

Stability Analysis of the Interface between Thermosetting and Thermoplastic Polymers Using Molecular Dynamics Simulations

Ryogo Konomi¹, Yutaka Oya², Naoki Yamada³, Maruri Takamura⁴, Jun Koyanagi⁵

¹Department of Materials Science and Technology, Graduate School of Advanced Engineering,
Tokyo University of Science

6-3-1 Nijjuku, Katsushika-ku, Tokyo 125-8585, Japan

First.8224509@ed.tus.ac.jp; Third.oya@rs.tus.ac.jp; Fourth.koyanagi@rs.tus.ac.jp

Abstract – In this Study, the interfacial energy between thermosetting and thermoplastic resins was evaluated using molecular dynamics (MD) simulations. The thermosetting resin used in this study was diglyceryl ether of bisphenol A (DGEBA), with 4,4'-diaminodiphenyl sulfones the curing agent. For thermoplastic resins, polyether ether ketone (PEEK) and polyphenylene sulphide (PPS) were selected. Two distinct interfacial structures were created by combining to the cured product of DGEBA and 4,4'-DDS with each of these thermoplastic resins. The origin of interfacial stability was investigated by analyzing the contributions of the Lennard-Jones potential and Coulombic energy to the total interfacial energy. As a result, it was determined that the interface of the DGEBA-PPS interfacial structure is more stable. It the knowledge of this research are expected to provide valuable insights into optimizing interfacial properties and guide the design of high-performance CFRP with enhanced interfacial bonding.

1. Introduction

Carbon Fiber Reinforced Plastics (CFRP) are widely utilized across various industries, including aerospace, automotive, and sports equipment, due to their exceptional specific strength, superior mechanical properties, and high design flexibility [1]. The resins used in CFRP are primarily classified into thermosetting and thermoplastic resins, each possessing distinct characteristics.

Thermosetting resins undergo a chemical curing process, forming a three-dimensional cross-linked structure. This structure imparts high rigidity, excellent heat resistance, and superior chemical resistance [2]. However, these resins cannot be reprocessed, limiting their recyclability and adaptability. In contrast, thermoplastic resins exhibit reversible behavior, softening upon heating and solidifying upon cooling. This reprocessability provides greater flexibility in manufacturing and design [3].

Achieving interfacial adhesion between thermosetting and thermoplastic resins is critical for integrating their complementary properties and enhancing the performance of CFRP. Such adhesion enables the development of composite materials that combine the rigidity and thermal stability of thermosetting resins with the flexibility and reprocessability of thermoplastic resins. However, achieving strong interfacial adhesion between these two types of resins poses significant challenges due to fundamental differences in their chemical interactions, insufficient molecular contact at the interface, and mismatches in physical and mechanical properties. For instance, while ultrasonic welding experiments have been conducted to bond thermoplastic and thermosetting resins, the establishment of such adhesion at the nanoscale or atomic level remains underexplored.

Addressing these challenges requires a deeper understanding of molecular-level behavior at the interface. Molecular dynamics (MD) simulations offer a powerful approach for analyzing such nanoscale behavior. This computational method treats atoms and molecules as particles and calculates their dynamic behavior by numerically solving Newton's equations of motion based on interatomic forces. MD simulations provide unique advantages, such as the ability to analyze interfacial phenomena that are difficult to observe experimentally and to reduce time and cost compared to traditional experimental methods [4] [5].

The primary objective of this study is to evaluate the adhesive properties of the interfacial structure between thermosetting and thermoplastic resins using molecular dynamics simulations. As a key metric, the interfacial energy, a critical factor in determining the mechanical strength of composite materials, is calculated. Interfacial energy serves as an essential indicator for assessing the stability and adhesive strength of the interface. By analyzing the calculated interfacial energy values, this study aims to elucidate the mechanisms of interfacial adhesion between thermosetting and thermoplastic resins. Furthermore,

the findings of this research are expected to provide valuable insights into optimizing interfacial properties and guide the design of high-performance CFRP with enhanced interfacial bonding.

2. Method

2.1. Modelling

In this study, the structural modelling was performed using the Winmostar software [6]. The thermosetting resin model was created using DGEBA and curing agent, 4,4'-DDS, with a ratio of DGEBA:4,4'-DDS = 2:1. The cross-linked structure of DGEBA + 4,4'-DDS will hereinafter be referred to simply as DGEBA. For thermoplastic resins, PEEK and PPS selected. DGEBA+4,4'-DDS has relatively higher mechanical properties than other thermosets, is more stable to reactions, and is widely used. The degree of polymerization was set to 50 for PEEK and 150 for PPS, ensuring that the molecular chain lengths of both resins were comparable. Figures 1 and 2 show the structure of the thermosetting resin and the two thermoplastic resins.

