Technical Report

Development of Practical Optimal Design and Comprehensive Evaluation Support Tool for Advanced Structural Polymer Materials

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Abstract

In this study, we developed the practical optimal design and comprehensive evaluation support tool for advanced structural polymer materials. The relationships between molecular structures and the mechanical performance of structural thermosetting polymers were examined by using this tool. The molecular structures of epoxy polymers are calculated using molecular dynamics (MD) simulations, and a database of the simulation results is constructed using an advanced mathematical method. The database can provide the relationships between the molecular structures and material heterogeneities that affect the mechanical performance of the materials.

1. Introduction

In order to improve the mechanical properties of resins, which generally have low elastic modulus and high thermal expansion properties compared to other materials such as metals and ceramics, a method of compounding a filler or reinforcing material with high elastic modulus and low thermal expansion properties into the matrix resin is widely used. A representative example of a composite material is a carbon fiber-reinforced plastic (CFRP), which is used as a primary structural member of aircraft. The physical properties and functions of composite materials depend on the physical properties of the resin matrix and reinforcing material, as well as the state of their interfaces.

In this study, we focused on the epoxy resin matrix and the filler interface. We developed a practical optimal design and comprehensive evaluation support tool for structural polymer materials that provides design guidelines for materials with high compressive elasticity, strength, and toughness, as well as guidelines for achieving the maximum properties of resins during high-speed molding.

2. Materials Integration

In the development of practical materials, it is useful to know the performance of materials and the time dependence of material performance in a short time, and the tool that makes this possible is materials integration. Materials integration is defined as a comprehensive materials technology tool that aims to support materials research and development from an engineering perspective by encompassing theory, experiments, analysis, simulation, databases, and practical experience to utilize the results of materials science and the latest ideas.

As **Fig. 1** shows, materials integration for polymeric materials is a tool that helps solve problems during research and development by taking a bird's-eye view while structuring a database to enable a unified understanding of the properties of polymeric materials at various spatial and temporal scales, and by leveraging a wide range of scientific and technological knowledge, including simulations, analytical formulas, and empirical equations. A novel mathematical database facilitates data exchange across different length and time scales. In addition, a number of parameters with physical meanings are used in the exchange. This enables the pseudo-inverse problem, allowing for the optimization of process conditions and material structures based on desired performance. Based on the concept of materials integration, we have developed a practical tool that sup-

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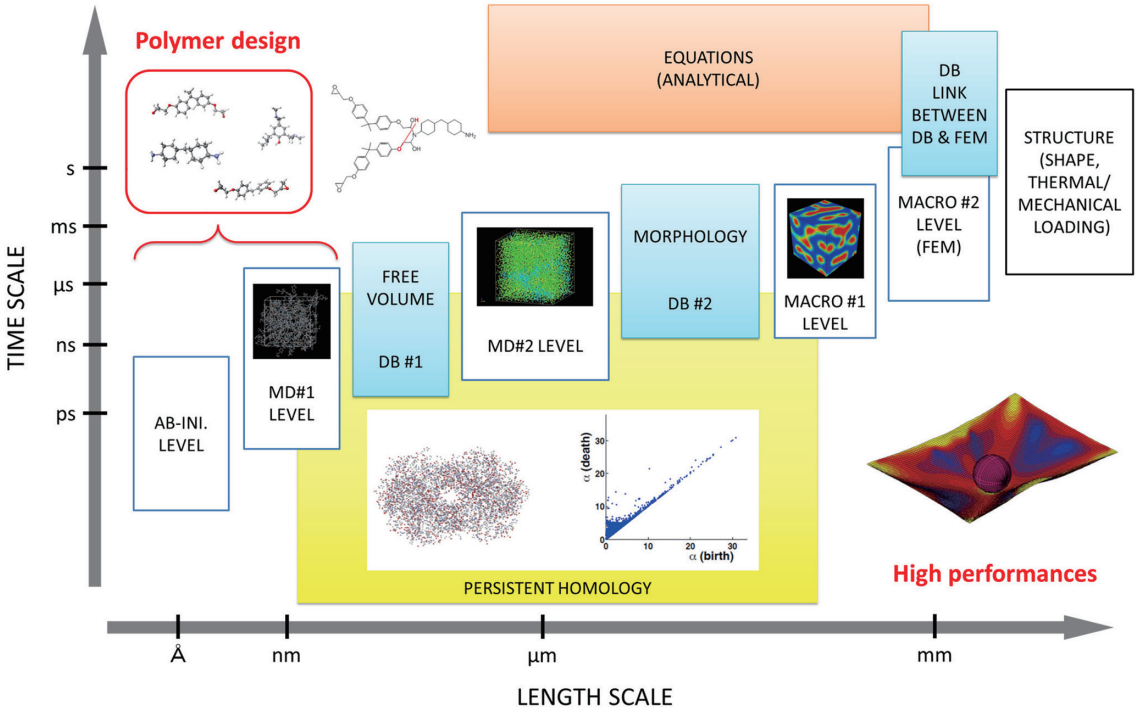

