

Molecular Dynamic Simulation Study on Glass Transition Temperature of DGEBA-THPA/SWCNTs Composites

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ABSTRACT

Molecular dynamic (MD) simulations were carried out to predict the thermo-mechanical properties of the cured epoxy network composed of diglycidyl ether bisphenol A (DGEBA) epoxy resin and tetrahydrophthalic anhydride (THPA) curing agent and their single-walled carbon nanotubes (SWCNT) reinforced the epoxy matrix composites. Different characters such as the density of the materials and mean square displacements (MSDs) were calculated to estimate the glass transition temperatures (T_g) of the materials. 365 K and 423 K of the T_g were obtained respectively, whereas the latter is much higher than the former. The simulation results indicated that the incorporation of SWCNTs in the epoxy matrix can significantly improve the T_g of the cured epoxy. The approach presented in this study is ready to be applied more widely to a large group of candidate polymers and nanofillers.

KEYWORDS

Molecular Dynamics Simulation; Glass Transition Temperature; Carbon Nanotubes Composites

1. Introduction

Glass transition temperature (T_g) is a key descriptor to evaluate the thermal properties of the heat-resistant materials, while the useability determined by the mechanical properties at high temperature. The ability to predict the T_g and mechanical properties is of great value in the selection and design of new materials. Conducting experiments to measure the T_g and mechanical properties is a reliable, however, time-consuming and expensive approach. Recently, molecular dynamics (MD) simulation has provided great insight into the T_g and elastic response of polymer and its composite materials.

Abu-Sharkh [1] conducted the rigid unit model and the explicit atom model to generate volume-temperature (V-T) data of poly (vinylchloride) respectively, which confirmed the validity of MD simulation in predicting the T_g of amorphous polar polymers. Wu *et al.* [2,3] calculated the density and elastic constants of diglycidyl ether bisphenol A (DGEBA) cured with isophorone diamine (IPD) using atomistic molecular simulation. The results indicated that both the use of COMPASS force-field and DREIDING force-field resulted in unrealistically high elastic constants whereas the former compared more favorably with the corresponding experimental values than the later. Fan *et al.* [4] used PCFF force-field to predict

the T_g, linear thermal expansion coefficients (LCTEs) and Young's modulus of cross-linked EPON862-TETA (triethylenetetramine) systems from MD simulations. Their results were in good agreement with the experimental values in the literature. Li *et al.* [5,6] and Bandyopadhyay *et al.* [7,8] studied the EPON862-DETDA (diethylene toluene diamine) systems. The simulation results indicated a significant increase in T_g, Young's modulus and yield stress with degree of polymerization, while the thermal expansion coefficient (CTE) decreased with the overall crosslink density, and the yield strain was less sensitive to it, however, there was no discernible influence of cross-link distribution on the elastic modulus and the LCTE. Shenogina *et al.* [9,10] employed a new method-dynamic deformation approach to simulate the thermo-mechanical constants and the elastic constants of DGEBA-DETDA systems. Results were in very good agreement with experimental data of actual cured polymers. The approach showed excellent improvement compared to constants calculated using the static deformation approach.

Epoxy resin matrix composites are of special interest in the aerospace industry for the current and future aircraft and spacecraft due to their good heat-resistance and outstanding mechanical properties, comparing to other

lightweight structural materials. It has been observed that the incorporation of CNTs [11] in the epoxy resin can significantly enhance its mechanical, thermal, and electrical properties, and thus, CNTs can be used as a potential reinforcement for epoxy. Gou *et al.* [12] investigated the interfacial bonding of single-walled carbon nanotube (SWCNT) reinforced epoxy resin composites in terms of stress transfer. A 250% ~ 300% increase in storage modulus with the addition of 20 ~ 30 wt% nanotubes was resulted. Liang *et al.* [13] found that both the EPON862 resin and DETDA molecules have attractive intercalations with (10, 10) SWCNT, and the aromatic ring structures of the molecules try to align the aromatic ring planes toward the SWCNT surface and wrap around it. Mittal *et al.* [14] found that the reinforcement of SWCNTs with different diameters, whereas the (8, 8) SWCNTs reinforced EPON862 resin composites exhibited the highest enhancement of the Young's modulus. Chakraborty *et al.* [15] investigated the properties of the composites of pure monomer and trimer polycarbonate and their mixtures with different weight percentages of embedded SWCNTs at different temperatures. It was seen that the diffusivity of solvent molecules decreased with increasing percentage of CNTs at a specific temperature; and the polymerization played a role in enhancement of binding energy.

