Chinese Journal of
POLYMER SCIENCE

ARTICLE

https://doi.org/10.1007/s10118-018-2114-y
Chinese J. Polym. Sci. 2018, 36, 991–998

Origin of Modulus Improvement for Epoxide-terminated Hyperbranched Poly(ether sulphone)/DGEBA/TETA Systems

Xue-Pei Miao[a*], Dao-Jian Cheng[b*], Ya-Dong Dai[c], Yan Meng[a,b], and Xiao-Yu Li[a,b*]

[a] *Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China*
[b] *State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China*
[c] *NeoTrident Technology Ltd (Beijing), Beijing 100190, China*

Electronic Supplementary Information

Abstract It has been experimentally shown that epoxide-terminated hyperbranched polyether sulphone (EHBPES) can significantly improve the mechanical properties of traditional diglycidyl ether of bisphenol A/triethylenetetramine (DGEBA/TETA) systems, but the origin of the improvement is still unclear. In this work, we used molecular dynamics (MD) simulations to gain a thorough understanding of the origin of modulus improvement for EHBPES/DGEBA/TETA systems. It is found that the modulus of EHBPES/DGEBA/TETA systems increases with the increase of EHBPES loading. In addition, the crosslinking density, cohesive energy density (CED), and free volume can be used to understand the modulus for EHBPES/DGEBA/TETA systems. It is shown that the highest modulus is achieved at 7 wt% EHBPES loading due to the highest crosslinking density and CED. When EHBPES loading is below 7 wt%, the higher CED and crosslinking density are responsible for the higher modulus. At higher loadings (> 7 wt%), the decreased modulus is closely related to the decreased crosslinking density and increased fractional free volume. It is expected that our results could be of great implications for designing high-performance epoxy materials.

Keywords Modulus; Molecular simulation; Epoxy resin

Citation: Miao, X. P.; Cheng, D. J.; Dai, Y. D.; Meng, Y.; Li, X. Y. Origin of Modulus Improvement for Epoxide-terminated Hyperbranched Poly(ether sulphone)/DGEBA/TETA Systems. Chinese J. Polym. Sci. 2018, 36(8), 991–998.

INTRODUCTION

Epoxy resin is a type of very important thermosetting resin and can be used in various applications due to their excellent properties, such as strong adhesion, low shrinkage and excellent electrical properties. With the increasing usage of epoxy resin in composite materials, epoxy resin with high mechanical properties is highly desired, but it still remains a challenge. Numerous research works have been focused on using additive to improve the mechanical properties of epoxy resin matrix[1−9]. Among various additives, hyperbranched polymer (HBP) is considered to be the most promising one due to its easy processing, low chain entanglements, abundant terminal groups which often prove useful for tuning compatibility, reactivity, and physical properties. Zhang and his coworkers[1−4] reported a series of epoxide-terminated HBPs with aromatic polyester backbones which could lead to the increase in toughness and strength. Jin and Park[5] reported a hyperbranched polyimide (HBPI) which could increase both the strength and toughness of diglycidyl ether of bisphenol A/diaminodiphenylmethane (DGEBA/DDM) system without forming phase separation and reducing glass transition temperature (T_g), and the optimum impact strength was achieved at 4 wt% HBPI. Our group reported several epoxide-terminated hyperbranched polymers[10−14] which could simultaneously improve toughness, tensile strength, elongation at break and T_g. It is worth noting that the optimum mechanical properties are always achieved at ~5 wt% HBP loading. This finding is very important for the design of higher performance composite material. However, the reason why the optimum mechanical properties are always achieved at ~5 wt% HBP loading still remains unclear. In addition, as the main factor of mechanical properties, the investigation on the modulus is still lacking. It is known that the whole curing process of epoxy resin system with hyperbranched polymers becomes much more difficult to study by experimental methods due to the more complex crosslinking process, which presents a big challenge for the design and prediction of high performance epoxy material. Therefore, it seems to be of great importance to get further understanding of the modulus for these complex systems (EHBPES/DGEBA/TETA systems) at a fundamental level in order to design new epoxy systems with higher performance.

---

* Corresponding authors: E-mail miaoxp@mail.buct.edu.cn (X.P.M)
E-mail chengdj@mail.buct.edu.cn (D.J.C)
E-mail lixy@mail.buct.edu.cn (X.Y.L.)