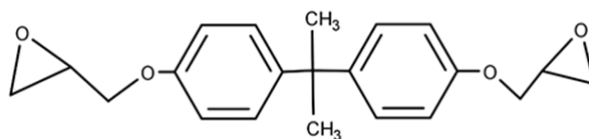


Fig.1 (a) Structure of DGEBA in base resins

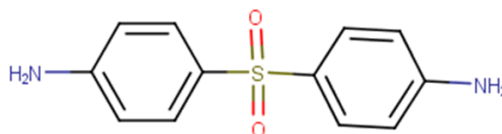


Fig.1 (b) Structure of 4,4'-DDS in thermosetting resins about the curing agent for DGEBA

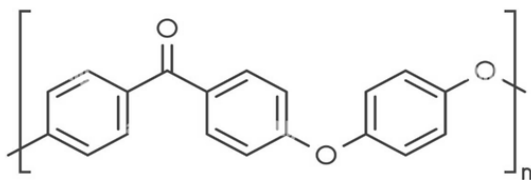


Fig.2 (a) Structure of PEEK in thermoplastic resins

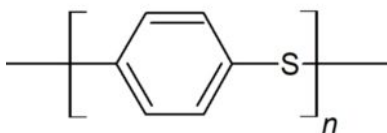


Fig.2 (b) Structure of PPS in thermoplastic resins

2.2. Simulation Method

Simulations were performed using LAMMPS [7]. The structures of both the thermosetting resin and the thermoplastic resin were equilibrated by performing shrinkage and increasing the density using the NVT ensemble. The NVT ensemble, also known

as the canonical ensemble, is a statistical mechanics framework where the number of particles (N), volume (V), and temperature (T) are kept constant. In molecular dynamics simulations, it is implemented using a thermostat to control the system's temperature, allowing the study of thermodynamic properties under constant thermal conditions. The temperature was maintained at a constant 300 K during this process. Next, the structures were equilibrated, and energy stabilization was achieved using the NPT ensemble, with the temperature kept constant at 300 K for relaxation. The NPT ensemble, or isothermal-isobaric ensemble, is a statistical mechanics framework where the number of particles (N), pressure (P), and temperature (T) are kept constant. In molecular dynamics simulations, it is implemented using a thermostat and a barista to control temperature and pressure, enabling the study of systems under realistic experimental conditions such as constant atmospheric pressure.

Next, the interface structure was constructed by combining the uncrosslinked DGEBA+4,4'-DDS model with thermoplastic resin models (PEEK and PPS). After the interface structure was constructed, the mixed structure of DGEBA and 4,4'-DDS was fixed, and the thermoplastic resin was relaxed to increase its density. Next, a chemical reaction of the mixed model of DGEBA+4,4'-DDS was performed to obtain a cross-linked network structure. Then, the entire structures of the thermosetting and thermoplastic resins with crosslinked networks were relaxed to obtain their equilibrium state. The base resin and curing agent are connected through synthesis, and the amine group in the curing agent. The successive reactions produce a cross-linked structure of thermosetting resin[8]. Finally, the interfacial energy was calculated from the interfacial structures of the two equilibrium structures.

In detail, the interfacial energy was calculated by subtracting the sum of the potential energies of each resin from the total potential energy E_{total} and then dividing by the cross-sectional area multiplied by 2. The multiplication by 2 accounts for the fact that there are two surfaces in contact at the interface. The following equation (1) was used to calculate the interfacial energy.

$$E_{interaction} = \frac{E_{total} - (E_{thermosetting\ resin} + E_{thermoplastic\ resin})}{2A} \quad (1)$$

$E_{interaction}$ represents the interfacial energy, E_{total} is the energy of the interfacial structure, $E_{thermosetting}$ is the energy of DGEBA, E_{PEEK} is the energy of PEEK, and A is the cross-sectional area.

3. Result and Discussion

3.1. Interfacial energy

First, the two types of interfacial structures, DGEBA-PEEK and DGEBA-PPS, were created, as shown in Figures 5 and 6. The interfacial energy was calculated based on these interfacial structures.

