

STUDY ON GLASS TRANSITION TEMPERATURE OF GRAPHENE REINFORCED SHAPE MEMORY POLYMER BY MOLECULAR DYNAMICS SIMULATIONS

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Keywords: Graphene reinforced SMP, Molecular dynamics, Glass transition temperature

ABSTRACT

Shape memory polymers (SMPs) possess unique shape-changing functionality that offer wide potential applications. However, SMPs with high mechanical strength are increasingly needed. For this purpose, graphene flakes can be used for strengthening the pure SMP materials. In this paper, full-atomistic molecular dynamics (MD) are used to study the shape-memory behaviour of a representative amorphous polymer. The glass transition temperature of graphene reinforced SMP (G-SMP) are investigated. The mechanical properties under uniaxial tension at different phases were obtained. The results show that the glass transition temperature of the G-SMP is higher than that of the non-reinforced SMP material.

1 INTRODUCTION

Stimuli-responsive shape memory polymers (SMPs) are promising smart materials that can recover their original shape and properties upon exposure to external stimuli, e.g., heat [1], light [2-4], pH [5], magnetic [6] fields and moisture fields [7,8]. Among various shape memory materials, SMPs have attractive features such as a wide elastic range, high recovery strain, enhanced processibility, light weight, and low cost. Owing to their prominent advantages, SMPs have wide potential applications, which are used for self-deploying structures [9], sensors [10], self-healing [11], smart fabrics [12], actuators, and smart devices.

Compared with other stimuli-responsive SMPs, thermal-responsive SMPs have been widely investigated and used on account of their relatively simple actuation. The temporary shape is fixed above the glass transition temperature. The polymer can keep deformation during cooling the material below the glass transition temperature. It is able to subsequently recover from the temporary stored shape above the glass transition temperature on the condition of stress-free heating. Shape memory effect is driving the change from rubbery state to glassy state when passing through the glass transition. This paper is studied the key element (glass transition temperature).

In order to improve and enhance the properties of shape memory polymers, extensive attention has been paid to the fabrication and design of new SMP materials and their composites, including SMP matrices [13-15], particle- or fibre-reinforced SMP composites [15,16]. Meanwhile, numerous works have reported the thermomechanical behaviour and shape memory effects of SMPs and their composites [17-20].

Many computational approaches have been proposed to describe the mechanical response of SMP with consideration of the molecular mechanism. Liu et al. [21] developed a three-dimensional small-strain internal state variable constitutive model to predict the thermomechanical behaviour of SMPs. The model can monitor the evolution of stress during the thermomechanical cycle.

Molecular dynamics (MD) simulation is a powerful technique to predict the change of the thermoelastic properties of polymers during thermal transition that allows practical problems to be explored in detail on the macromolecular scale for polymers to obtain information that cannot be

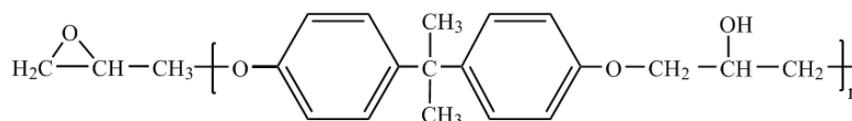
extracted directly from experiments. MD simulations can also consider the vibrational modes of individual atoms and calculate many fundamental atomic interactions at the individual chain level, which cannot be obtained by other numerical simulation methods, such as the finite element method. Diani et al. [22] used a full atomistic simulation of the shape-memory behaviour of polyisoprene to study the strain storage and energy evolution. Instead of real SMPs, a virtual polyisoprene was constructed in their model, in which entropy dependent shape storage and recovery was confirmed. Ghobadi et al. [23, 24] set the atomistic modeling schemes of the shape memory creation procedures of poly (L-lactide) to predict the shape-memory behavior and its cyclic uniaxial thermomechanical test. Abberton et al. [25] elucidated the effects of phase fraction and temperature on the shape recovery of copolymer system with coarse-grained potentials using a two-phase molecular model. Choi et al. [26] discussed the filler-size effect on the glass transition and the thermoelastic behaviors of epoxy-based nanocomposites.

SMP-resin-based composites reinforced by continuous fibers are regarded as the most promising materials for deployable structures in future space applications [27]. Although, there are still great challenge in improving the load-carrying properties the SMP materials. The fabrication of high-performance SMP epoxy systems is essential. A series of shape memory epoxy systems tailored with different thermomechanical properties and shape transition temperatures have been synthesized. Recently, Yang et al. [28] presented MD simulations to investigate the influence of the ratio of curing agent to epoxy resin on the thermomechanical properties of SMP based on the molecular mechanism of shape memory. However, an understanding of how the enforcements affects these properties remains elusive. Few studies have been carried out that deal with the relationship between the molecular state and the macroscopic changes of polymer during shape recovery behavior. This is because the shape memory behaviors of polymer structures are significantly affected by the thermomechanical history during the prestretching process [29].

