



Molecular dynamics simulations of key physical properties and microstructure of epoxy resin cured with different curing agents

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ABSTRACT

The molecular structure of curing agents significantly influences the properties of epoxy resins. In this article, the effect of the molecular structure of curing agents on the thermomechanical (TM) properties of an epoxy resin was investigated by a molecular dynamics method. First, the influence of the sizes of 3D systems on the performance of cured systems was preliminarily analyzed. From the results, four kinds of fully atomistic models were constructed and simulated. The effects of curing agents' molecular chain lengths, polar groups, side-chain groups on the TM properties of epoxy resin systems were analyzed from various perspectives. The results showed that the longer the molecular chain and the smaller the group polarity, the inferior the TM properties of the cured system, and vice versa; further, the side-chain group significantly weakened the movement ability of the chain, which has a primary effect on cured system TM properties. Molecular structures of curing agents have little effect on thermal expansion coefficient and thermal conductivity of epoxy curing systems.

Introduction

Epoxy resins are widely used directly or indirectly in almost all industrial fields; e.g., they are used for coatings, adhesives, and molding materials in electrical and mechanical equipment manufacturing. The macroscopic thermomechanical (TM) properties of epoxy resin systems are very sensitive to the

microstructure of epoxy resins themselves and curing agents [1]. With the rapid development of chemistry and testing technology recently, several high-performance epoxy resins and curing agents are being synthesized. The molecular structure of an epoxy resin system can be adjusted by adding different curing agents [2–6]. There are many kinds of epoxy resin curing agents, e.g., imidazoles, amines, anions,

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cations, phenolics, mercaptan, and isocyanates. It is difficult to confirm high-performance epoxy resins or curing agents as well as analyze the relationships between the molecular structure and macroscopic properties of epoxy resin systems experimentally due to the time complexity, cost, and low efficiency [7, 8].

Several studies on the structure and properties of epoxy resin systems have been reported via molecular dynamics (MD) [2–6], which allows for more efficient screening of high-performance epoxy resins and curing agents. This is due to the rapid development of computers, as well as the constant perfection and development of modeling methods and simulation force fields. MD simulations have been shown to be useful in elucidating the relationship between the microstructure and macroscopic properties of epoxy resins. In addition, they offer improved security and efficiency in the process of creating novel materials [9, 10].

Recently, MD simulations have attracted enormous attention, and the relationship between the microstructures and properties of epoxy resins has been extensively studied. The main work of microstructure and properties are shown in the following: the relationship between structure and properties [2–6], failure mechanism [11–14], interface and properties of composite materials [15–17].

Soni [18], Sirk [19], Li [20] et al. discussed the influence of curing agent chain length and flexible on the glass transition temperature, and the results showed that the longer and the more flexible of the curing agent molecular chain, the lower of the glass transition temperature of curing system. Masoumi [21] employed MD to study the crosslinking process and TM properties of Bisphenol A diglycidyl ether (DGEBA) using polypropylene diamine as the curing agent in the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field and found that the glass transition temperature, thermal expansion coefficient, and elastic constants, calculated using a static method, were close to experiment results. Fu [22] studied the TM properties of an epoxy resin cured with different anhydride curing agents using both MD and experiment methods; the results showed that slight changes in the molecular structure of the curing agents significantly influenced the performance of epoxy resin systems.

In this article, first, the effect of the size of fully atomistic models on the TM properties of epoxy/

amine curing systems was investigated. Considering the high calculation accuracy and computing capability of the workstation, an appropriate size was selected to construct an epoxy/amine fully atomistic curing system with different molecular structure aromatic amine curing agents for further simulation.

Methodology

Construction of pre-crosslinking model

DGEBA/4,4'-diaminodiphenylsulfone (DDS) models with different sizes (containing different numbers of molecules) were constructed using material studio 2017 (MS) (Fig. 1).

DGEBA, curing agents, and 3D pre-crosslinking models shown in Fig. 2 are constructed using MS. Particularly, four kinds of 3D amorphous models of epoxy/amine systems containing DGEBA and curing agent molecules—4,4'-diaminodiphenylether (DDE), 3,3-Bis(4-(4-aminophenoxy)phenyl)phthalide (BAPP), DDS, 1,4-bis(4-aminophenoxy)benzene (BAPB)—were constructed using the amorphous cell tools of MS to analyze the TM properties of epoxy resin systems. MD studies have shown that the effect of the polymerization degree of epoxy resins on the properties of epoxy resin systems is negligible [23]. Therefore, in this study, we set the polymerization degree of DGEBA to zero [24, 25].