Received November 17, 2017; Accepted January 26, 2018; Published online April 13, 2018

Molecular dynamics (MD) simulation studies provide an effective means for aiding the understanding of the origin of the modulus improvement for these complex cured systems. Meanwhile, molecular simulation has become a particularly important and simple way to predict network formation and macroscopic properties[15−23]. Tam and Lau[16] proposed an effective dynamic cross-linking algorithm, which can be used to construct the SU-8 epoxy network with crosslinking degree higher than 80%. Results showed that the calculated mechanical properties are in good agreement with the various experimental studies. Khare and coworkers[17] investigated the volumetric and thermal properties of crosslinked epoxy systems consisting of diglycidyl ether of bisphenol A (DGEBA) and poly(oxypropylene) (POP) diamines of four different lengths ranging from 3 units to 68 units by MD simulations. Li and Strachan[18] studied EPON862/DETDA epoxy system and predicted significant enhancement in T_g, stiffness and yield stress with conversion. Tsige and Stevens[19] investigated the effect of cross-linker functionality and interfacial bond density on the fracture behavior of highly crosslinked polymer networks bonded to solid surface through large-scale molecular dynamics simulations. Qu and Yang[20] reported the effectiveness of molecular dynamic simulations to study the thermomechanical properties of an epoxy molding compound formed by curing tri/tetra-functionalized EPN1180 with Bisphenol-A. The research works discussed above have proven that MD simulation is an effective method for investigating the structure-property relationships of cured epoxy resin. To our best knowledge, no simulation work has been focused on using hyperbranched polymer as additive to improve the modulus of epoxy resin. Therefore, understanding of the origin of the modulus improvement for these complex systems (EHBPES/DGEBA/TETA systems) by MD simulation is necessary.

In the present study, we conduct MD simulations to investigate the epoxy resin system including epoxy resin DGEBA, EHBPES, and TETA (as curing agent). Several properties such as T_g, Young's modulus, bulk modulus, shear modulus, and Poisson's ration are investigated. Meanwhile, effects of EHBPES loading on modulus are systematically studied. The origin of modulus improvement for EHBPES/DGEBA/TETA system is investigated by analyzing how the crosslinking density, intermolecular interaction and free volume affect the modulus of cured epoxy resin.

MODELING AND SIMULATION METHODOLOGY

Molecular Structures

In this simulation work, DGEBA was chosen as epoxy, hyperbranched polymer EHBPES as additive and TETA as curing agent. Their chemical structures are shown in Fig. 1. TETA has six end-groups and is capable of reacting with six epoxide groups at most. DGEBA has two epoxide groups. EHBPES has eight epoxide groups according to GPC and epoxy value titration results[13].

Simulation Methods

All simulation works were carried out using Material Studio software v6.0 (Accelrys Inc., USA). The Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force-field was employed in all simulations works, which is very effective in predicting polymer performances[24, 25]. Epoxy resin and stoichiometric ratio of curing agent molecules were packed into a cubic periodic simulation cells at 300 K through the use of the Amorphous Cell module with the initial density of 1.1 g/cm^3, which is a typical value for epoxy system. The total amount of atoms in the studied EHBPES/DGEBA/TETA systems is approximately 1.15×10^4–1.3×10^4 atoms. The mass fractions of EHBPES are 3 wt%, 5 wt%, 7 wt%, 10 wt% (based on total weight of DGEBA), respectively. The study on free volume was carried out by using the "Atom Volume & Surfaces" tool in Materials Studio software.

Crosslinking simulation

The uncrosslinked epoxy system was equilibrated in the isothermal and isochoric ensemble (NVT) at 300 K for 500 ps, then was equilibrated in the isothermal and isobaric ensemble (NPT) at 300 K and 0.1 MPa for another 1 ns to obtain a full equilibration of temperature and density, respectively. The corresponding integration time step is 1 fs. Geometry optimization was conducted before and after equilibration. During the dynamic equilibration process, temperature and pressure were controlled by Nose-Hoover thermostat and Berendsen barostat, respectively. The minimum cutoff distance and maximum cutoff distance were set to be 3.0 and 8.0 Å, respectively. Once the uncrosslink systems were equilibrated, the crosslinking procedure was performed, which is fully described in Ref. [26]. And the

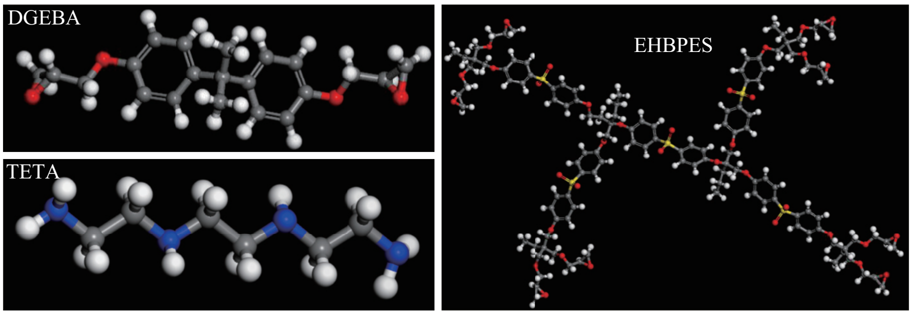

Fig. 1 Chemical structures of DGEBA, TETA, and EHBPES (Red, blue, white, gray, and yellow ball represent oxygen, nitrogen, hydrogen, carbon, and sulphur atom, respectively.)

detailed crosslinking procedure is shown in the flowchart in Fig. S1 (in electronic supplementary information, ESI). It should be mentioned here that all of the epoxy systems were crosslinked under the same simulation condition.