In this study, molecular dynamic (MD) simulations were carried out to predict the thermo-mechanical properties of the cured epoxy network composed of diglycidyl ether bisphenol A (DGEBA) epoxy resin and tetrahydrophthalic anhydride (THPA) curing agent and single-walled carbon nanotubes (SWCNT) reinforced the epoxy matrix composites, respectively. Density of the materials and mean square displacements (MSDs) were calculated to estimate the glass transition temperatures (T_g s) of the materials.

2. Molecular Dynamic Simulation

MD simulations were conducted using the Materials Studio 5.5 (Accelrys Inc.) software. COMPASS force-field was used in the simulation, which has been shown to provide accurate predictions of thermo-mechanical properties of thermosetting polymers [3,4,10]. The non-bond interactions with a cutoff distance of 9.5 Å, including van der Waals and electronic static forces, were applied. The atom approach was used for the dispersion interactions.

The cured epoxy network is composed of DGEBA resin and THPA curing agent. Chemical structures of the resin and hardener segments are shown in **Figure 1**. During the curing reaction, the acid anhydride groups of the curing agent molecules reacted with the epoxide groups of the epoxy resin. Initially, one THPA molecule reacted with one epoxide group. As the reaction contin-

ued, more cross-links were generated between the epoxy resin and the curing agent. The cross-linking activity expanded in all directions and formed a network of macromolecules. Schematic of the curing reactions are shown in **Figure 2**.

In this study, the polymer model was dynamically built by assumptions. Firstly, 8 epoxy segments and 16 hardener segments containing reactive sites with a density equal to 1.2 g/cm³ were packed into a 3D periodic cell box using the Amorphous Cell tool. This formulation was then mixed using the ensembles of the constant number of particles, constant volume and constant temperature (NVT) MD simulation for 100 ps performed at 298 K after initial molecular minimization (MM) based

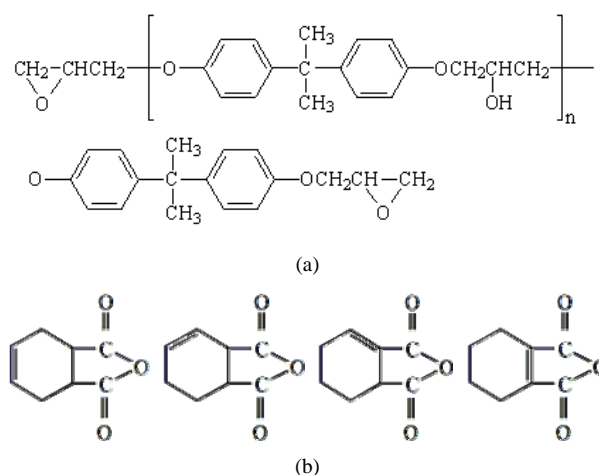


Figure 1. Chemical structures of the resin, hardener. (a) DGEBA; (b) THPA.

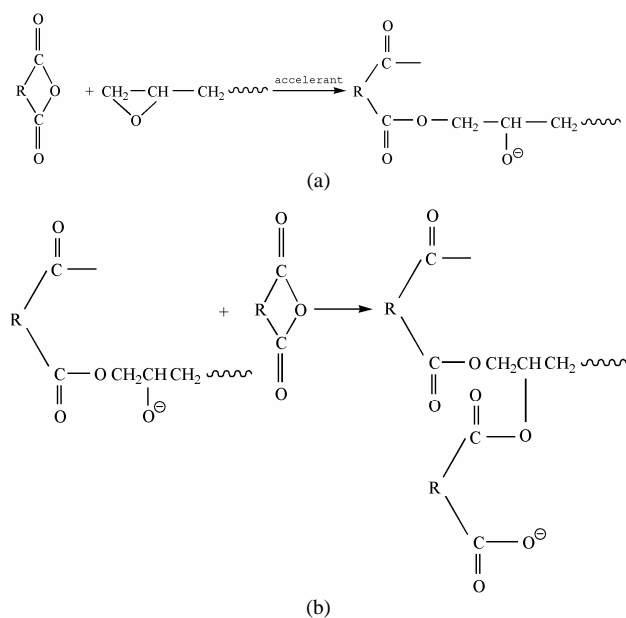


Figure 2. Schematic of the curing reactions.

on COMPASS force-field. Under close proximity, covalent bonds were formed between the nearest reactive pairs within the reaction cutoff distance of 9.5 Å considering the removal of ring catenation or spearing. Repeating these steps to form bonds for several times, a 19.33 Å × 19.33 Å × 19.33 Å cross-linked polymer network with a conversion of 80% was finally obtained. For the CNT composites, a zigzag SWCNT (4,0) with the diameter of 3.13 Å and length of 34.08 Å consisting of 196 atoms is embedded into the above amorphous DGEBA-THPA systems with a density equal to 1.0 g/cm³, followed by the cross-linking activities. The resulting model system has a cell dimension of 21.52 Å × 21.52 Å × 21.52 Å with a conversion of 60%. Periodic boundary conditions are applied in all three directions for both models.