Crosslinking parameters

The initial density of the models was set to 0.5 g/cm^3 . Geometry optimization allowed us to minimize the energy of the models. In addition, dynamics equilibrate was conducted in a constant volume and temperature (NVT) ensemble for 25 ps at 298 K and constant pressure and temperature (NPT) ensemble for 50 ps at 1 atm. The main parameters—the minimum crosslinking radius, maximum crosslinking radius, step crosslinking radius, iterations per radius, target degree of crosslinking, and crosslinking temperature—were set to 4 Å, 12 Å, 1 Å, 3, 90%, and 500 K, respectively. A high simulation temperature aided molecular segment movement in the cross-linked system and could significantly reduce the simulation time [26]. The Andersen and Berendsen methods were, respectively, used for temperature (thermostat) and pressure (barostat) controls. The

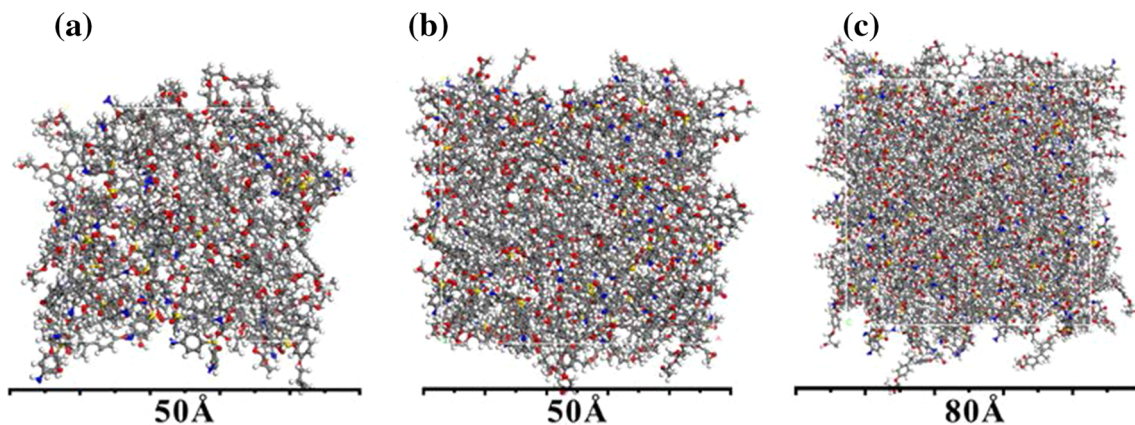


Figure 1 Different sizes of the DGEBA/DDS fully atomistic models: **a** 64DGEBA/32DDS; **b** 128DGEBA/64DDS; **c** 256DGEBA/128DDS. Color legend: hydrogen H (white); nitrogen N (blue); carbon C (gray); oxygen O (red); sulfur S (yellow).