Annealing simulation

The crosslinked epoxy systems obtained above firstly experienced an equilibration for 1 ns at 600 K in NPT ensemble, in which temperature and pressure were adjusted by the Nose-Hoover thermostat and Berendsen barostat, then experienced an annealing simulation, and detailed annealing procedures are described below. Crosslinked epoxy system was cooled down from 600 K to 300 K with a cooling rate of 20 K/200ps, and simulated *via* MD simulations, for 0.2 ns at each temperature point. The average density at each temperature point was calculated based on the trajectory generated at each temperature.

Mechanical properties calculation

Mechanical properties can be calculated by static (constant-strain minimization), fluctuation formula, and dynamics (constant-stress MD), by MD simulations[27]. In this study, the static method was used to calculate elastic constants of these crosslinked epoxy networks. The stress-strain behavior in linear elastic materials can be described by Hook's law:

$$\sigma_i = C_{ij}\varepsilon_j \tag{1}$$

where, $i, j = 1, 2, 3$. σ_i and ε_j are stress and strain vectors, respectively, and C_{ij} is 6-dimentional stiffness matrix. The system was strained with triaxial extension, and the maximum strain amplitude in this calculation was set to be 0.003. The stress components were calculated using the so-called virial expression[28]:

$$\sigma_{ij} = -\frac{1}{V}\sum_{k}\left[m^{\mathrm{k}}\left(u_i^{\mathrm{k}}u_i^{\mathrm{k}}\right)+\frac{1}{2}\sum_{l\neq k}\left(r_i^{\mathrm{kl}}\right)f_j^{\mathrm{lk}}\right] \tag{2}$$

where V is the volume; m^{k} and u^{k} stand for the mass and velocity of the k^{th} particle, respectively; r^{kl} is the distance between k^{th} and l^{th} particles, and f^{lk} denotes the force exerted on the l^{th} particle by the k^{th} particle. Given the static conditions, the first term on the right hand side was omitted. The elastic modulus was then obtained by the first derivative of the virial stress equations regarding the strain, $\partial\sigma/\partial\varepsilon$. In other words, the full 6 × 6 stiffness matrix was formed from the slopes of $\partial\sigma/\partial\varepsilon$ in tension and shear[29].

Lamé coefficients λ and μ can be calculated by the following equations[30]:

$$\lambda = \frac{1}{6}(C_{12}+C_{13}+C_{21}+C_{23}+C_{31}+C_{32}) \approx \frac{1}{3}(C_{12}+C_{23}+C_{13}) \tag{3}$$

$$\mu = \frac{1}{3}(C_{44}+C_{55}+C_{66}) \tag{4}$$

$$\lambda + 2\mu = \frac{1}{3}(C_{11}+C_{22}+C_{33}) \tag{5}$$

The other elastic modulus and properties can be calculated from the above coefficients:

$$E = \frac{\mu(3\lambda+2\mu)}{\lambda+\mu} \tag{6}$$

$$K = \lambda + \frac{2}{3}\mu \tag{7}$$

$$G = \mu \tag{8}$$

$$\upsilon = \frac{\lambda}{2(\lambda+\mu)} \tag{9}$$

where E, K, and G is Young's, bulk, and shear moduli, respectively; υ illustrates the Poisson's ratio.

RESULTS AND DISCUSSION

Modeling Certification

In order to confirm the validity of the model structures, the crosslinked structure and glass transition temperature of cured epoxy system obtained in our molecular simulations were compared with simulation works or experimental values. Detailed analysation about the crosslinked structure and glass transition temperature are given below.

Crosslinked structure

The crosslinked structure for EHBPES/DGEBA/TETA system at 7 wt% EHBPES loading is shown in Fig. S2 (in ESI), and the ultimate conversion degree for EHBPES/DGEBA/TETA system is 84%, which agrees well with other simulation works[31]. Fig. 2 shows the snapshot of atomistic configuration of EHBPES/DGEBA/TETA system containing 7 wt% EHBPES with different conversion degrees. It is clear that crosslink points increase with the increase of conversion