Although coarse-grained models with reduced degrees of freedom can reduce the computational time and are less limited by the temporal and spatial scales, we adopted all-atom-based MD simulations to examine the glass transition temperature. These incur massive computational cost compared with simplified models. However, chemically realistic microscopic conformations can be obtained with the energetically rigorous force-fields. We constructed SMPs models reinforced with graphene contents to investigate the influence of graphene on the glass transition temperature and to describe the different state and investigated the changes of microscopic chain. The simulation results are also compared with related experimental data [30]. Our investigation allows elucidation of the underlying mechanism that accounts for such thermomechanical properties.

2 MATERIALS AND SIMULATION DESCRIPTION

In the paper, thermoset epoxy and curing agent, 4, 4'-methylenedianiline (DDM), are used to build shape memory polymer. Single-layer graphene flake is used as the reinforcement. The molecular structures of epoxy, DDM and graphene flake are shown in Figure 1.



(a) Epoxy

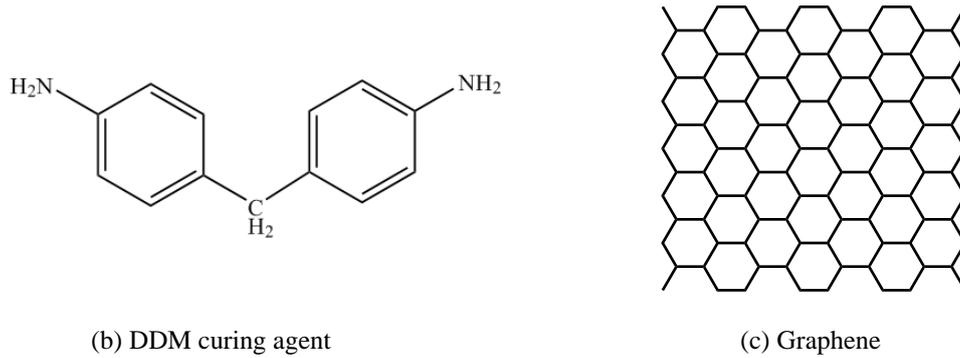


Fig. 1 Molecular structures of epoxy, DDM curing agent, and graphene

Materials Studio was used to build the initial molecular model, and further MD simulation was performed using LAMMPS [31]. The epoxy and DDM repeat units are shown in Figure 2, free metals represent a head and a tail linkage, respectively. Formulations of the shape memory epoxy systems are shown in Table 1. According to the mass ratios listed, the molecular numbers of epoxy: DDM in each system were 10:3. Using the random copolymer builder and amorphous cell generator program in Materials Studio, an epoxy/DDM random copolymer system was constructed. Firstly, periodic amorphous G-SMP models consisting of epoxy, DDM and graphene were constructed in Materials Studio. The size of graphene flake is $15.62\text{\AA} \times 14.76\text{\AA}$ in polymer amorphous cell.

Then, these initial models were equilibrated using NVT and NPT ensembles sequentially at a high temperature (500 K) with a timestep of 0.1 ps. Simulations were performed using polymer consistent force field. Simulations were carried out using a polymer consistent force field (PCFF), which is parameterized for a large class of organic molecules involving H, C, O, S, P, F, Cl, and Br, allowing it to be applied to synthetic polymers [32]. It has been found that the PCFF leads to accurate geometries for various polymeric systems. The cutoff distance was set to 9.5\AA [33]. The shape memory effect in SMPs arises from the glass transition of the materials owing to the change of material temperature. All simulations in this work focused on the glassy (below the glass transition temperature) and rubbery (above the glass transition temperature) states of the materials. In this work, we focus on the influence of graphene on composite material.

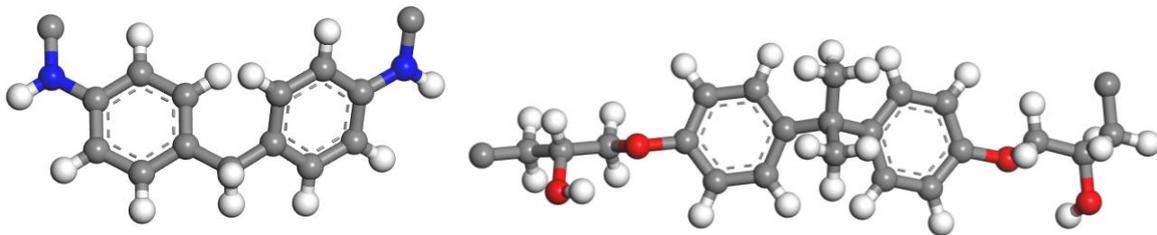


Fig. 2 repeat elements of DDM curing agent and epoxy

Content	Mass ratio
epoxy	81.4
DDM	14.6
Graphene	4.0

Table 1: Formulations of the prepared shape memory epoxy systems (mass ratio)

3 RESULTS AND DISCUSSION

It is well known that the glass transition temperatures (T_g) is one of the most important parameters for shape memory polymers. The shape recovery processes are closely correlated with T_g of the

materials. In order to determine T_g for the present two types of SMP materials with different mass fractions of graphene, V-T curves were obtained based on MD simulations with NPT ensemble at a fixed pressure. The volumes at each temperature were obtained by cooling the system with a decrement of 10 K.