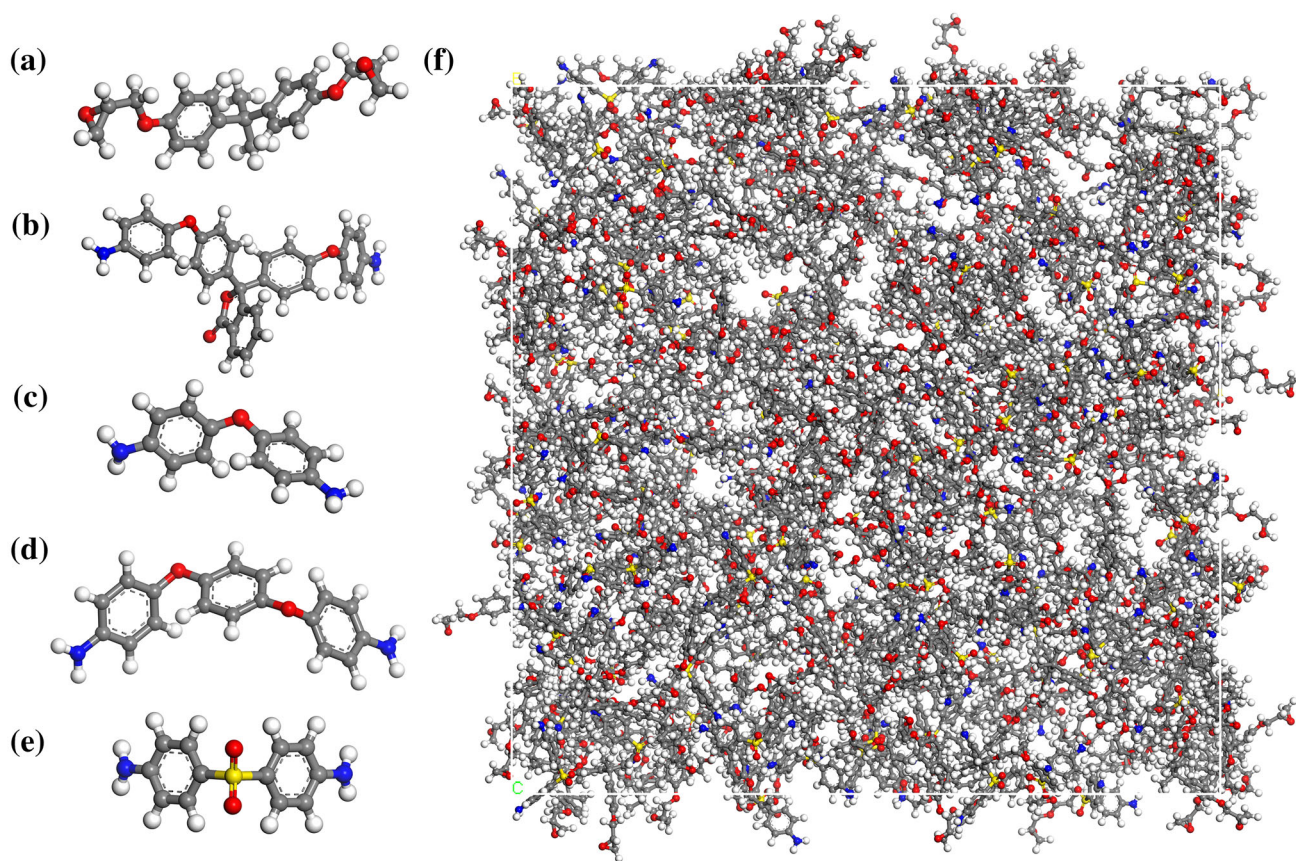


Figure 2 Ball and stick models of epoxy and curing agent molecules: **a** DGEBA; **b** BAPP; **c** DDE; **d** BAPB; **e** DDS; **f** Pre-crosslinking model. Color legend: hydrogen H (white); nitrogen N (blue); carbon C (gray); oxygen O (red); sulfur S (yellow).

degree of crosslinking is the ratio of the number of newly formed C–N bonds to the theoretically formed C–N bonds. The TM properties of the epoxy resin systems strongly depended on the polymer networks formed during curing, where the modulus and glass

transition temperature (T_g) increased with the increase in the degree of crosslinking [27]. Thus, it was necessary to set a uniform degree of crosslinking parameter as 90% for all models. All simulation task qualities were ultrafine.

The force field reflects the microchemical environment of the particular atom. By matching combinations of force field types, parameters for various potential energy terms can be assigned, ultimately leading to a full potential energy surface that can be used to calculate the forces between atoms which is the core of mechanical simulation [28]. The COMPASS force field is a quantum mechanics ab initio force field [29–31]. The COMPASS force field can not only simulate the structure and vibration frequency of isolated molecules but also more accurate values for the structure and TM properties of the macromolecular condensed state. Simulation results of inorganic or organic systems in the COMPASS force field agreed well with experiment results [16, 22, 24, 32–37]; therefore, the COMPASS force field was selected. The various functional forms in this force field have been discussed by Sun [30] and Singh [38].

Crosslinking procedure

The crosslinking script was written by Perl. Both primary and secondary amines in aromatic amine were assumed to have the same reactivity in the crosslinking process [31]. The detailed crosslinking procedure is as follows.

Step 1 Designate C atoms on epoxy rings and N atoms on curing as reactive atoms by labeling them R1 and R2, respectively. Construct and optimize the initial fully atomistic crosslinking models. Set up the simulation parameters.

Step 2 (A) Open epoxy rings and form new C–N bonds if there are R1 and R2 within the reaction cutoff distance. Relax the fully atomistic crosslinking models with geometry optimization. Equilibrate in NVT and NPT ensembles within the cutoff distance. *(B)* Increase the cutoff distance (step 0.5 Å) if there are no unreacted atoms within the reaction cutoff distance and repeat Step 2 (A) until the target degree of crosslinking or maximum cutoff is reached.

