

COMPUTATIONAL INTERPRETATION OF SHAPE MEMORY EPOXY: PROCESSING AND ITS OPERATION

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Abstract. The shape forming and restoration mechanisms of shape memory epoxy originate from the molecular-scale dynamics that epoxy molecules undergo during thermomechanical processes. In this study, the microstructural changes that occur at the molecular scale caused by heat and load during the programming and operation of the epoxy network were investigated using molecular dynamics simulations. The mechanical behaviors of each molecule were analyzed by classifying it into translation, rotation, and deformation based on the classical kinematic framework. Specifically, depending on its structural properties, each molecular component was rearranged to different levels, forming local residual stresses. The principle leading to shape recovery as the subsequent thermal load breaks the equilibrium of residual stresses and resulting changes in the mechanical anisotropy of entire epoxy network were also analyzed through a subcontinuum perspective. This study has the potential to be extended to a method for designing epoxy resins that satisfy desired physical properties and shape recovery performance.

1 INTRODUCTION

Shape Memory Polymers (SMPs) are innovative materials capable of remembering and reverting to pre-set shapes under specific conditions [1,2,3]. When an external force and heat

are applied, these polymers can be temporarily reconfigured. Among these, Shape Memory Epoxy (SME) is the most extensively studied due to its highly crosslinked network composed of chemical covalent bonds, which offers several advantages, including high chemical resistance, excellent mechanical properties, and remarkable shape restoration. Due to these characteristics, SMEs have significant potential in various applications, such as soft robotics, space-deployable structures, and 4D printing [4,5,6].

SMEs operate by alternating between the rubbery phase and the glassy phase based on their glass transition temperature (T_g). This process involves two main stages: programming, in which the material is shaped, and recovery, where it returns to its original shape when reheated. During this process, the competition between polymer chain mobility and network rigidity defines the performance of SMEs.

Previous studies have explored the molecular mechanisms underlying shape memory behavior, focusing on morphological changes in polymer chains and structural changes during thermomechanical cycles [7,8,9]. These investigations highlighted the role of atomic potential energy changes in triggering the shape memory effect. However, the complex behavior of highly crosslinked SMEs cannot be fully explained by atomic bonding properties alone. Recently, a new subcontinuum analysis methodology using virial stress has been developed to study the topology of cross-linked epoxy networks and their mechanical properties [10]. Based on this approach, this study evaluates strain energy distribution, storage, and release within the molecular network.

The present study reveals that SME network responses can be understood through translational motion, rotational motion, and internal deformation of molecular components. This provides a comprehensive understanding of the molecular-scale factors influencing SME behavior and guiding the design of SME operation processes for specific applications.

2 SIMULATION MODEL

To investigate microstructural changes during the shape memory process, an all-atom molecular dynamics (MD) model of shape memory epoxy was prepared. The epoxy components included diglycidyl ether of bisphenol A (DGEBA) as the resin and 4,4-diaminodiphenylmethane (DDM) as the hardener. A total of 250 DGEBA and 125 DDM molecules were dispersed in a cubic cell with periodic boundary conditions. The crosslinked epoxy networks were formed by bonding reactive atoms within a set reaction radius, which was incrementally increased until a 60% crosslinking ratio was achieved.

The shape memory effect was characterized through MD simulations of programming and recovery processes as shown in **Figure 1**. During programming, the equilibrated epoxy model was heated to T_g+30K , uniaxially elongated to 30% strain, cooled to 300 K, and then relaxed. Recovery involved reheating the programmed network to T_g+120K and then cooling it back to 300 K.

