

Recovery of Mechanical Properties in an Epoxy Vitrimer: Molecular Dynamics Simulations and Experimental Measurements

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Abstract - This study investigates the self-healing mechanism in vitrimer materials by integrating molecular dynamics (MD) simulations with experimental methods. We focus on elucidating the self-healing properties of epoxy vitrimers containing disulfide bonds and understanding their underlying mechanisms, aiming to contribute to the design of high-performance materials. MD simulations reproduce the molecular structure of epoxy vitrimers synthesized from tetraglycidyl diaminodiphenylmethane (TGDDM) and 4-aminophenyl disulfide (AFD). Tensile simulations show bond cleavage under external forces, and subsequent simulations demonstrate the recombination of cleaved disulfide bonds, restoring the material's mechanical properties. "Compression and tensile tests conducted after the repair confirmed the recovery of the material's ability to withstand stress. These results highlight the critical role of disulfide bonds in the self-healing process. Double cantilever beam (DCB) tests are experimentally performed to quantitatively evaluate self-healing. The results show a marked recovery of fracture toughness after heating, confirming the self-healing process. These experimental findings align with MD simulation predictions, reinforcing the importance of disulfide bonds in the self-healing behavior.

Keywords: Vitrimer, dynamic covalent bonds, disulfide bonds, molecular dynamics simulations, self-healing, fracture toughness, healing mechanism.

1. Introduction

Carbon fiber-reinforced plastics (CFRPs) are materials that combined a resin matrix with carbon fibers as a reinforcing component. They have gathered significant attention in various industries, particularly the aerospace sector, due to their excellent mechanical properties [1]. The thermosetting resins used in CFRPs form chemical cross-links during the manufacturing process, enabling them to achieve superior mechanical and thermal properties. However, cured resins cannot be reshaped or dissolved, making recycling and repair highly challenging, which poses significant limitations from both practical and environmental perspectives. To address these issues, vitrimers have been developed as a novel material that combines the reprocessability and recyclability of thermoplastic resins with the mechanical properties of thermosetting resins [2][3][4].

Among the various vitrimer systems, epoxy-based vitrimers containing disulfide bonds have attracted particular attention due to their ease of synthesis, the availability of precursors, and many other advantages. Previous studies have shown that disulfide bonds (S-S) promote dynamic bond exchange reactions, which greatly contribute to the exceptional self-healing properties of these materials [5].

From the perspective of molecular dynamics (MD) simulations, the self-healing mechanisms of vitrimers can be investigated at the atomic level by simulating bond breaking and reformation under various conditions. MD simulations enable detailed analysis of how external forces and thermal activation influence dynamics of a covalent bond, providing insights into the recovery of mechanical properties after damage. Furthermore, these simulations highlight the critical roles of bond exchange kinetics and thermal activation in achieving efficient self-healing [6].

The self-healing behavior of vitrimers is evaluated through mechanical testing and fracture toughness measurements before and after damage via DCB testing. Heat treatment is commonly used to activate the bond exchange process and promote material recovery. Experimental results validate the predicted mechanisms and complement MD simulations by quantitatively assessing properties such as fracture toughness recovery and mechanical strength.

This study aimed to elucidate the self-healing properties of epoxy-based vitrimers containing disulfide bonds by integrating MD simulations and experimental research.

2. Methods

2.1. Model Creation

The epoxy vitrimer used in this study was prepared with tetraglycidyl diaminodiphenylmethane (TGDDM) as the base resin and 4-aminophenyl disulfide (AFD) as the curing agent. The structural formulas of TGDDM and AFD are shown in Fig. 1.