Step 3 Repeat Steps 2 (A) and (B). Relax the final fully atomistic crosslinking models with NVT/NPT ensemble and anneal them using a temperature cycle. Save all projects and exit.

Results and discussion

Model size effect

The size of models has a certain effect on the performance of curing agents [39], so it is significant to choose an appropriate model size to obtain more accurate and convincing simulation results. Three pre-crosslinking models containing 256DGEBA and 128DDS, 128DGEBA and 64DDS, 64DGEBA and 32DDS were constructed; their stoichiometric ratios of N–H bonds to epoxy rings were equal. The parameters of the simulations were consistent. The mechanical properties of the different sizes of the DGEBA/DDS curing systems are shown in Fig. 3.

Epoxy/amine curing systems can be considered isotropic materials within an error range allowed [25]. The simulation results showed that the larger the model size, the more perfect the curing system, which manifested in the following two aspects. (1) The modulus of the X, Y, and Z directions tended to be uniform, meaning the curing systems tended to exhibit isotropic features with the increase in the model size. (2) The modulus of the X, Y, and Z directions increased with the increase in the model size. Considering the high calculation accuracy and computing capability of the workstation, four kinds of fully atomistic models containing 256 DGEBA and 128 curing agents were constructed to analyze TM properties of epoxy/amine curing systems with different curing agents.

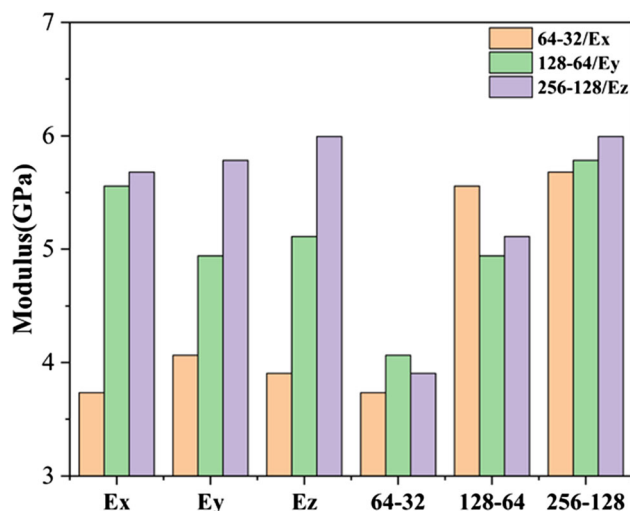


Figure 3 Effect of model size on the performance of epoxy resin system.

Coefficient of thermal expansion and thermal conductivity

Thermal expansion occurs when the volume of a substance increases with temperature under a certain pressure. The coefficient of thermal expansion (CTE) reflects how easily a material expands or contracts when heated. It is very important to clarify the thermal expansion coefficient of materials to further clarify the application environment. Prevent the failure of internal stress caused by expansion or contraction of assembly due to large temperature change. The CTE is given by

$$CTE = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)_p \tag{1}$$

where V_0 is the initial volume of the system (at 300 K), and V is the volume of the system at temperature T , and the pressure is 1 atm. The slope was obtained by fitting temperature-volume. Volume parameters at different temperatures are obtained in Sect. 3.1 simulate procedure. The CTE of each system in the glassy and rubbery states is shown in Fig. 4.

In essence, heat conduction is a process in which energy is transferred from the high temperature part of the object to the low temperature part, or from the high temperature object to the low temperature object, due to the collision of a large number of molecules in the material. The thermal conductivity reflects the degree of difficulty of the thermal conductivity of the material. The thermal conductivity parameter of crosslinking system was simulated by

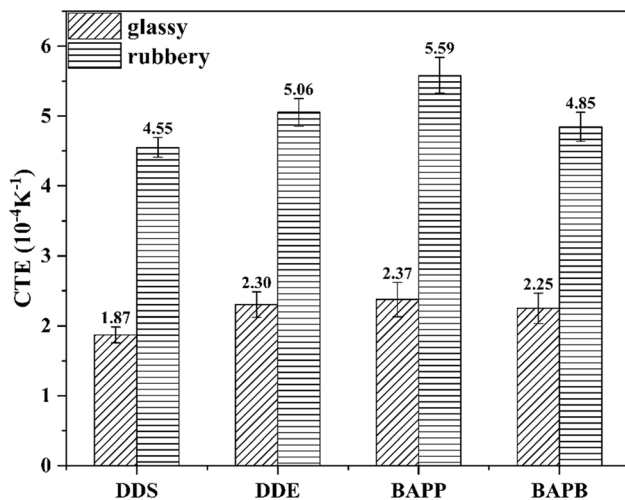


Figure 4 CTE of epoxy/amine curing system in the glassy and rubbery states.