Fig. 1 Conceptual diagram of materials integration for polymer

ports optimal design and comprehensive evaluation by combining analytical and simulation technologies to achieve optimum performance under service conditions and environments for polymeric composite materials.

3. Overview of Developed Tools and Main Findings

3.1 Overview of developed tools

In this study, we are working on the development of a simulation module for the structure of the resin matrix of the CFRP and the curing reaction at the interface layer, leading to the development of technology (including process technology) that can fully utilize the covalent bonding capabilities of polymer materials. In developing a practical "design and evaluation tool for structural polymer materials," approaches relying on individual techniques like experiments, measurements, and simulations had limitations. Therefore, we adopted a novel approach, unconstrained by conventional thinking. This involved integrating diverse methodologies from fields such as chemistry, mathematics, materials science, physics, mechanical engineering, drug discovery, and measurement to achieve a breakthrough. These technologies are combined to develop a unique set of practical modules in which measurements and simulations are fused through mathematics at each scale, as shown in Fig. 1.

Focusing on epoxy-based structural polymer materials, we have produced model cured products of epoxy-based thermosetting resins and performed various mechanical property evaluation tests, free volume measurement by positron annihilation spectroscopy (PAS),[1] nanoindentation AFM analysis, and molecular dynamics (MD) analysis[2–4] to clarify the relationship between their molecular structure and mechanical properties. We have performed persistent homology analysis[5] on the results of these measurements and analyses to quantify the heterogeneity of the materials, compiled them into a database, and are considering applications to various inverse problems. The parameterized heterogeneity is reflected in macroscopic property parameters, establishing a link to mechanical frameworks relevant to structural materials, such as fracture mechanics and damage mechanics. This has resulted in a practical polymer material design and evaluation tool comprising a suite of modules capable of correlating spatial and temporal scales.

3.2 Main findings

3.2.1 Microscale (to nm)

The reaction process where three-dimensional crosslinks are formed during the curing reaction of epoxy resins, etc., is extremely challenging to analyze directly, unlike the reaction process of thermoplastic resins, as the entire system undergoes macrogelation, becoming insoluble and infusible. Therefore, a simulation approach is essential. We thus first completed a simulation module for the curing reaction process using the all-atom molecular dynamics method (MD#1), as shown in **Fig. 2**. In the figure, the yellow area represents the free-volume space where no atoms or molecules exist. The simulation results revealed that as curing progresses, the resin network forms a three-dimensional distorted structure, with the interstitial spaces constituting the free volume. After curing, the free volume space is surrounded by crosslinking points that are generated as the reaction proceeds. **Figure 3** shows the relationship between the curing conversion rate and the free volume fraction. **Figure 4** shows a snapshot of the distribution of the free volume space at a conversion rate of 89%. The free volume space increases as the reaction progresses, and the increase rate of the free volume fraction at a conversion rate of 20% to 89% is 23%. PAS measurements showed a similar trend, with the average free volume size in an 89% conversion sample being 20% greater than in a 14% conversion sample. **Figure 5** shows the frequency distribution of inscribed spheres virtually filling the free volume (cavity diameters) shown in Fig. 4, compared to that in the uncured state (at a conversion rate of 0%). While the overall size distribution pattern remained similar after