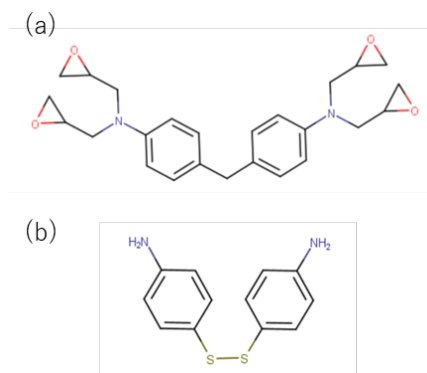


Fig.1: Structure formula of (a) TGDDM, (b)AFD

TGDDM and AFD were mixed in a functional group molar ratio of (AFD: TGDDM = 1:1) and approximately 20,000 particles were evenly distributed in the simulation box. Subsequently, energy relaxation calculations were performed to stabilize the intermolecular interactions ($P=1\text{atm}$, $T=300\text{K}$). Next, a crosslinking reaction was simulated between pairs of molecules where the epoxy group of TGDDM and the amino group of AFD were within $5.0\text{ \AA}$. This process reconstructed the covalent bonds between the epoxy and amino groups. After the crosslinking formation, further energy relaxation was performed, and the equilibrium structure of the epoxy vitrimer was obtained. The resulting thermosetting resin's crosslinked structure is shown in Fig. 2.

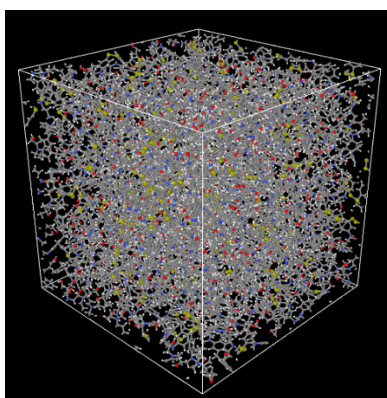


Fig. 2: Structure of thermosetting resin

2.2. Tensile Simulation and Fracture

Uniaxial tensile simulations were performed on the crosslinked structure obtained in Section 2.1 to evaluate its mechanical behaviour under two distinct conditions. In the first condition, a model without bond fracture considerations was utilized, and uniaxial tensile simulation was conducted under a strain rate of 5×10^8 . In the second condition, a model incorporating bond fracture mechanisms specific to disulfide bonds, C–C bonds (excluding those within aromatic rings),

C–N bonds, and C–O bonds was employed to simulate the degradation behavior at the same strain rate as the first condition. This bond fracture algorithm was designed to model the breaking of disulfide bonds when their length extended to 1.1 times the equilibrium bond length, thereby capturing the failure process under tensile loading [7].

2.3. Repair

Following the compression of the crosslinked network containing fractured disulfide bonds, as described in Section 2.2, the deformed structure was reverted to its original simulation box dimensions. The repair process was subsequently modeled using a two-step approach.

In the first step, a bond reformation algorithm specifically targeting disulfide bonds was implemented. This algorithm allowed for the dynamic reconnection of previously cleaved disulfide linkages based on spatial proximity and bonding criteria. To facilitate relaxation of the system and promote the formation of new crosslinks, energy minimization followed by molecular dynamics simulations were conducted under isothermal conditions. The simulation was run for 1 nanosecond to monitor the progression of the repair and to evaluate the structural recovery of the polymer network.

2.4. Mechanical Characterization After Repair

To assess the mechanical performance of the repaired vitrimer network, a uniaxial tensile simulation was performed after the disulfide bonds had been reformed, as described in Section 2.3. This tensile test employed the same conditions and strain rate as in the original deformation simulation in Section 2.2, allowing for direct comparison of mechanical properties before damage and after repair.

The simulation involved elongation of the restored system along the z-axis under periodic boundary conditions, with temperature held constant to isolate the effects of network reconstruction. The resulting stress–strain response was analyzed to determine the extent of mechanical recovery.

The post-repair tensile behavior exhibited a significant restoration of stiffness and tensile strength relative to the damaged state. In particular, the initial linear region of the stress–strain curve closely resembled that of the pristine sample, indicating effective re-establishment of the network structure through disulfide bond exchange. These findings confirm the material's inherent self-healing capability and its potential for use in applications requiring both structural integrity and reparability.

2.4. Fabrication of Specimens and DCB Testing

After preparing the epoxy polymer with disulfide bonds as shown in Fig. 3, a release film (polyimide film) of approximately 30 mm in length was inserted to introduce a pre-crack, and the material was heat-pressed for 1 hour.