Perl script. The system is divided into 10 parts in one direction (X, Y, or Z), and simulation time is 100 ps. The thermal conductivity of each system is shown in Fig. 5.

Different molecular structures of curing agents have little effect on thermal expansion coefficient and thermal conductivity of epoxy curing systems. The higher coefficient of thermal expansion and thermal conductivity of epoxy curing system can be obtained by filling metal micro-nano particles [40] and carbon nanomaterials [41].

Free volume

The actual polymer volume is much larger than the volume of all atoms contained in a polymer because of the limitations of packing density and constraints of intermolecular forces. Generally, the volume of a polymer contains two parts: the occupied and free volumes [42]. The free volume is an essential factor affecting the TM properties of polymer materials. Commonly, the increase in free volume aids the movement of molecular chain segments, and polymers can complete the transition from the glassy to rubbery states by a small temperature increase. In other words, the smaller the fraction free volume (FFV), the better the TM performance of a polymer, and vice versa. In this article, the Atom Volume & Surface tool in MS was used to obtain the free volume of the curing systems by Connolly surface, and the grid interval parameter was set to 0.2. The free

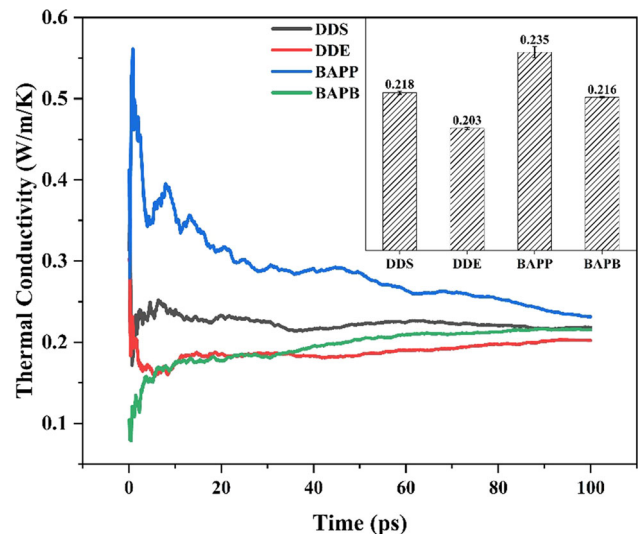


Figure 5 Thermal conductivity of different systems at room temperature (300 K).

volume of an epoxy resin system is shown in Fig. 6 (schematic of DGEBA/BAPP system), and the FFV (%) is shown in Table 1. The gray and blue regions indicate the free volume and the border of the free volume, respectively [43].

The FFV was inversely proportional to the density of the DDS, DDE, BAPB systems, but the presence of side groups in the phthalide cardo structure increased the stiffness of the BAPP system, which caused the FFV of the BAPP system to be slightly larger than that of the other systems. Moreover, the introduction of polar groups made the molecular structure of the curing systems more closely stacked with a larger physical density, for instance, the density of the DDS system was more than that of the DDE system. For non-bond energy, the Van der Waals energy of DDS was more negative, and the electrostatic energy of DDS was positive, which both indicated that the DDS system has higher stacking density.

In addition, the molecular spatial configuration was another factor affecting the free volume of the curing systems, e.g., the dihedral angle between the two benzene rings in the DDS system was larger than that in the DDE system, and the degree dihedral angle of DDS and DDE is 75.75° and 65.58° , respectively.