After the initial microstructure was generated, the minimization of the potential energy of the model was carried out, where COMPASS force-field was used. Then simulated annealing was performed by raising the temperature from 500 K to 900 K and cooling down to 500 K with steps of 20 K and an annealing time of 50 ps. After that, geometric optimization of 10000 steps and NVT MD simulation of 200ps were performed at a temperature above the T_g, such as 523 K in Forcite modules, and repeated for several times to relax the polymer chains.

In order to imitate the thermal performance in a kinetic process, simulation of cooling process was performed. The system was cooled stepwise from 523 K to 283 K with the rate of 10 K/200 ps. At each temperature, 10000 steps geometric optimization simulation was performed to relax the polymer chains, followed by the ensembles of the constant number of particles, constant pressure and constant temperature (NPT) MD simulation under a pressure of 0.1 MPa for 200 ps to obtain the optimized density. In terms of non-bonding interaction treatments, atom-based direct cutoff of 9.5 Å and a buffer of 0.5 Å were used depending on the accuracy and efficiency of the computation. Velocity Verlet algorithm with a time step of 1fs was used for the integration of the atom motion equations throughout all simulations. Nose thermostat and Anderson barostat with cell time constant of 1.0 ps have been adopted. Each subsequent simulation was started from the final configuration obtained at the preceding temperature. The simulation in each case was performed with an interval of 1 femtosecond (fs) in each simulation step.

3. Results and Discussion

Various energies can be calculated from the MD simulations, which are used to analyze the roles of them in glass transition. The simulated results of total energy, potential energy and kinetic energy of the system against the tem-

perature are plotted in **Figure 3**. It can be seen that the plots of these energy increases almost linearly with increasing temperature in the whole temperature range, indicating that the total energy, potential energy and kinetic energy play no distinctive roles in the glass transition process of the epoxy resin and its CNT composites.

Densities of the epoxy resin and the composites at room temperature were calculated to be 1.228 g/cm³ and 1.012 g/cm³, respectively, which are in good agreement with the appointed values. The evolution of density as a function of temperature of the DGEBA-THPA/SWCNT composites is plotted in **Figure 4**. A steady increase of the density with decreasing temperature and a clear change in the slope of the density curve were observed. The kink in the density vs temperature slope is defined as the