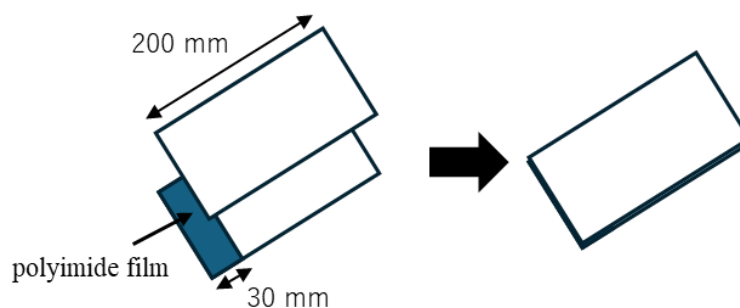


Fig. 3: Fabrication of Epoxy polymer containing vitrimers

Subsequently, the resulting material was cut into specimens of 200 mm in length, 2 mm in width, and 4 mm in thickness using a diamond cutter. The jig was fitted to the specimen, and a DCB test was conducted as shown in Fig. 4.

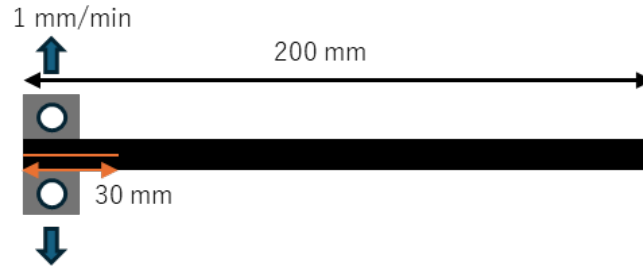


Fig. 4: Schematic diagram of DCB

The testing machine used was a SHIMADZU EZ-X, and the loading rate was set to 1 mm/min. The double cantilever beam (DCB) specimens were subjected to a stepwise loading-unloading procedure. Specifically, the opening displacement was increased incrementally to predetermined values—3.0 mm, 3.5 mm, 4.0 mm, 4.5 mm, and 5.0 mm. At each step, loading was paused once the target displacement was reached, followed by unloading at a rate of 25 mm/min. This procedure was repeated for each displacement increment to observe the crack propagation behavior at discrete stages.

For fractured specimens, thermal pressing was performed again to activate the self-healing mechanism. The same DCB testing protocol was then applied to evaluate the healing performance.

3. Result and Discussion

3.1. Molecular Dynamics (MD) simulation

In this study, tensile analysis was performed on the constructed structures under three different simulation conditions: (1) tensile testing without considering bond fracture. (2) tensile testing with fracture criteria introduced, and (3) tensile testing after recombining the fractured disulfide bonds.

First, tensile simulations were conducted on the structures under conditions (1) and (2), and the resulting stress-strain diagrams are shown in Figure 5.

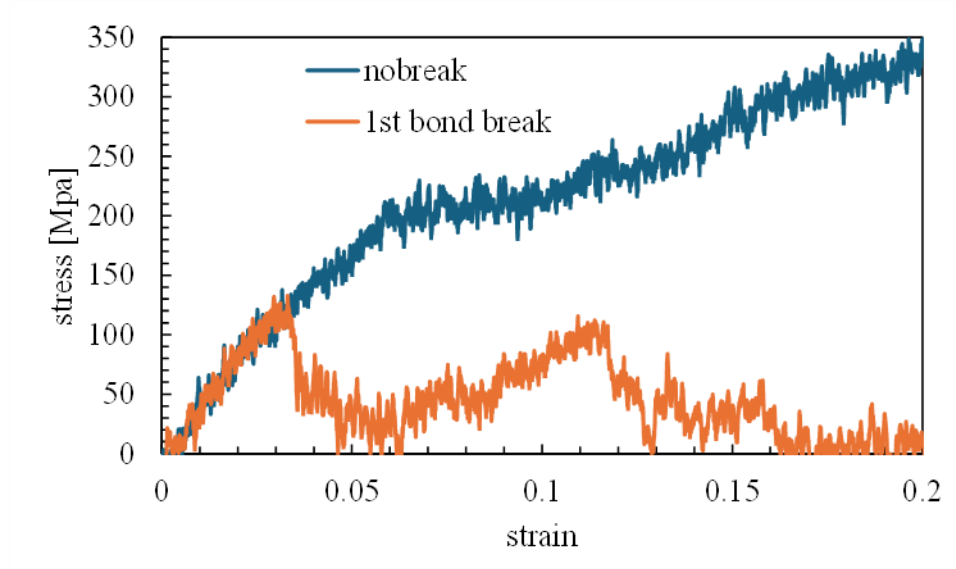


Fig. 5: under conditions (1) and (2), stress-strain diagrams

This figure shows that under condition (2), the stress rapidly decreases at a strain of 0.02 due to the fracture of the disulfide bonds. Next, the fractured disulfide bonds were recombined. The number of SS bonds prior to fracture, the number

of disulfide bonds fractured under tensile testing with the introduced fracture criteria, and the number of disulfide bonds recombined after fracture are presented in Table 1.