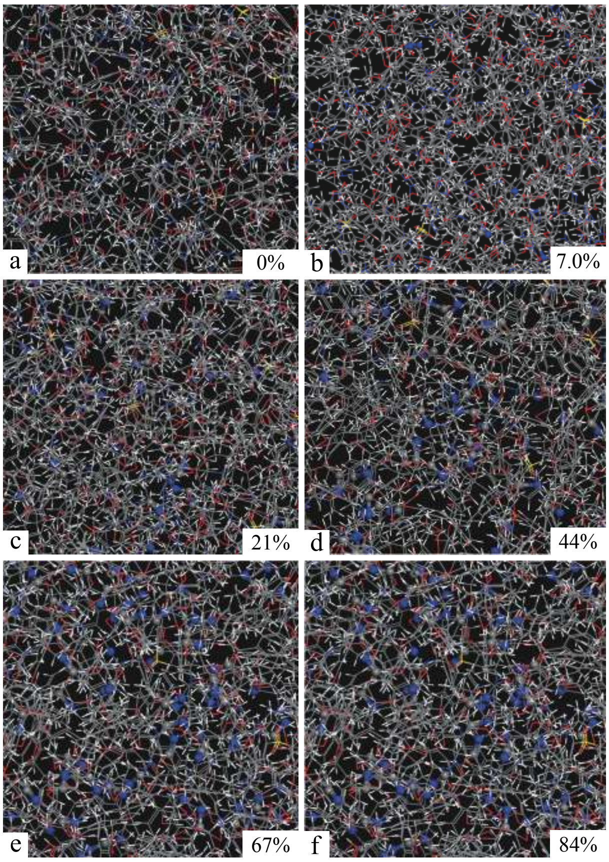

Fig. 2 Snapshot of atomistic configuration of EHBPES/DGEBA/TETA system containing 7 wt% EHBPES with different conversion degrees (Crosslink points are reprsented by the ball-stick.)

https://doi.org/10.1007/s10118-018-2114-y

degree, and crosslink points distribute uniformly in the cured epoxy network, which indicates a good crosslink result obtained by using the models established in this work.

Glass transition temperature

T_g is one of the important thermal properties of epoxy polymers, and T_g can be determined by using several experimental methods, such as differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermomechanical analysis (TMA). Recently, atomistic MD simulations have been widely used to predict T_g values of specific systems based on established cross-linking models[32−36]. T_g can be estimated from either the density-temperature plot or volume-temperature plot. In our simulation works, density-temperature plot was used to predict T_g and the results are displayed in Table 1 and Fig. 3. Fig. 3 plots the comparison of experimental and simulated T_g. Comparing the T_g obtained by MD simulation with the experimental values, the simulation values are higher than experimental ones, which can be explained by the relatively faster cooling rate (20 K/200ps) in simulation. It can be found that T_g increases with the increasing of EHBPES loading. EHBPES/DGEBA/TETA system with 10 wt% EHBPES shows the highest T_g, which is 19.2 °C higher than that of EHBPES/DGEBA/TETA system with 0 wt% EHBPES, indicating that EHBPES has a positive effect on the T_g of EHBPES/DGEBA/TETA system. It has to be stressed that the simulation values and the experimental values show nearly the same trend. This consistency proves the validity of the atomistic models.

Table 1 Conversion degree of EHBPES/DGEBA/TETA epoxy systems

EHBPES content	Conversion degree (%)	T_g (K)	
		Experiment (Ref. [13])	Simulation
0 wt%	73	419.35	440.35 ± 5.5
3 wt%	78	426.45	449.89 ± 6.3
5 wt%	81	436.25	457.67 ± 4.1
7 wt%	84	–	464.55 ± 3.5
10 wt%	80	438.55	466.78 ± 5.7

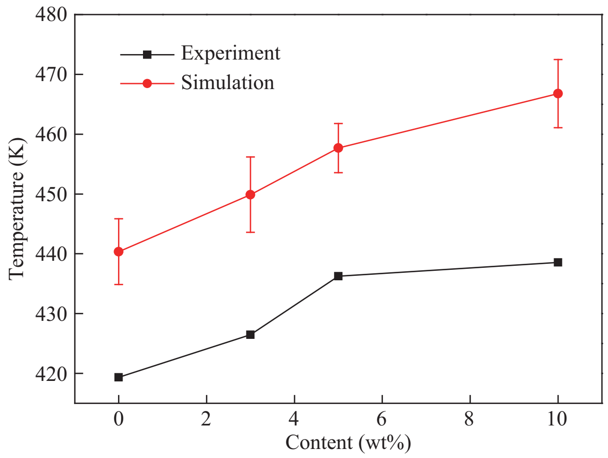

Fig. 3 The comparison of experimental and simulated T_g

Effects of EHBPES Loading on Modulus

In order to understand the origin of modulus improvement for EHBPES/DGEBA/TETA systems, we investigate the effects of EHBPES loading on the modulus of cured epoxy system. The estimated moduli of epoxy systems containing different EHBPES loading are listed in Table 2. It can be found that modulus of EHBPES/DGEBA/TETA system has a strong dependence on EHBPES content. Young's, bulk and shear moduli all increase first and then decrease with the increase of EHBPE loading. The highest modulus is achieved at 7 wt% EHBPES loading. Compared with the EHBPES/DGEBA/TETA system with 0 wt% system, Young's, bulk and shear moduli of the EHBPES/DGEBA/TETA system with 7 wt% EHBPES show 24.5%, 83.9%, and 20.3% increase, respectively. This indicates that EHBPES can significantly improve the moduli of the EHBPE/DGEBA/TETA system. In addition, it can be found that the value of Poisson's ratio of EHBPES/DGEBA/TETA systems is in the range of 0.3 to 0.36, which is a typical range for epoxy resin. With the increase of EHBPES, Poisson's ratio shows an increasing trend. Generally, the reduction of Poisson's ratio can be used as a damage index[37, 38]. Thus, it can also be predicted that the incorporation of EHBPES is beneficial for the mechanical performance, especially for the modulus of EHBPES/DGEBA/TETA system. It is worth noting that these simulation results show good agreement with the experimental results. This agreement offers a good guidance on the origin of the modulus improvement for EHBPES/DGEBA/TETA systems.