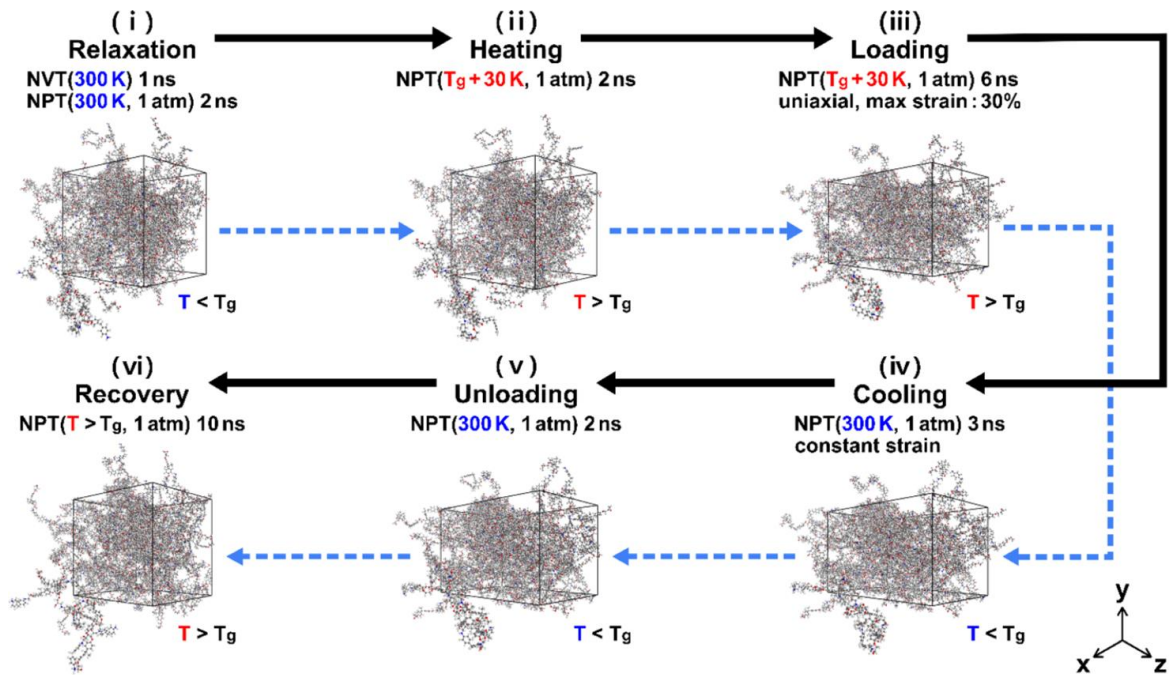


Figure 1: A Simulation process for SME through molecular dynamics. The process of setting the epoxy network in a temporary shape (steps (i) to (v)) and recovering to its original shape (steps (vi) to (vii)).

3 RESULTS AND DISCUSSION

Model validation was performed through the glass transition temperature (T_g), which determines the operating temperature of shape memory epoxy. At T_g , the polymer transitions from a glassy state to a rubbery state, resulting in a significant increase in mobility [11]. The MSD curve, which represents the average displacement of atoms, showed a significant gap between 380K and 390K, indicating a state change. By applying this to the density–temperature profile and performing linear fitting, the T_g was calculated to be 387.7K, similar to previously reported results [12].

As shown in **Figure 2**, monitoring the center of mass, orientational order, and atomic stress response revealed that under high temperature and external load, both the center of mass and orientational order increased linearly in the forming direction. This deformation energy propagation led to increased anisotropy, which was maintained during cooling and unloading, resulting in a permanent network modification.

The epoxy network was categorized into DDM and DGEBA, with DGEBA further divided into aromatic and epoxide groups. The virial stress for each group was calculated, revealing that during loading, stress values increase monotonically, remaining high until cooling. Upon unloading, stress was quickly released, indicating minimal residual stress across the entire network. However, this zero-stress state is deceptive, as DDM and DGEBA components formed residual stresses in opposite directions. This asymmetric energy storage enhanced material anisotropy, enabling actuation forces to be stored for subsequent stimuli.