Table. 1: Number of disulfide bond repairs by reaction		
SS bonds before fracture	Broken SS bonds	Recombination SS bonds
216	87	52

It was confirmed that approximately 60 % of the fractured disulfide bonds were restored. Subsequently, tensile simulations were conducted on the recombined structure, and the resulting stress-strain diagram is shown below. For comparison, tensile simulations under condition (2) are also included.

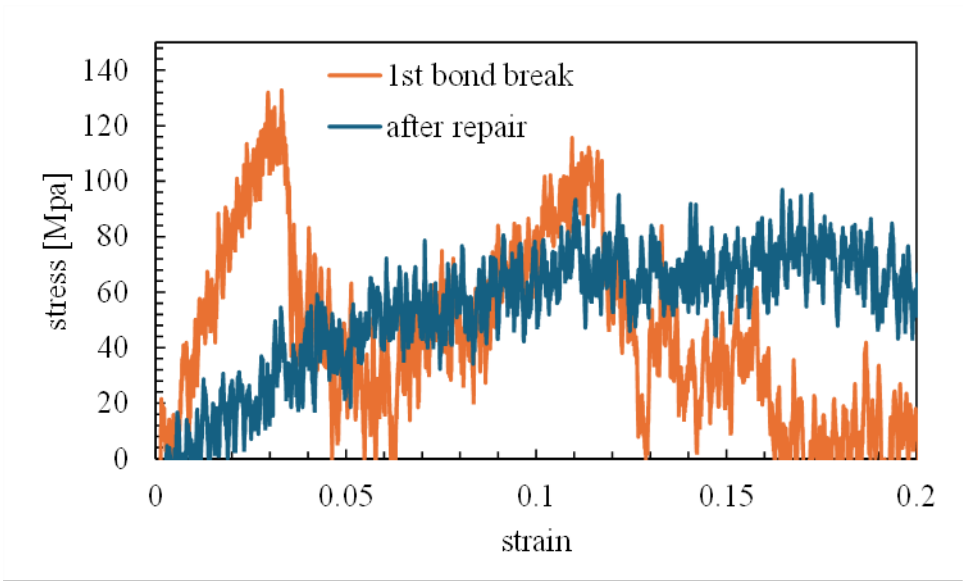


Fig. 6: (2) and (3), stress-strain diagrams

From Figure 6, it was confirmed that the structure recovered stress compared to the degraded structure due to the recombination of disulfide bonds. This result suggests that the recombination of disulfide bonds contributes to the recovery of mechanical properties.

3.2. DCB Testing

In this study, specimens fabricated through heat pressing were subjected to DCB testing, followed by repeated heat pressing and fracture tests. Figure 7 illustrates the opening displacement-load curve obtained from the DCB test.