In our previous studies[12−14], when the loading is low, tensile and impact strength increase with the increase of EHBPES loading. The possible explanation we have offered is the increase of crosslinking density due to the higher overall reactivity of terminal epoxy groups of EHBPES. At higher loadings of EHBPES (10 wt% and 15 wt%), tensile and impact strength decrease with the increase of EHBPE loading, and the possible explanation is incomplete cure due to steric hindrance effects caused by the unreacted terminal epoxide groups at excessive loading. It is believed that crosslinking density, intermolecular interaction and fractional free volume of the polymer networks can affect the modulus of epoxy systems. In general, epoxy systems with higher crosslinking density, higher intermolecular interaction and lower free volume show a higher modulus. In order to

Table 2 Modulus of EHBPES/DGEBA/TETA system

	EHBPES content				
	0 wt%	3 wt%	5 wt%	7 wt%	10 wt%
Young's modulus (GPa)	4.08 ± 0.42	4.51 ± 0.58	4.76 ± 0.61	5.08 ± 0.62	5.04 ± 0.65
Bulk modulus (GPa)	3.12 ± 0.63	3.57 ± 0.56	4.46 ± 0.52	5.74 ± 0.59	4.17 ± 0.60
Shear modulus (GPa)	1.53 ± 0.51	1.99 ± 0.51	1.74 ± 0.60	1.84 ± 0.57	1.82 ± 0.55
Poisson's ratio	0.30 ± 0.05	0.29 ± 0.03	0.33 ± 0.03	0.36 ± 0.04	0.36 ± 0.05

https://doi.org/10.1007/s10118-018-2114-y

understand the origin of modulus improvement of the EHBPES/DGEBA/TETA system, crosslinking density, intermolecular interaction and fractional free volume of the EHBPES/DGEBA/TETA system are systematically investigated in the following part.

Understanding the Origin of Modulus Improvement

Crosslinking density

In order to understand how the crosslinking density affects the modulus of the EHBPES/DGEBA/TETA system, we will discuss the relationship between crosslinking density and modulus in this section. Generally, crosslinking density can be defined as the number of effective crosslinks per unit volume. It is dependent on the number of reactive sites (functionality), the molecular distance and chain mobility between functional sites, and the percentage of these sites that enter into reaction. Degree of conversion is expressed as the percentage of the conversion of reactive species (atoms). It is clear to see that degree of conversion and crosslinking density are directly related to each other. The higher the degree of conversion, the higher the crosslinking density. Therefore, relationship between crosslinking density and modulus can be roughly replaced by relationship between conversion degree and modulus. It is believed that modulus increases with increasing crosslinking density. In order to investigate such dependence on crosslinking density, we calculate the modulus of the EHBPES/DGEBA/TETA system with 7 wt% EHBPES at different conversion degrees and the results are shown in Fig. 4 and Table S1 (in ESI). As shown in Fig. 4, Young's, bulk, and shear moduli all increase with increasing conversion degree, proving that crosslinking density has a strong positive correlation to the modulus of the EHBPES/DGEBA/TETA system within the scope of our study.

For the EHBPES/DGEBA/TETA systems with different EHBPES loading, effects of crosslinking density on modulus are also investigated. Comparison of the ultimate conversion degree of EHBPES/DGEBA/TETA systems with different EHBPES loading is given in Table 1 and Fig. S3 (in ESI). As shown in Table 1, the conversion degree increases first then decreases with increasing EHBPES loading, and the highest conversion degree is achieved at 7 wt% EHBPES loading. Interestingly, these results agree quite well with the modulus results. It means the higher the crosslinking density, the higher the modulus. Therefore, it can be predicted that the increased crosslinking density contributes to the improved modulus of the EHBPES/DGEBA/TETA systems.

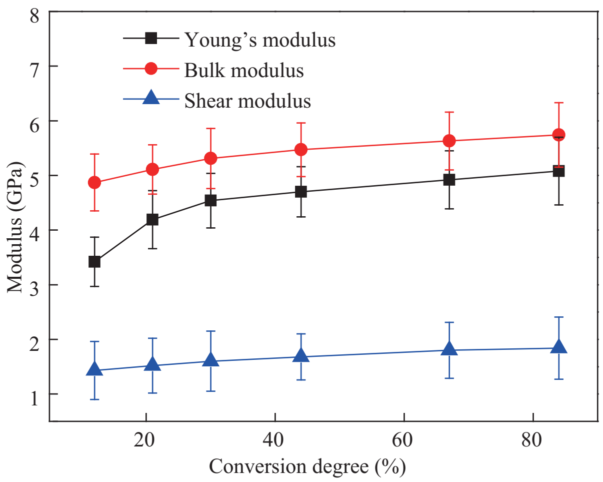

Fig. 4 Young's, bulk and shear moduli of EHBPES/DGEBA/TETA system as a function of conversion degree