Glass transition temperature

The glassy and rubbery states can be transformed to one another with temperature increase or decrease. The temperature range corresponding to the two

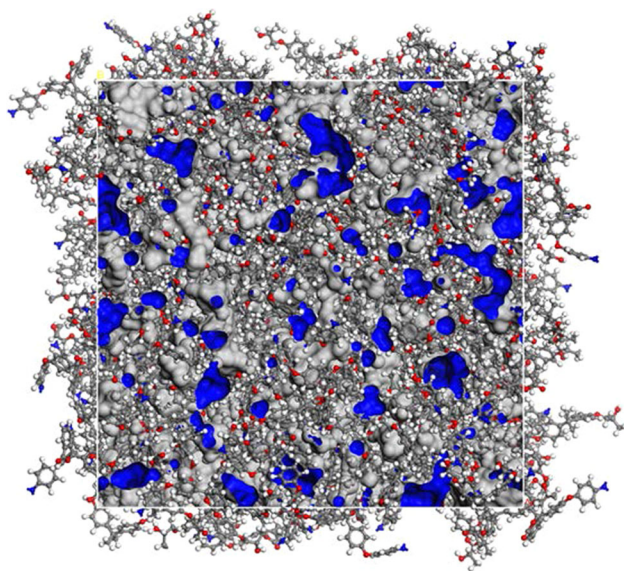


Figure 6 Free volume (gray part) of epoxy crosslinking system.

Table 1 FFV and density of epoxy/amine curing system

Properties	DDS	DDE	BAPB	BAPP
FFV (%)	16.85	17.17	17.87	18.31
Density (g/cm^3)	1.1775	1.1522	1.1468	1.1601

physical state changes is called the glass transition temperature (T_g); however, we generally regard the temperature corresponding to the maximum slope of the heat flow curve as T_g . Glass transition is always accompanied by changes in physical properties, such as specific volume, as well as thermal, mechanical, and electrical properties. Therefore, the T_g of an epoxy resin system is usually obtained by fitting temperature–volume or temperature–density in MD simulation [44–47]. An anneal simulation was conducted in the NPT ensemble at a cooling rate of 40 K/40 ps. The temperatures and densities of the models were output per 2000 steps for further thermal performance analysis. The densities corresponding to different temperatures and the fitting curves of the models are shown in Fig. 7. The piecewise function is used to fit the temperature–density data in Origin software.

There were approximately 12 orders of magnitude differences between simulation and experiment in the heating or cooling process. According to the Williams–Landell–Ferry equation [48], the difference in T_g between the simulation and experiment was approximately 22 K. The correction data of T_g are shown in Table 2.

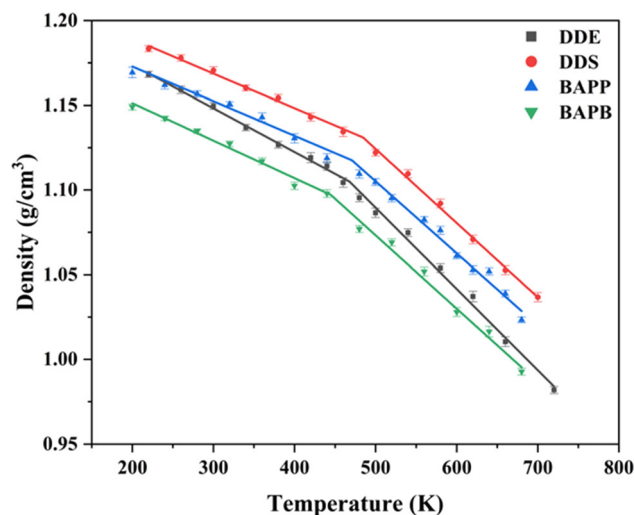


Figure 7 Densities corresponding to different temperatures and fitting curves of epoxy resin systems.

The simulation and experiment Tg values were close; the maximum difference was 8 K. Just as the results, generally, the Tg simulation results are slightly higher than the experiment data obtained from the literature (Table 2). Ring-opening polymerization reacted among high reactivity epoxides themselves during the experiment, resulting in an imperfect crosslinking structure; consequently, the experiment Tg value was slightly lower than the simulation Tg value. The simulation results reflected the reliability of MD in predicting the properties of polymers.

The linear chain molecules are DDE, DDS, and BAPB, whereas the BAPP molecule contains a side-chain group. For linear chain molecules, first, the molecular structure of DDS and DDE was almost the same, but their polar groups significantly differed, following the descending order of $-SO_2- > -O-$. This conclusion also applies to the BAPP and BAPB systems. The group polarity agreed with the Tg of the corresponding curing system. Second, the DDE and BAPB molecules had the same atomic species and molecular chain conformation, but the BAPB molecules had a longer molecular chain structure. From Table 2, the simulation results showed that the higher the molecular chain flexibility of the curing agent, the lower the Tg of the curing system [18–20].