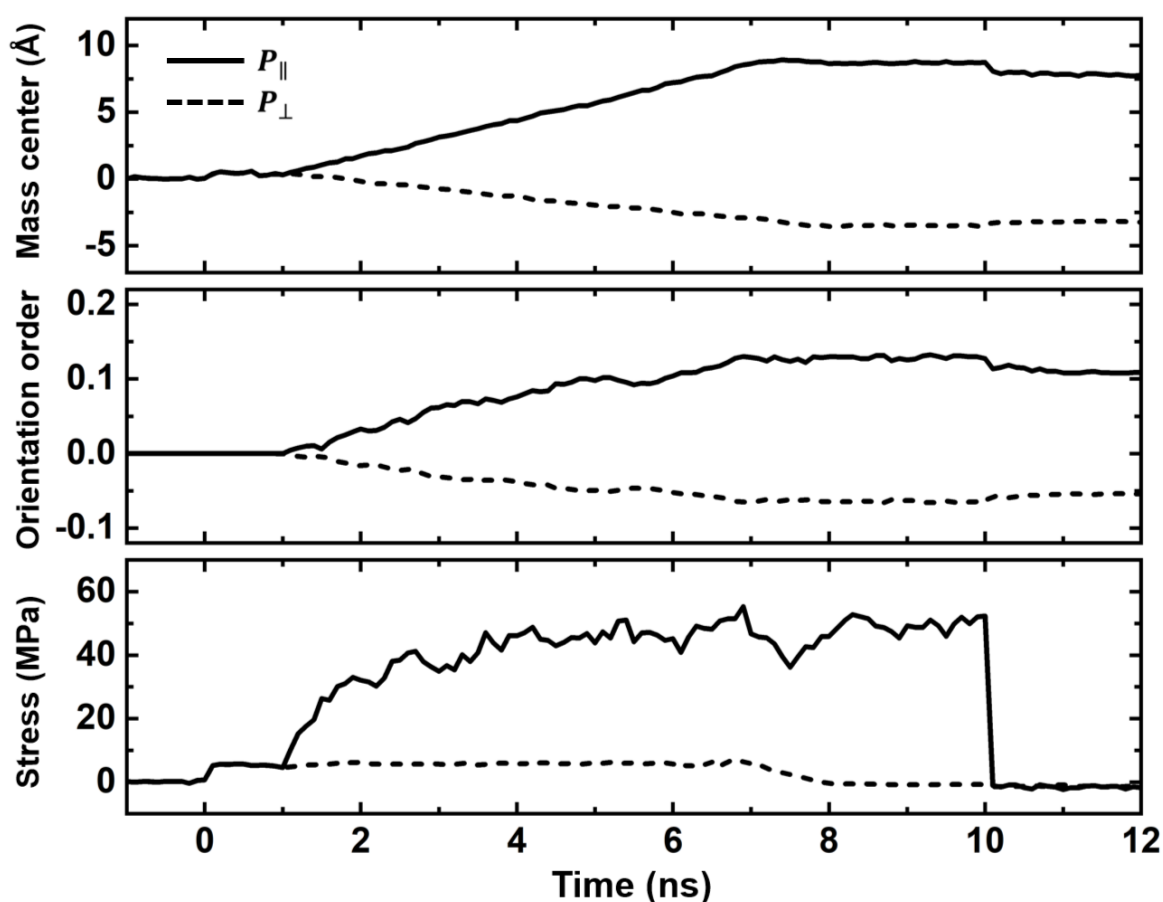


Figure 2: Changes in center of mass, orientation order and stress during the shape programming process.

The significant difference in the center of mass and orientational order between the tensile and vertical directions gradually disappeared upon reheating, as shown in **Figure 3**. The atomic stress profile also responded immediately to the applied temperature. The recovery process involved sequential deformation, rotation, and translation of molecular components, with complete recovery points identified at 2.6 ns for deformation, 3.5 ns for rotation, and over 10 ns for translation. This sequence aligns with observations of rapid stress recovery and slower specimen shrinkage at high temperatures.

Residual tensile stresses remained in the aromatic rings of DDM and DGEBA during programming, balanced by the flexible side chains of DGEBA. Upon reheating, this residual energy was fully released, enabling structural reconstruction. Internal stresses in DDM, DGEBA, and related components disappeared, indicating effective activation of the shape memory effect.