Figure 3 shows the MD simulation results for the dependence of reinforced material and non-reinforced material on temperature. The molecular numbers of epoxy: DDM was 70:21. The T_g values of the materials can be determined from the intersection of the two straight lines, as shown in Figure 3. The T_g values obtained from the MD simulations are 363K, 443K, respectively. The results show that glass transition temperature of graphene reinforced material is higher than that of the materials without graphene. Figure 3 also reveals the molecular structure of the two materials in the different state. These results indicates that the chains are more flexible in the rubbery state. It is obvious that T_g of shape memory polymer composites have been improved with graphene. The presence of graphene slows down the volume change caused by the decrease of the polymer with temperature. There is a gap between the simulation results and the experimental results. It is possible that the model size is too small to reach the entangled state of the real material.

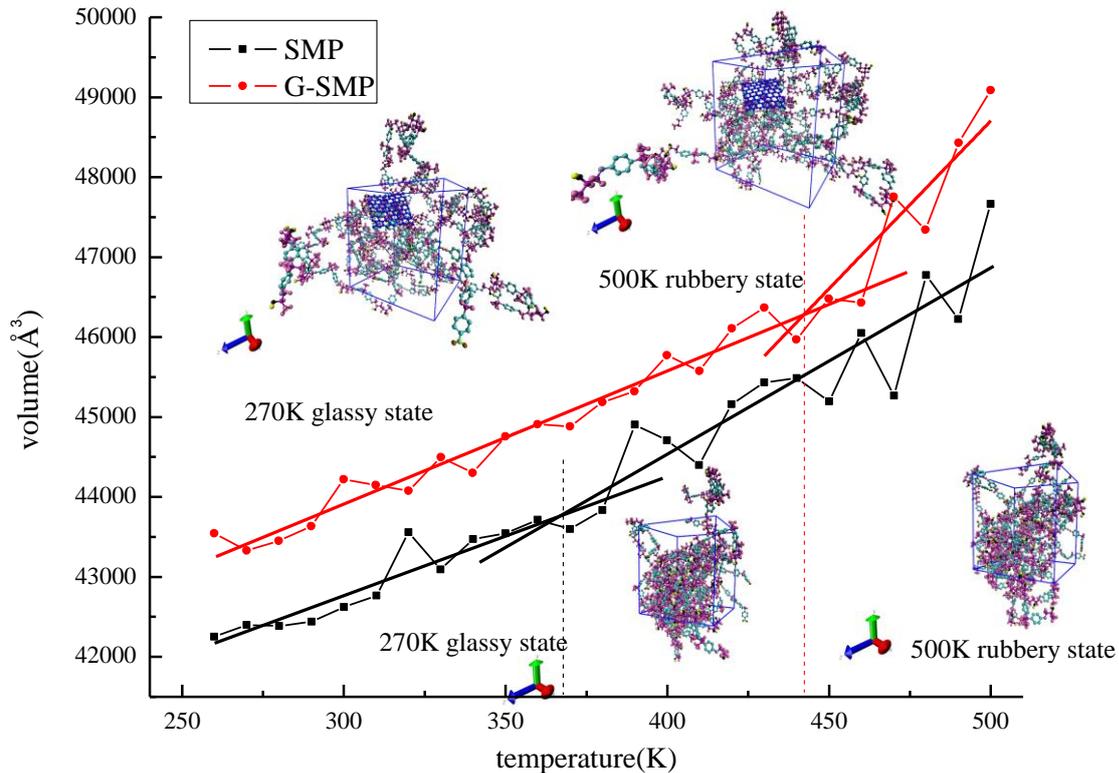


Fig. 3 Temperature-volume curves of SMP and G-SMP

ACKNOWLEDGEMENTS

The paper is the first time written by me after I study molecular dynamics simulation method. I extend my sincere gratitude to my supervisor professor Yang for his constant support throughout my work on this thesis and for his informed guidance. I am also most grateful to teacher Liu without whose support and patience this thesis would not have been completed. She has solved the problem for me many times. At the same time, Shang Junjun also provides a lot of help for me and make a contribution to the paper.

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