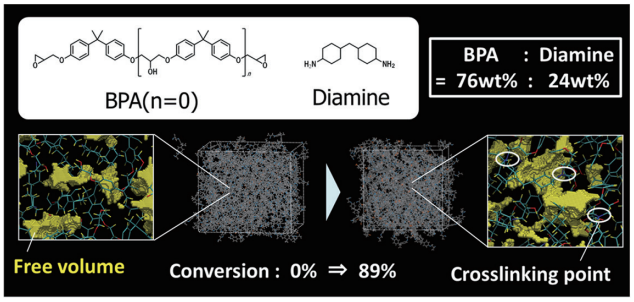

Fig. 2 Full atom molecular dynamics (MD#1) analysis

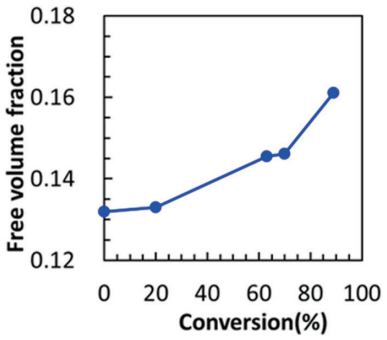

Fig. 3 Free volume fraction vs. conversion by MD#1

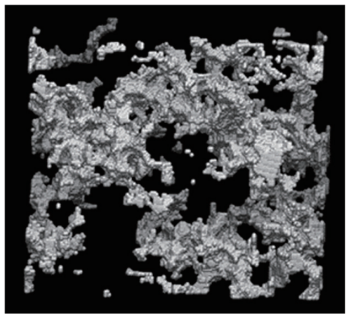

Fig. 4 Distribution of free volume at 89% conversion by MD#1

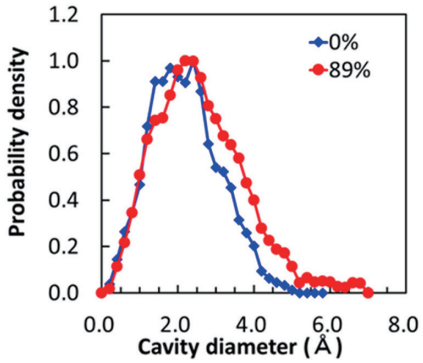

Fig. 5 Distribution of free volume size by MD#1

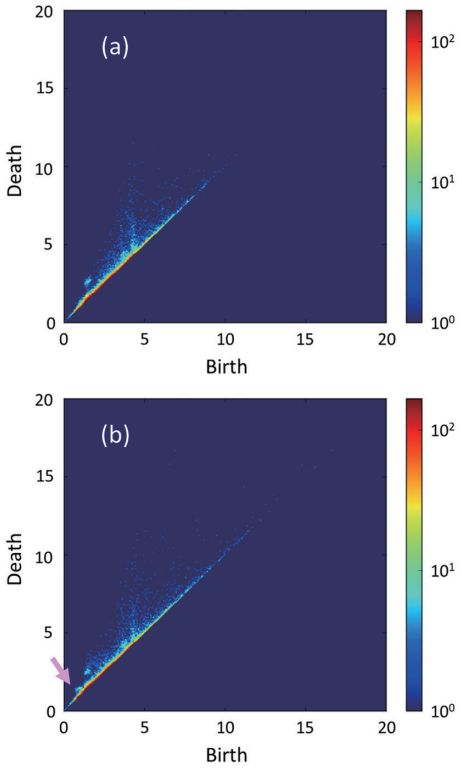

Fig. 6 2-dimensional persistence diagrams of (a) 0% and (b) 89% conversion epoxy resin by MD#1 results

curing, the absolute size of the free volume spaces increased. The average size of the inscribed spheres was also compared with the results of the free volume measurement by PAS, and the increase in the average size of the inscribed spheres showed good quantitative agreement.