Cohesive energy density (CED)

The cohesive energy of a system of molecules, E_{coh}, is the average energy required to separate all molecules to infinite distance from each other. The cohesive energy density, CED, is simply the cohesive energy per unit of volume. The cohesive energy density is calculated by the following equation:

$$\mathrm{CED} = E_{\mathrm{coh}}/V \tag{10}$$

$$< E_{\mathrm{coh}} > = < E_{\mathrm{inter}} > = < E_{\mathrm{total}} > - < E_{\mathrm{intra}} > \tag{11}$$

where E_{inter} is the total energy between all molecules, which is the total energy of a system, E_{total}, minus the intramolecular energy, E_{intra}. The brackets <...> represent an average over a NPT or NVT ensemble.

Cohesive energy density is commonly used to characterize the intermolecular interaction. Generally, the larger CED value reflects the larger intermolecular interaction[39, 40]. It is believed that the cohesive energy density can also significantly affect the modulus. The small cohesive energy density can result in low modulus. Therefore, in order to understand the effect of CED on the modulus, we calculated the CED of EHBPES/DGEBA/TETA system. CED of all EHBPES/DGEBA/TETA systems are presented in Table 3. It can be found that the EHBPES/DGEBA/TETA system with 0 wt% EHBPES loading shows the lowest CED, indicating that the intermolecular interaction forces of EHBPES/DGEBA/TETA system with higher EHBPES loading (> 3 wt%) are higher than that of the EHBPES/DGEBA/TETA system with 0 wt% EHBPES loading. In addition, CED of the EHBPES/DGEBA/TETA system increases with EHBPES loading, indicating that the EHBPES/DGEBA/TETA system with higher EHBPES loading has higher intermolecular interaction force. The stronger intermolecular interaction force of EHBPES/DGEBA/TETA system limits the chain segment motion, so the EHBPES/DGEBA/TETA system with higher CED could show higher modulus. However, as discussed before, the modulus decreases with increasing EHBPES at higher EHBPES loading (10 wt%). Besides CED, it is believed that other factors such as free volume and crosslinking density also affect the modulus. Thus, it can be predicted that effects of crosslinking density and free volume on modulus may override the contribution of CED, and result in a low modulus at higher EHBPES loading (10 wt%).

Free volume

It is believed that the fractional free volume exhibits a close relationship with the mechanical properties and chemical

Table 3 Cohesive energy density of the EHBPES/DGEBA/TETA system

	EHBPES content				
	0 wt%	3 wt%	5 wt%	7 wt%	10 wt%
CED (J/cm^3)	239.8	241.2	242.4	284.7	296.4

https://doi.org/10.1007/s10118-018-2114-y

structure of polymers in glassy state. An increase in free volume can enhance the toughness of epoxy resins[13], while decrease in free volume can induce a higher modulus due to the weak mobility of molecular chains. It should be stressed that free volume also has a strong dependence on the crosslinking density. When the crosslinking density is lower, the crosslinking favors the packing of molecule, thereby causes a lower free volume. When the crosslinking density is higher, 3D network formed by crosslinking will limit the packing of molecule, thus the free volume will increase with crosslinking density. However, when it exceedes a critical crosslinking density, the free volume will decrease with the increase of crosslinking density.

In order to understand the relationships between the fractional free volume and the crosslinking density, we calculated the fractional free volume of EHBPES/DGEBA/TETA system with different conversion degrees. Taking the EHBPES/DGEBA/TETA system with 7 wt% EHBPES loading as an example, fractional free volumes of the EHBPES/DGEBA/TETA system with different conversion degrees are shown in Table S2 (in ESI). It can be found that when the conversion degree is lower than 30%, the free volume decreases from 14.99% to 14.02%; at 67% conversion degree, the free volume increases from 14.02% to 14.71%; however, at higher conversion degree (84%), the free volume decreases from 14.71% to 14.15%. Occupied volume (V_t – V_f) decreases with the increasing conversion degree. And fractional free volume shows the same trend with free volume, indicating that fractional free volume has a strong dependence on the crosslinking density.

In order to understand how the fractional free volume affects the modulus of EHBPES/DGEBA/TETA systems, the fractional free volume of EHBPES/DGEBA/TETA systems with different EHBPES loading are investigated and the results are given in Table 4 and ploted in Fig. 5. For cured system, it can be found that the fractional free volume of the system with higher EHBPES loading (> 3 wt%) is higher than that of the one without EHBPES, indicating that the incorporation of EHBPES could increase the fractional free volume of the system. It has been reported that addition of HBPs can increase the fractional free volume of epoxy system due to the internal cavities nearby the branching points inside the HBPs[9, 41]. In order to understand the effects of EHBPES loading on the fractional free volume of EHBPES/DGEBA/TETA system, we also calculated the fractional free volume of uncrosslinked EHBPES/DGEBA/TETA system and the results are also shown in Table 4. It can be found that the fractional free volumes of uncrosslinked EHBPES/DGEBA/TETA systems with higher EHBPES loading (> 3 wt%) are higher than that of the uncrosslinked EHBPES/DGEBA/TETA system with 0 wt% EHBPES loading, indicating that the incorporation of EHBPES can indeed increase the fractional free volume of the EHBPES/DGEBA/TETA system.