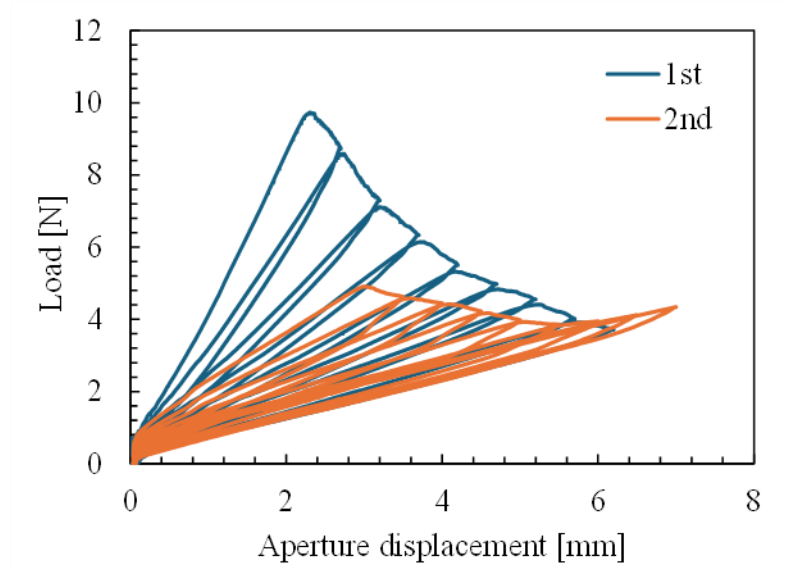


Fig. 7: Opening Displacement-Lord Diagram

The results in Figure 7 show that the maximum load for the first fracture was 10 N, while the maximum load for the second fracture was 5 N. Based on these results, the modified compliance calibration method was employed to calculate the fracture toughness (G_{1c}). In this method, the following equations (1) and (2) hold [8].

$$\frac{a}{2h} = \alpha (bC^{app})^{\frac{1}{3}} + \beta. \quad (1)$$

$$G_{1c} = \frac{3}{2(2h)} \left(\frac{P_y}{b} \right)^2 \frac{\sqrt[3]{(bC^{app})^2}}{\alpha}. \quad (2)$$

Here, a represents the crack length, h is the specimen thickness, b is the specimen width, δ is the opening displacement, P_y is the load, and C_{app} is the compliance. The relationship between crack length and fracture toughness, calculated using these equations, is shown in Figure 8.

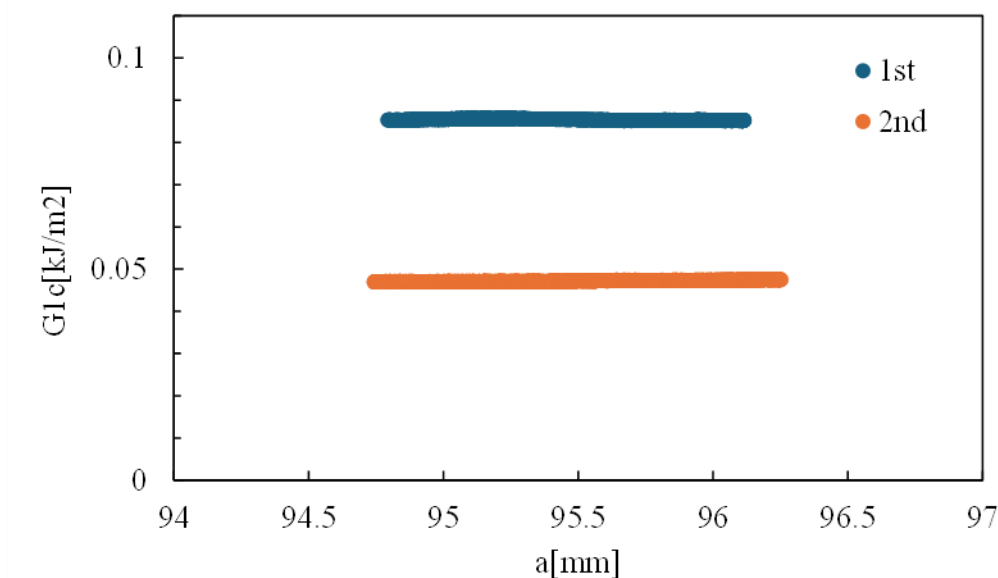


Fig. 8: R-curves obtained by DCB test

From the data in Figure 8, it was confirmed that the fracture toughness values, as indicated by the disulfide bonds reformed through heat pressing, were 0.0855 kJ/m² for the first fracture and 0.0473 kJ/m² for the second fracture. This suggests that the dynamic covalent disulfide bonds reformed during the heat pressing process, leading to the bonding of the specimen.

4. Conclusion

In this study, we elucidated the self-healing mechanisms in epoxy vitrimer materials by combining MD simulations with experimental approaches. MD simulations reproduced the behavior of disulfide bond cleavage under external forces and demonstrated their reformation through thermal treatment and energy relaxation processes, confirming the recovery of mechanical properties. Experimentally, DCB tests revealed significant recovery of fracture toughness after heat treatment, highlighting the critical role of disulfide bonds in the self-healing process. Furthermore, the agreement between MD simulation predictions and experimental results validated the fundamental mechanisms of self-healing in epoxy vitrimer systems.

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