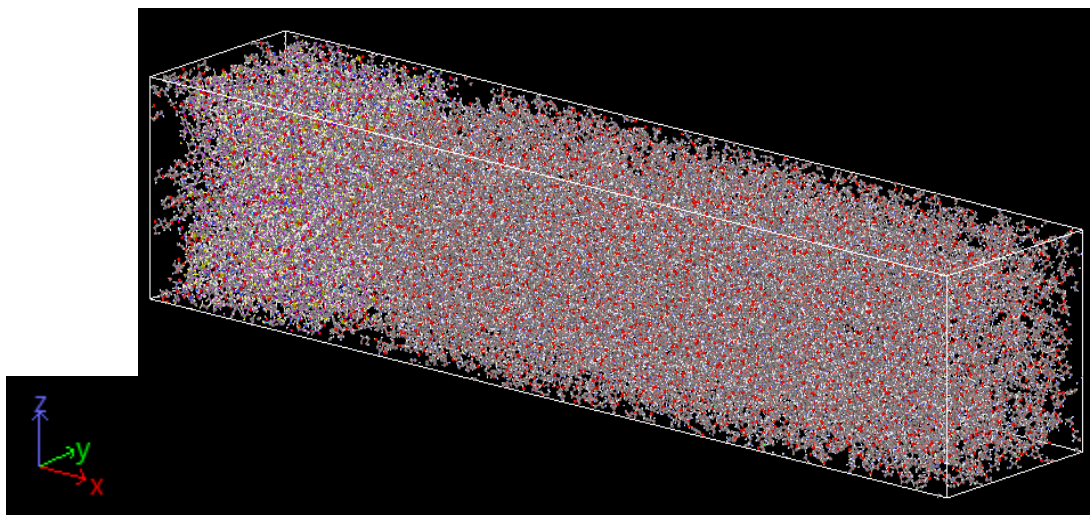


Fig.5 Interfacial structure of DGEBA-PEEK

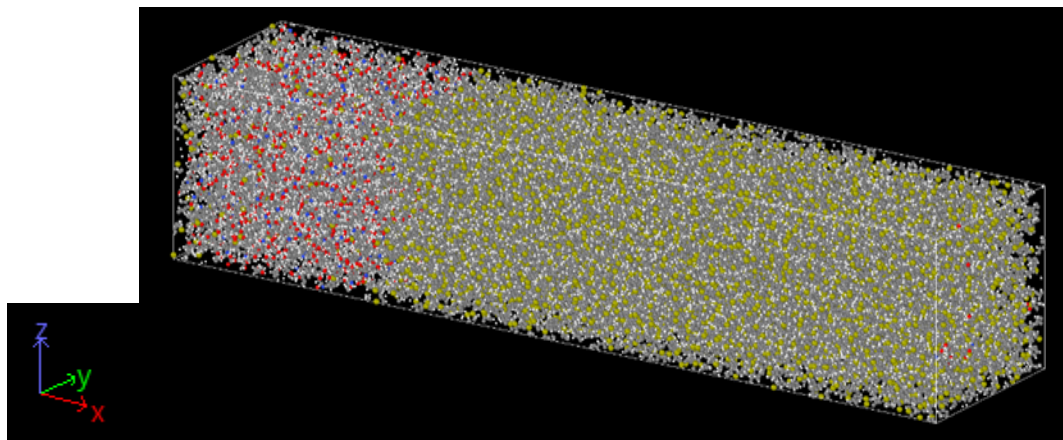


Fig.6 Interfacial structure of DGEBA-PPS

Next, Table 1 shows the interfacial energies for DGEBA-PEEK and DGEBA-PPS, respectively.

Table 1: Comparison of interfacial energies for each interfacial structure

Types of resins	DGEBA-PEEK	DGEBA-PPS
Interface energy (J/m ²)	-0.155	-0.081

A negative overall interfacial energy indicates interfacial adsorption. Furthermore, a large the absolute value of the interfacial energy, the stronger the interfacial adhesion. Based on the results, the interfacial energy of DGEBA-PPS exhibits, a greater absolute value compared to that of DGEBA-PEEK. This indicates that the interfacial stability of thermosetting resin DGEBA is higher when bonded with PPS (DGEBA-PPS).

3.2. Potential energy analyzed

The interfacial energy is obtained by summing the Lennard-Jones Potential and the Coulomb Potential. Therefore, in addition to comparing the whole interfacial energy, it is also important to compare the potential energy contributions in order to clarify a mechanism for the interfacial stability at the interface. Figures 7 and 8 show a comparison of the LJ and Coulomb potentials of DGEBA-PEEK and DGEBA-PPS at each interface structure.