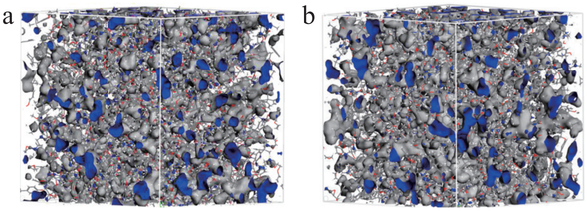

Fig. 5 The image of free volume of the unit cells: (a) EHBPES/DGEBA/TETA with 0 wt% EHBPES loading and (b) EHBPES/DGEBA/TETA 7 wt% EHBPES loading (The blue area represents the free volume.)

Besides the internal cavities, it is believed that the increased distance between crosslink points also contributes to the increase of fractional free volume due to the larger molecular weight of EHBPES. As stated, the EHBPES/DGEBA/TETA system with higher fractional free volume will result in a lower modulus. Thus, when EHBPES loading is below 7 wt%, it is predicted that fractional free volume has little contribution to the increased modulus because the effect from other factors such as CED and crosslinking density on modulus overrides the contribution of fractional free volume to the modulus; however, at higher EHBPES loading, the increased fractional free volume contributes much more to the decreased modulus.

Table 4 The fractional free volume of EHBPES/DGEBA/TETA systems

		EHBPES content				
		0 wt%	3 wt%	5 wt%	7 wt%	10 wt%
Before crosslinking	Free volume V_f (Å^3)	33787.82	35567.97	36828.79	37968.54	40695.02
	Total volume V_t (Å^3)	135706.90	133452.09	137821.41	141405.54	150443.68
	$f \times 100\%$	24.90	26.65	26.72	26.85	27.05
After crosslinking	Free volume V_f (Å^3)	13668.61	14535.13	18098.05	19138.28	21011.27
	Total volume V_t (Å^3)	111915.01	114169.75	127942.04	128272.67	136083.38
	$f \times 100\%$	12.21	12.73	14.15	14.92	15.44

CONCLUSIONS

In this study, molecular dynamics (MD) simulation has been used to study the origin of modulus improvement of EHBPES/DGEBA/TETA systems. The results obtained from our MD simulation provide a full understanding. Effects of EHBPES loading on the modulus of EHBPES/DGEBA/TETA system indicate that EHBPES has a positive influence on the modulus of the EHBPES/DGEBA/TETA system, which increases with the increasing EHBPES loading. Accordingly, the crosslinking density, cohesive energy density (CED), and free volume can be used to understand the modulus for EHBPES/DGEBA/TETA systems. It is found that the highest modulus is achieved at 7 wt% EHBPES loading, which can be attributed to its higher crosslinking density and CED. When the EHBPES loading is below 7 wt%, it is predicted that crosslinking density and CED contribute to the increased modulus. However, at higher loadings (> 7 wt%), the increased fractional free volume and decreased crosslinking density contribute a lot to the decreased modulus. From the above analysis, we believe that our results can be useful for designing high-performance epoxy materials.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-018-2114-y.

ACKNOWLEDGMENTS

This work was financially supported by CHEMCLOUD-COMPUTING and the National Natural Science Foundation of China (No. 51173012).

REFERENCES

1 Zhang, D.; Chen, Y.; Jia, D. Toughness and reinforcement of diglycidyl ether of bisphenol-A by hyperbranched poly(trimellitic anhydride-butanediol glycol) ester epoxy resin. Polym. Compos. 2010, 30(7), 918−925.

2 Zhang, D.; Jia, D. Toughness and strength improvement of diglycidyl ether of bisphenol-A by low viscosity liquid hyperbranched epoxy resin. J. Appl. Polym. Sci. 2010, 101(4), 2504−2511.

3 Chen, S.; Zhang, D.; Jiang, S.; Jia, D. Preparation of hyperbranched epoxy resin containing nitrogen heterocycle and its toughened and reinforced composites. J. Appl. Polym. Sci. 2012, 123(6), 3261−3269.

4 Zhang, D.; Wu, H.; Li, T.; Zhang, A.; Peng, Y.; Jing, F. Preparation of high-performance flame-retardant hybrid material by hyperbranched polyphosphate ester. Polym. Compos. 2011, 32(1), 36−43.

5 Jin, F. L.; Park, S. J. Thermal properties and toughness performance of hyperbranchedpolyimidemodified epoxy resins. J. Polym. Sci., Part B: Polym. Phys. 2006, 44(23), 3348−3356.