By applying persistent homology[5] (PH), a topological data analysis method, to the molecular structure results from the all-atom MD analysis (MD#1), the heterogeneity at the molecular level was quantitatively analyzed.[6] PH is a topological data analysis technique capable of quantitatively extracting structural information about voids, such as rings and cavities contained in a structure.[7,8] **Figure 6** shows an example of a 2-dimensional persistence diagram in which PH was applied only to oxygen and hydrogen atoms in the all-atom MD analysis (MD#1) results at curing conversion rates of 0% and 89%. The persistence diagram shows an expansion of the plot range near the diagonal and the emergence of a new cluster of plots (indicated by the red arrow) as a result of the curing reaction. These observations suggest the increase in the free volume space size (Fig. 5) and the formation of new microvoids due to molecular distortion near the crosslinking points (Fig. 2). Free volume information from these MD analyses is stored in a database (DB#1) using this persistence diagram format.

3.2.2 Mesoscale (nm to μm)

In order to practically simulate the structure of the resin matrix in CFRP or the interface between the resin matrix and filler, we established a simulation technology platform (MD#2) based on the user-friendly coarse-grained molecular dynamics (CGMD) method, capable of accurately handling mesoscale phenomena while minimizing computational costs. **Figure 7** shows coarse-grained models. The coarse-grained models are built by considering the state of distortion of the structure obtained by the all-atom MD (MD#1) analysis. **Figure 8** shows a snapshot of an enlarged view of the reaction site after the curing reaction. A red line in the figure indicates the reaction site. Prior to examining the mechanical properties through CGMD analysis, we validated the CGMD model. The glass transi-

tion temperature (Tg) was calculated for various curing conversion rates and compared with experimental data. The obtained results are shown in **Fig. 9**. While discrepancies were observed below a 20% curing conversion rate, possibly due to structural instability, the CGMD model showed good agreement with experimental Tg values above 40%, indicating its thermodynamic stability. **Figure 10** shows the results of the simulation of the uniaxial tensile and compression tests by the CGMD model. **Figure 11** shows the results of the uniaxial tensile test. Comparison showed good agreement between simulation and experimental results. This suggests that the CGMD model can predict macroscopic mechanical properties with sufficient practical accuracy, taking into account the influence of molecular structure. **Figure 12** shows the results of the elastic modulus distribution of the respective samples obtained by nano-palpation AFM analysis. The sample with a 60% conversion rate, which exhibited the highest toughness in Fig. 11, displayed an elastic modulus distribution close to a normal distribution (Fig. 12). A correlation was observed between toughness and the randomness of the elastic modulus distribution.

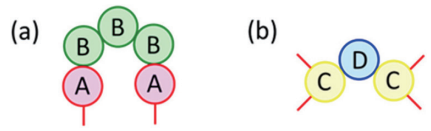

Fig. 7 Coarse-grained model of (a) Bisphenol A type epoxy resin (BPA) and (b) diamine

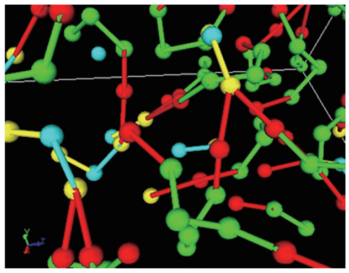

Fig. 8 Snapshot of CGMD (MD#2) analysis

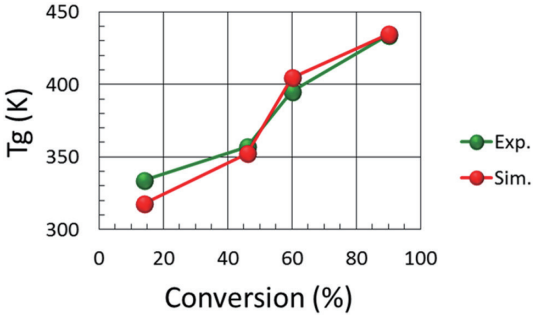

Fig. 9 Comparison of CGMD (MD#2) simulation and experiment with respect to glass transition temperature (Tg)