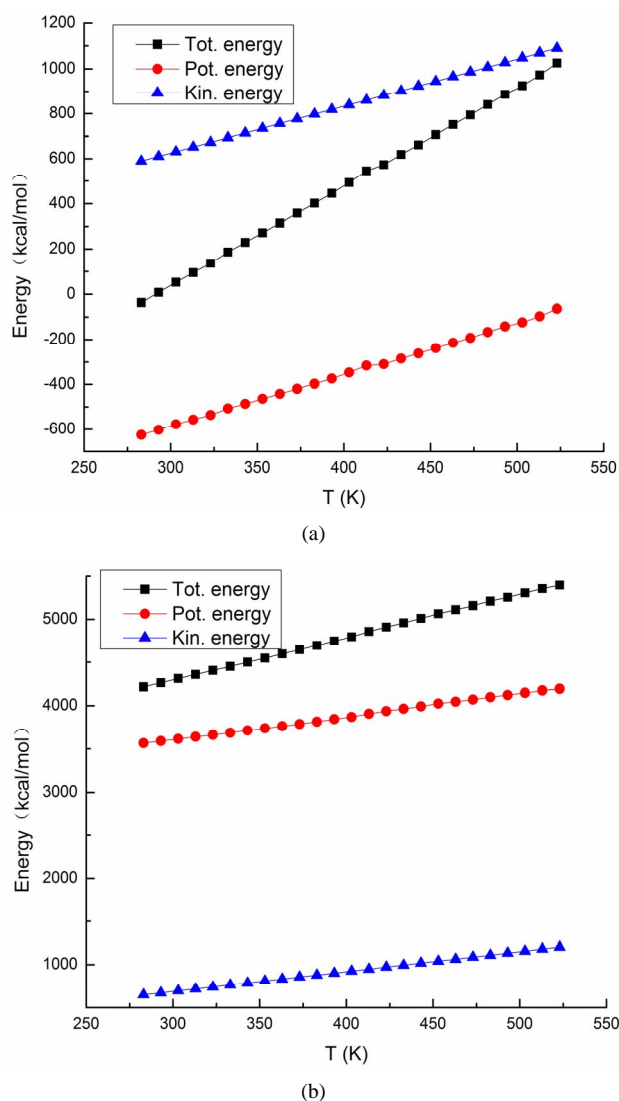


Figure 3. Energy variations as a function of temperature. (a) DGEBA-THPA polymer; (b) DGEBA-THPA/SWCNTs composites.

values of T_g , which occurs at approximately 423 K, where the epoxy resin passes from the glassy state to the rubbery state.

The cross-reactions in the epoxy resin make significant differences in structure and properties from other linear polymers. It is instructive to analyze the motion of these cross-links in the model systems as a function of temperature. Because of incomplete reaction, segments on the polymer chains can be classified as cross-linked and free ones. Generally, the cross-linked segments exhibit much lower mobility than the free ones due to topological constraints. The value of T_g is correlated well with the polymer rigidity, namely the segmental mobility in polymer chain. The mean square displacements (MSDs) of the epoxy resin chains at 30 ps were calculated, which is plotted in **Figure 5**. The turning point of MSDs indicated T_g of the DGEBA-THPA polymer, which occurs around 365 K.

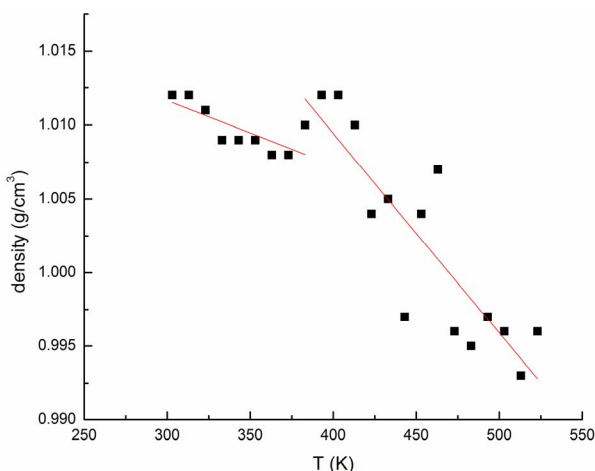


Figure 4. Density of DGEBA-THPA/SWCNT composites variation as a function of temperature.

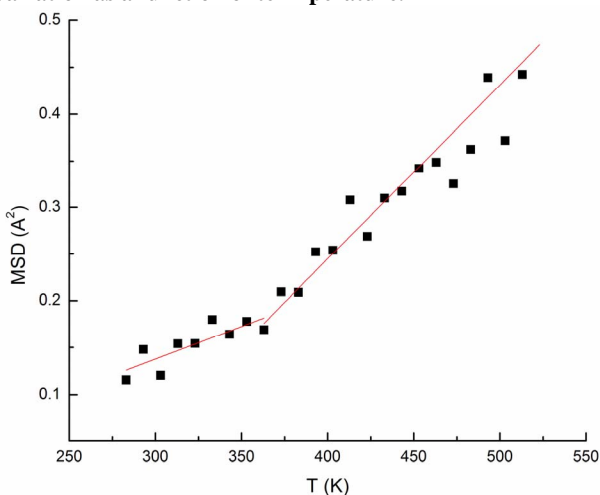


Figure 5. MSDs of the epoxy resin chains variation as a function of temperature.

From the MD simulations, T_g of the DGEBA-THPA/SWCNT composites is much higher than the DGEBA-THPA polymer, which is consistently with the fact.

It is very inspiring to see that the MD simulation method can be successfully applied to investigate the thermomechanical properties of the CNT/polymer composites. Once established, this approach can be applied more widely to a large group of candidate polymers and nanocomposites, proving a much more cost-effective way to narrow the fabrication and testing efforts to the selected best performers predicted by the MD simulations.

4. Conclusion

In the current study, two models of DGEBA-THPA cross-linked resin and its CNT composites were investigated by MD simulations. Different characters were calculated for the two models. The calculated results showed that the T_g of the two systems are 365 K and 423 K, respectively, whereas the value of latter is much higher than the former, which is consistent with the fact. It can be expected that the method would be employed in further molecular simulation of structure and properties for cross-linked epoxy resin or other cured polymer network and their CNTs composites.

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