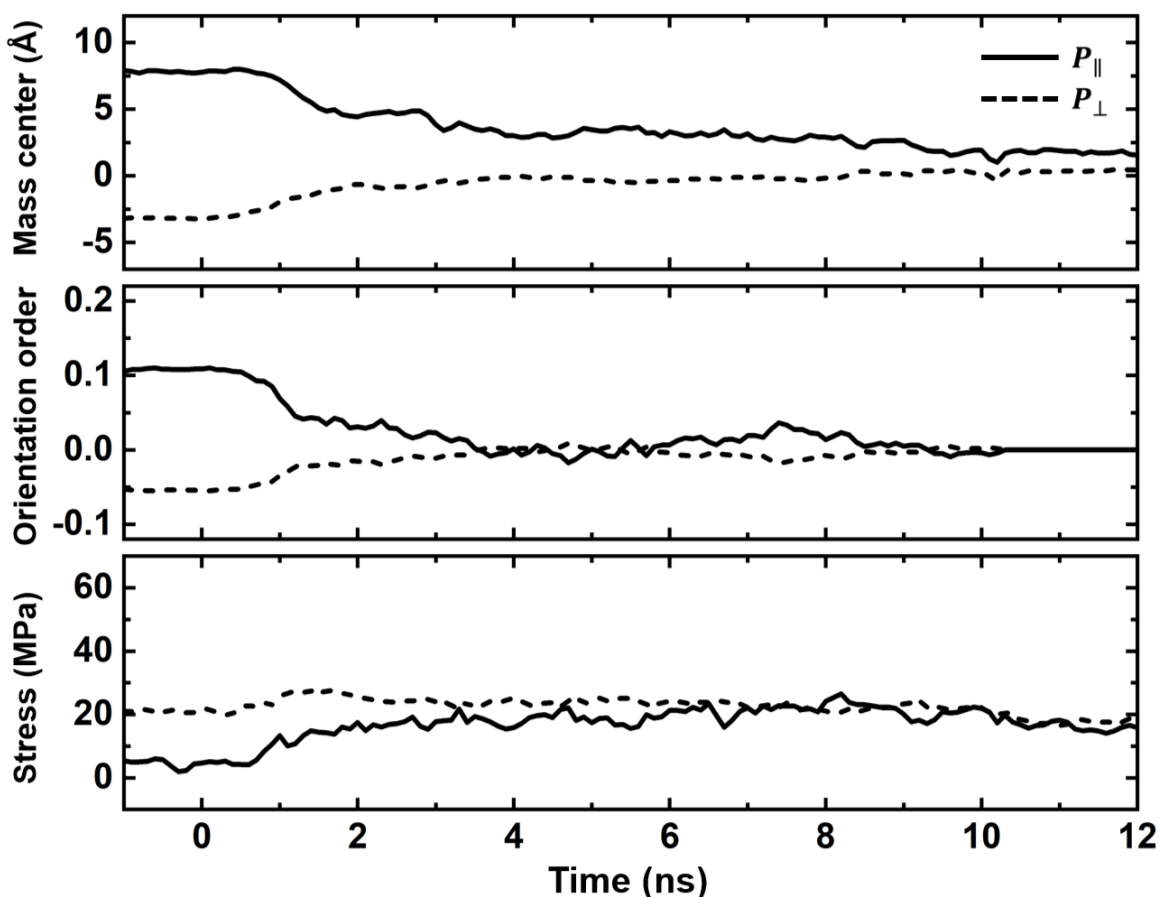


Figure 3: Changes in center of mass, orientation order and stress during the shape recover process.

4 CONCLUSIONS

In this study, we investigated the structural changes in thermosetting polymer resin during the shape memory effect's programming and restoration phases. Using an all-atom MD model of a crosslinked epoxy network, we simulated processes of heating, loading, cooling, and reheating. We analyzed the material's response based on molecular position changes, orientational order, and virial stress distribution.

Our findings show that the subcontinuum aspects of epoxy networks can be effectively described using a classical kinematic framework. The complex microstructure formed by the epoxy resin and crosslinking agent was explained through translation, rotation, and stretching of individual molecules. During the shape memory process, a permanent increase in orientation order and mechanical anisotropy was observed. Notably, asymmetric residual stress was found within the molecular components, with tensile stress in rigid aromatic rings balanced by compressive stress in flexible epoxide groups.

Residual stress stored during shape forming drives the anisotropic network to return to its original form upon reheating. This process eliminates residual stresses and restores the network's initial shape, confirmed by isotropic mechanical properties and the return of

molecular centers of mass to their original positions.

This work provides the first theoretical analysis of shape memory polymers at the molecular scale, systematically classifying the mechanical effects on crosslinked epoxy networks. The proposed model elucidates the structural factors influencing shape memory and the resulting material property changes. This study offers a methodological guide for designing thermosetting resins with specific physical properties and shape recovery performance.

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