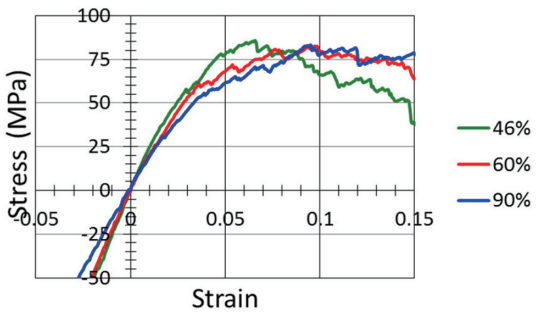

Fig. 10 Simulation results using CGMD (MD#2) simulating the uniaxial tensile and compression test

3.2.3 Macroscale (μm and up)

The molding conditions were studied by the resin transfer molding (RTM) simulation shown in **Fig. 13**. A multiscale simulation framework, hierarchically integrating CGMD and the finite element method (FEM), was developed. This framework enables the prediction of key parameters for the actual RTM molding process, such as mold temperature, injection time, and viscosity changes. Furthermore, it facilitates the examination of the molded CFRP's phase structure (morphology) and its impact on performance. This simulation framework allows for the analysis of tensile and compressive properties of polymer materials, considering the phase structure af-

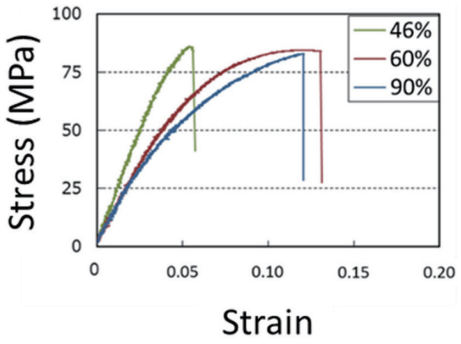

Fig. 11 Results of uniaxial tensile test

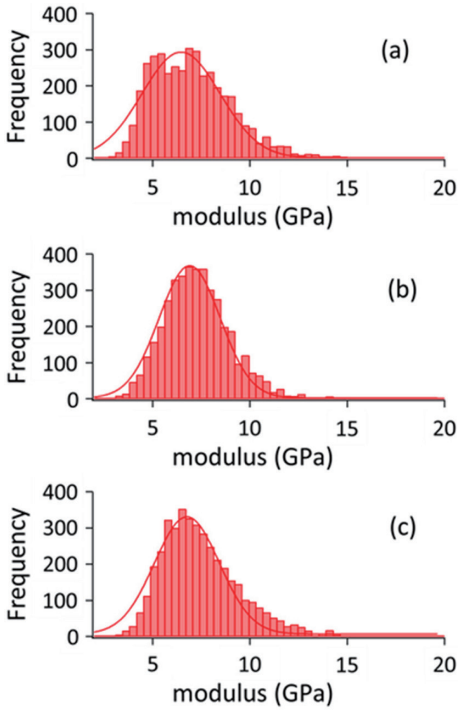

Fig. 12 Nano palpation AFM analysis results at conversion: (a) 46%, (b) 60%, (c) 90%