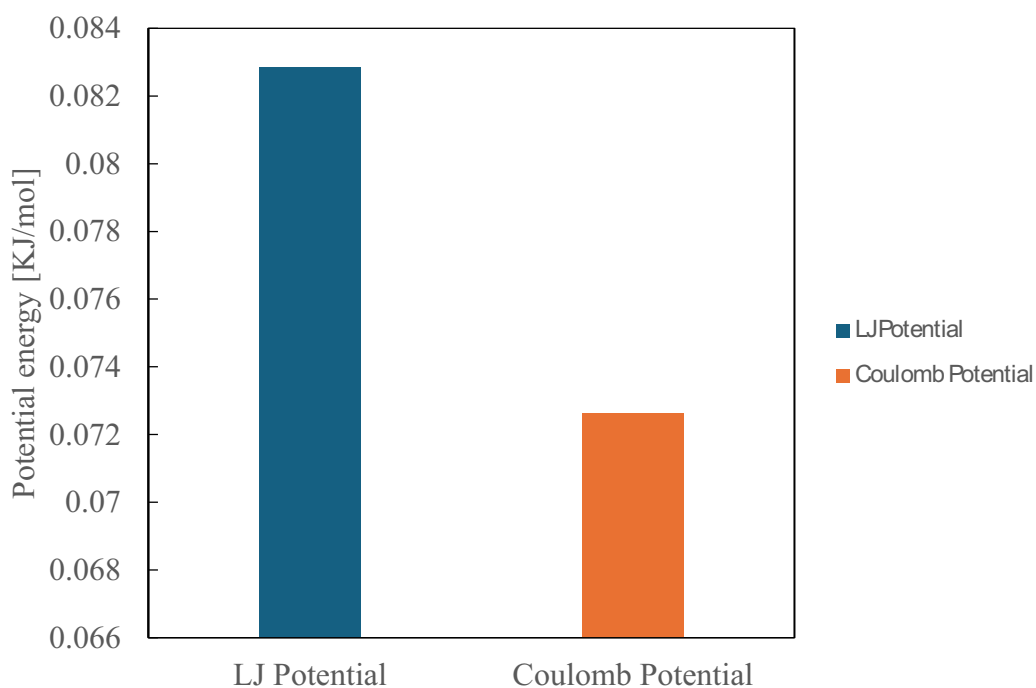


Fig7. Comparison of LJ Potential and Coulomb Potential in DGEBA-PEEK

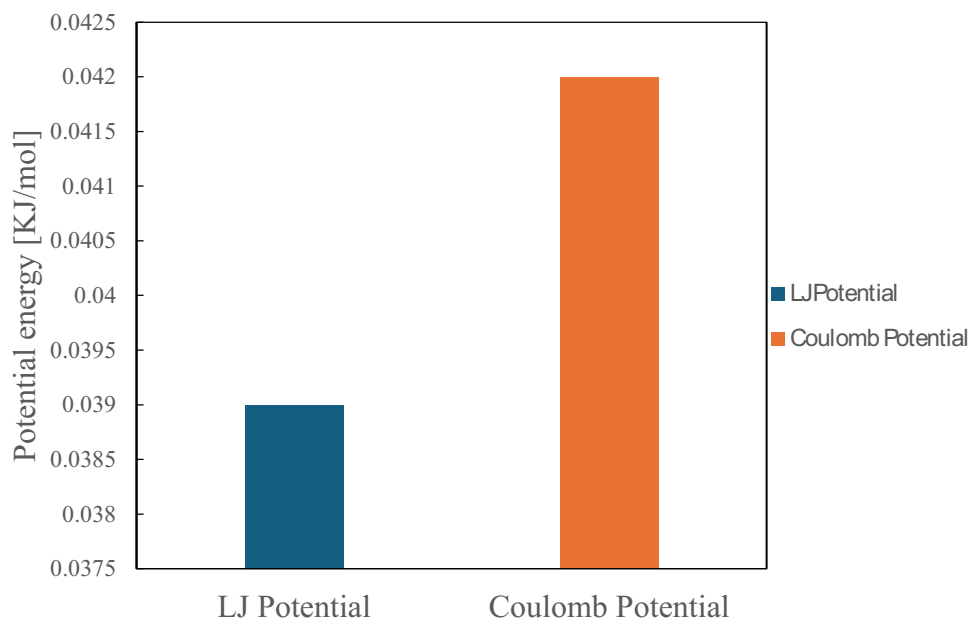


Fig8. Comparison of LJ Potential and Coulomb Potential in DGEBA-PEEK

Comparison of the potentials at the two interfacial structures shows that the LJ Potential is larger in DGEBA-PEEK. This is thought to be due to the fact that both DGEBA and PEEK have aromatic rings, and the stabilization by LJ is stronger

due to π - π stacking. In addition, the electronegativity of sulfur in PPS is lower than that of oxygen in PEEK, so the Coulomb Potential interaction is thought to be larger due to the local charge distribution.

4. Conclusion and Future Perspectives

In this study, the interfacial energy between thermosetting polymer and the thermoplastic resins PEEK and PPS were calculated using molecular dynamics (MD) simulations. By comparing the interfacial energy values, it was determined that the DGEBA-PPS interface exhibits higher interfacial stability and is more suitable for interfacial adhesion.

Given the limited research on interfacial adhesion between thermosetting and thermoplastic resins using molecular dynamics (MD) simulations, future studies should aim to expand and explore more thermoset and thermoplastic resin combinations. By varying interfacial adhesion patterns, it will be possible to conduct more comprehensive comparisons of interfacial behaviours across a wider dataset. Such efforts will contribute to a deeper understanding of the interfacial phenomena and provide valuable insights for optimizing composite material design.

5. References

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