For side-chain group molecules, in terms of molecular structure, BAPP was more like two DDE molecules linked by a phthalide cardo side-chain group structure. The angle was close to the vertical between the phthalide cardo structure plane and main chain plane, making it difficult to obtain a linear structure with a straight molecular chain. The introduction of phthalide cardo structure increases the rigidity of the polymer molecular chain and improves the heat resistance of the polymer [50]. Although a longer chain structure could weaken the Tg of a curing system to some extent [18, 52], the Tg of the BAPP system was slightly higher than that of the DDE system, indicating that the phthalide cardo structure improve the heat resistance of epoxy resin systems.

Table 2 Tg of epoxy/amine curing system

Crosslinking system	Simulation (K)	Correction (K)	Experiment (K)
DGEBA-DDS	484 ± 11	462 ± 11	457 [49]
DGEBA-BAPP	470 ± 19	448 ± 19	443 [50]
DGEBA-DDE	465 ± 14	443 ± 14	440 [51]
DGEBA-BAPB	446 ± 17	424 ± 17	–

The nonbond energy comprise of the electrostatic and Van der Waals interactions, which both have some certain influence on the TM properties of the crosslink system. The energy are shown in Table 3. For non-bond energy, the Van der Waals energy was more negative, and the electrostatic energy was positive, which both indicated that the distance of the atom or group was closer and the system has higher stacking density. The nonbond energy may be one of the more important factors affecting the Tg in the crosslink system.

Mechanical properties

In this article, the constant strain method was used to calculate the mechanical properties of epoxy resin systems; a 0.02 small strain was applied to the epoxy resin systems. For an isotropic material, the stiffness matrix can be described by only two independent coefficients. The simplified stiffness matrix can be expressed as follows:

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix} = \begin{bmatrix} \lambda + 2\mu & \lambda & \lambda & 0 & 0 & 0 \\ \lambda & \lambda + 2\mu & \lambda & 0 & 0 & 0 \\ \lambda & \lambda & \lambda + 2\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{bmatrix} \tag{2}$$

where λ and μ are the Lamé coefficients in matrix 1. For the isotropic case, the familiar elastic modulus E , bulk modulus K , and shear modulus G can be expressed in terms of the Lamé coefficients as follows:

$$E = \mu \left(\frac{3\lambda + 2\mu}{\lambda + \mu} \right) \tag{3}$$

Table 3 Energy of epoxy/amine curing system

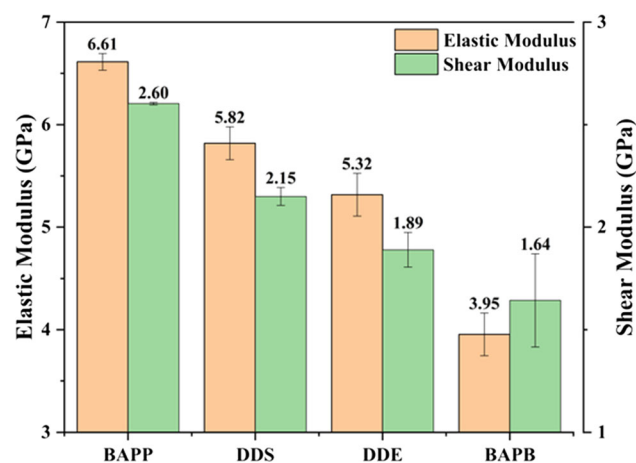
Energy (kcal/mol)	DDS	DDE	BAPB	BAPP
Van der waals	– 2487.25	– 2006.42	– 1024.06	– 2554.54
Electrostatic	4446.69	– 2763.01	– 4600.23	– 3451.95
Total cross terms	– 3342.37	– 3419.85	– 3520.68	– 6616.28

$$K = \lambda + \frac{2}{3\mu} \quad (4)$$

$$G = \mu \quad (5)$$

The mechanical properties of the epoxy/amine curing systems are shown in Fig. 8.

