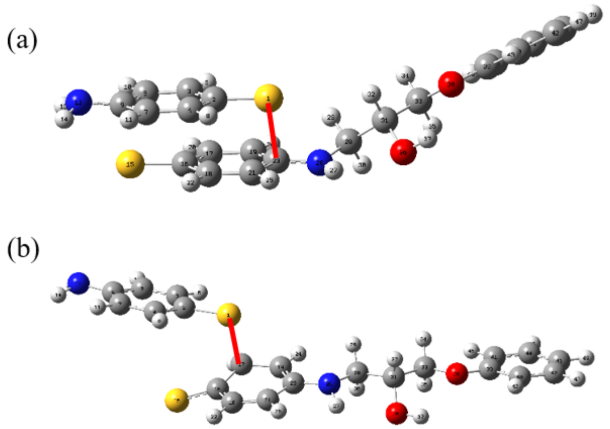

Fig. 4: Bonding of sulfur atoms to the (a) para (b) ortho position

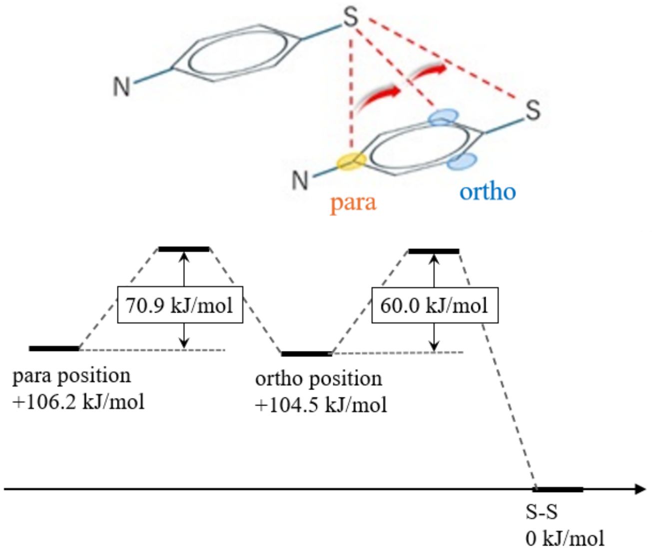

Fig. 5: Reaction pathways by QC calculations

Figure 5 shows that the disulfide bond, ortho-addition, and para-addition are more stable in that order, and that activation barriers of about 60 kJ/mol and 71 kJ/mol exist between each stable structure, respectively. These activation barriers are sufficiently lower than the activation energy associated with the disulfide bond exchange reaction (192.9 kJ/mol) [13], which is often considered in conventional MD calculations. Therefore, we can conclude that covalent bond transitions such as those shown in Figure 5 can occur predominantly.

3.2. Molecular Dynamics (MD) Simulations

In the MD calculation, considering the results of the QC calculation above, tensile analysis is performed on the following four types of structures.

(1) Structure in which disulfide bonds are repaired through reactions at the para and ortho positions of benzene ring in addition to direct recombination.

(2) Structure in which disulfide bonds are repaired only by direct recombination.

(3) Degraded structure (all disulfide bonds are dissociated).

(4) Undegraded (no disulfide bonds are dissociated) crosslinked structure.

First, the results of the disulfide bond repairing calculations for the reaction length in the simulations (1) and (2) are shown in Table 1.

Table 1: Number of disulfide bond repairs by reaction length

Reaction length [Å]	Simulation (1)	Simulation (2)
3.0	112	7
3.1	154	87
3.2	170	139

Table 1 shows that, for each reaction length, the reaction pathway that repairing disulfide bonds via para- and ortho-position reactions of benzene ring in addition to direct recombination can repair more disulfide bonds than the reaction pathway that repairs only direct recombination. This suggests that the reaction pathway we found enhances vitrimer self-repair.

Furthermore, the stress-strain curves obtained by performing tensile simulations on the four types of structures mentioned above are shown in Fig. 6. Tensile simulations were performed for structures (1) and (2) with a reaction length of 3.1 Å.

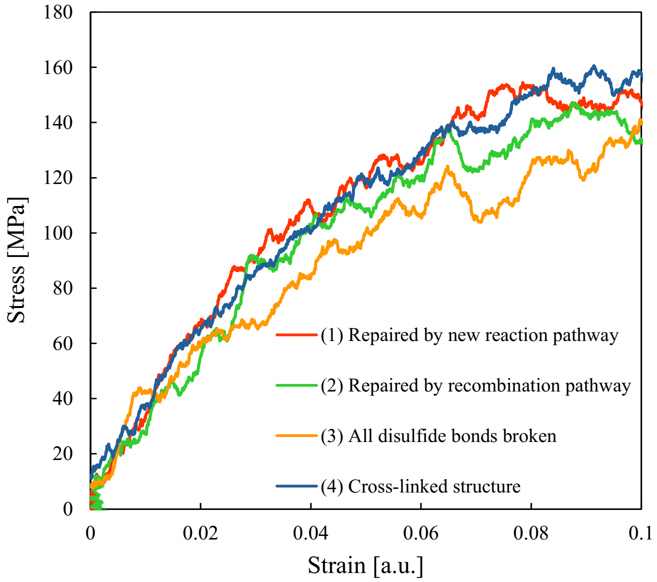

Fig. 6: Stress-strain curves by MD

Comparing (1) and (3), the structure repaired by our finding reaction pathway shows stress recovery from the degraded structure. Furthermore, the comparison between (1) and (2) shows that the structure repaired by reaction pathway we found exhibits higher stress than the structure repaired by the direct recombination-only reaction pathway.

4. Conclusion

QC calculations were used to investigate the reaction pathways of the vitrimers, revealing that the sulfur atom forms stable bonds to carbon atoms at the ortho and para positions of a benzene ring in addition to disulfide bond recombination. It was also found that this reaction pathway occurs predominantly over the bond exchange reaction. MD simulations show that the structure with the reaction pathway we found repairs more disulfide bonds and exhibits higher stress in tensile simulations than the structure with the direct recombination-only repair mechanism.

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