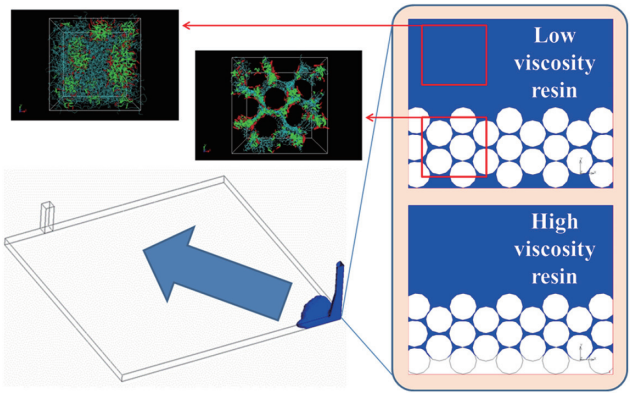

Fig. 13 Example of RTM process simulation

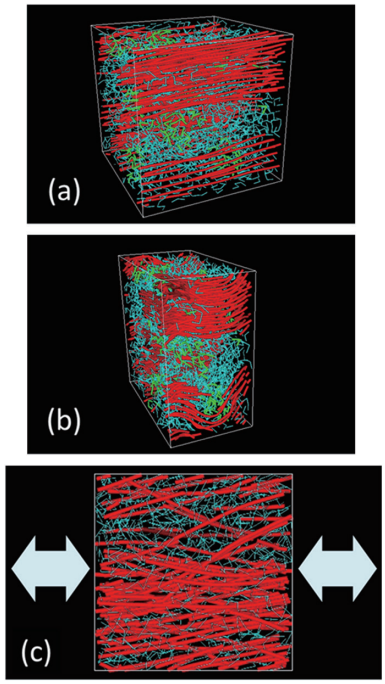

Fig. 14 Example of CGMD (MD#2) model of CFRP (a) before deformation, (b) after compressive deformation, (c) vibration

ter curing and molding. It also enables the relatively straightforward analysis of complex yet practically important behaviors of CFRP, such as compressive deformation and vibration damping. **Figure 14** shows an example of the CGMD (MD#2) model. In the figure, the carbon fibers are displayed in red, and the matrix resin is displayed in blue and green. In Fig. 14(b), the complex local buckling deformation of the carbon fibers under compressive deformation can be seen. **Figure 15** shows an example of the results of a uniaxial compressive deformation simulation of the CFRP using CGMD (MD#2). The figure shows that after the initial buckling deformation, which corresponds to the first compressive stress peak, the stress gradually decreases through subsequent minor local buckling events. **Figure 16** shows an example of the results of a vibration simulation of uniaxial tension and compression of the CFRP using CGMD (MD#2). The plot shows a hysteresis curve indicative of viscoelastic behavior. These CGMD analysis techniques have been further developed into research connecting vehicle macroscale characteristics to material microscale properties[9] and are being implemented as practical

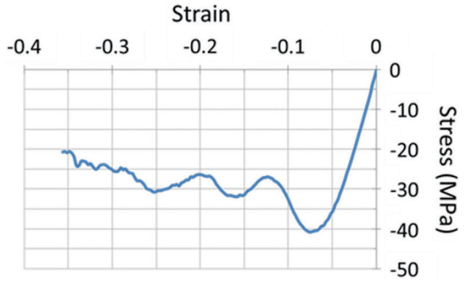

Fig. 15 Example of CFRP compression deformation simulation results using CGMD (MD#2)

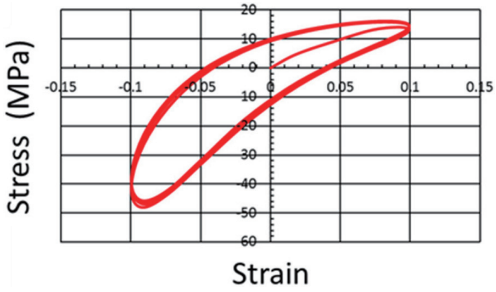

Fig. 16 Example of CFRP vibration simulation results by CGMD (MD#2)

analysis tools.

4. Conclusions

Applying the concept of coarse-graining from a top-down (macroscale) perspective, aligned with currently evaluable spatial and temporal scales, significantly reduced computational costs. This reduction surpasses what could be achieved by simply extending existing bottom-up (microscale, atomic/molecular level) approaches. This enables its direct application at the macro level during component development. Furthermore, utilizing this simulation module to investigate real resin formulations and filler surface conditions allows for the derivation of ideal material designs based on fundamental scientific principles, without extensive experimentation. It also aids in understanding deviations from ideal system behavior. Moreover, the tool enables the consideration of in-service temperature environments and the prediction of various deformation and failure modes at the nano- to micro-scale, potentially guiding innovation in resin and fiber-reinforced plastic (FRP) material development.

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