The simulation data of mechanical properties are shown in Table 4. The variation trend of mechanical properties basically agreed with that of Tg, except for the BAPP system. Not only atomic distance but chemical bond and atomic groups torsion parameter changed during tensile deformation, so it is possible more convincing to analyze the relationship between nonbond and total cross terms energy in Table 2 and mechanical properties of crosslink system. Total cross terms are almost equal of DDS, DDE, and BAPB system, but the stacking density of DDS is biggest, the smallest of BAPB, so, the modulus of DDS is biggest. On the other hand, the total cross terms of BAPP is more negative than that of DDS, which may be the one of the reasons that he modulus of BAPP is bigger than DDS. Notably, the performance of the curing system was not determined by a single factor. Although the molecular chain of BAPP was longer than those of DDS, DDE, and BAPB, the presence of side groups in the phthalide cardo structure increased the stiffness of the BAPP system and

**Figure 8** Modulus of epoxy/amine curing system.**Table 4** Modulus of epoxy/amine curing system

Properties	DDS	BAPP	DDE	BAPB
E (GPa)	5.82	6.61	5.32	3.95
G (GPa)	2.15	2.60	1.89	1.64
K (GPa)	3.97	3.93	3.67	4.89
K/G	1.85	1.51	1.94	2.98

entanglement of the 3D crosslinking model, thereby resulting in the superior mechanical properties of the BAPP system. The ratio of bulk modulus to shear modulus (K/G) can be used to characterize the toughness of a system; the higher the ratio, the tougher the system [53]. The ratio of the BAPP system was the smallest, which also indicated that the stiffness of the BAPP was higher.

Mean square displacement

Mean Square Displacement (MSD) analysis is a technique to determine the mode of displacement of particles over time. The MSD becomes linear during the particle diffusion process. Its slope defines the system diffusion coefficient D , shown in Eq. 7. The MSD can be obtained directly from the particle positions in MD simulation. The MSD calculation formula [54, 55] is as Eq. 6.

$$\text{MSD} = \frac{1}{3N} \sum_{i=1}^N \langle |\vec{R}_i(t) - \vec{R}_i(0)|^2 \rangle \quad (6)$$

$$D = \frac{1}{6} \lim_{\Delta t \rightarrow \infty} \frac{d\text{MSD}}{d\Delta t} \quad (7)$$

where are the position of the i -th atom at the instant t and the initial position, respectively; N is the total number of atoms in the epoxy/amine crosslinking system. The MSD curves of the four systems using 200-ps simulation at 300 K are shown in Fig. 9.

The MSD is agree with the FFV for BAPB and DDE system, and, The smaller the free volume, the harder of atoms to move. For BAPP, because of the introduction of phthalide cardo structure increasing the

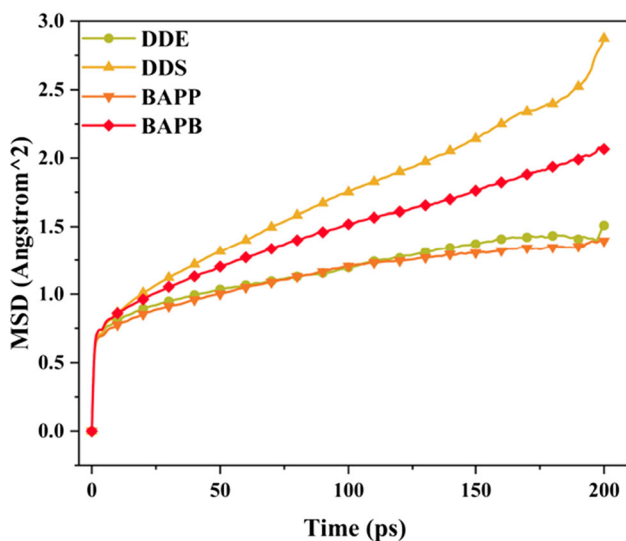


Figure 9 MSD of epoxy/amine curing systems.

rigidity of the polymer molecular chain and the existence of side-chain group making cross-linked network difficult to move, as a consequence, the MSD of BAPP is relatively small. It is interesting that the DDS system has Minimum FFV, but the MSD is biggest. We speculate that the possible reason is positive electrostatic energy which caused stronger intermolecular repulsion.

Conclusions

In this study, we investigated the Key Physical Properties and Microstructure of epoxy resin cured by different curing agents. The simulation results showed good consistency. First, the anisotropy of the material could be weakened with a large simulation size. Therefore, it was paramount to choose an appropriate simulation size for further simulations. Second, a slight difference in the molecular structure of curing agents significantly influenced the TM properties of the epoxy/amine curing system. Third, the influence of phthalide cardo structure side-chain groups on the TM properties of the epoxy resin systems was enormous. Conclusively, many factors can affect TM to some extent, such as molecular chain entanglement, group polarity, and side-chain groups, nonbond energy which have certain significance to accurately control the TM properties of epoxy resin systems by designing the molecular structure of curing agents; this will be a focus of our further studies.

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Declarations

Conflict of interest There are no conflicts to declare.

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