6 Gan, W.; Zhan, G.; Wang, M.; Yu, Y.; Xu, Y.; Li, S. Rheological behaviors and structural transitions in a polyethersulfone-modified epoxy system during phase separation. Colloid. Polym. Sci. 2007, 285(15), 1727−1731.

7 Pillai, J. P.; Pionteck, J.; Häβbler, R.; Sinturel, C.; Mathew, V. S.; Thomas, S. Effect of cure conditions on the generated morphology and viscoelastic properties of a poly(acrylonitrile-butadiene-styrene) modified epoxy-amine system. Ind. Eng. Chem. Res. 2012, 51(6), 2586−2595.

8 Nguyen, F. N.; Berg, J. C. Novel core-shell (dendrimer) epoxy tougheners: Processing and hot-wet performance. Composites. Part A 2008, 39(6), 1007−1011.

9 Gao, C.; Yan, D. Hyperbranched polymers: from synthesis to applications. Prog. Polym. Sci. 2004, 29(3), 183−275.

10 Lv, J.; Meng, Y.; He, L.; Qiu, T.; Li, X.; Wang, H. Novel epoxidized hyperbranched poly(phenylene oxide): synthesis and application as a modifier for diglycidyl ether of bisphenol A. J. Appl. Polym. Sci. 2013, 128(1), 907−914.

11 Luo, L.; Meng, Y.; Qiu, T.; Li, Z.; Yang, J.; Cao, X.; Li, X. Dielectric and mechanical properties of diglycidyl ether of bisphenol a modified by a new fluoro-terminated hyperbranched poly(phenylene oxide). Polym. Compos. 2013, 34(7), 1051−1060.

12 Miao, X.; Meng, Y.; Li, X. Epoxide-terminated hyperbranched polyether sulphone as triple enhancement modifier for DGEBA J. Appl. Polym. Sci. 2015, 132(17), 41910−41920.

13 Miao, X.; Meng, Y.; Li, X. A novel all-purpose epoxy-terminated hyperbranched polyether sulphone toughener for an epoxy/amine system. Polymer 2015, 60, 88−95.

14 Liu, T.; Nie, Y.; Zhang, L.; Chen, R.; Meng, Y.; Li, X. Dependence of epoxy toughness on the backbone structure of hyperbranched polyether modifiers. RSC Adv. 2015, 5(5), 3408−3416.

15 Komarov, P. V.; Chiu, Y, T, C.; Chen. S. M; Khalatur, P. G.; Reineker, P. Highly cross-linked epoxy resins: an atomistic molecular dynamics simulation combined with a mapping/reverse mapping procedure. Macromolecules 2007, 40(22), 8104−8113.

16 Tam, L.; Lau, D. A molecular dynamics investigation on the cross-linking and physical properties of epoxy-based materials. RSC Adv. 2014, 4(62), 33074−33081.

17 Soni, N. J. Lin, P. H.; Khare, R. Effect of cross-linker length on the thermal and volumetric properties of cross-linked epoxy networks: A molecular simulation study. Polymer 2012, 53(4), 1015−1019.

18 Li, C.; Strachan, A. Molecular dynamics predictions of thermal and mechanical properties of thermoset polymer EPON862/DETDA. Polymer 2011, 52(13), 2920−2928.

19 Tsige, M.; Stevens, M. J. Effect of cross-linker functionality on the adhesion of highly cross-linked polymer networks: a molecular dynamics study of epoxies. Macromolecules 2004, 37(3), 630−637.

20 Yang, S.; Qu, J. Computing thermomechanical properties of crosslinked epoxy by molecular dynamic simulations. Polymer 2012, 53(21), 4806−4817.

21 Shudo, Y.; Izumi, A.; Hagita, K.; Nakao, T.; Shibayama, M. Structure-mechanical property relationships in crosslinked phenolic resin investigated by molecular dynamics simulation. Polymer 2017, 116, 506−514.

22 Tam, L. H.; Lau, D. Moisture effect on the mechanical and interfacial properties of epoxy-bonded material system: An atomistic and experimental investigation. Polymer 2015, 57, 132−142.

23 Vo, V. S.; Nguyen, V. H.; Mahouche-Chergui, S.; Carbonnier, B.; Tommaso, D. D.; Naili, S. From atomistic structure to thermodynamics and mechanical properties of epoxy/clay nanocomposites: Investigation by molecular dynamics simulations. Comp. Mater. Sci. 2017, 139, 191−201.

24 Zhang, Q. G.; Liu, Q. L.; Huang, S. P.; Hu, W. W.; Zhu, A. M. Microstructure-related performances of poly(vinyl alcohol)-silica hybrid membranes: a molecular dynamics simulation study. J. Mater. Chem. 2012, 22(21), 10860−10866.

25 Yu, B.; Fu, S.; Wu, Z.; Bai, H.; Ning, N.; Fu, Q. Molecular dynamics simulations of orientation induced interfacial enhancement between single walled carbon nanotube and aromatic polymers chains. Composites Part A 2015, 73, 155−165.

26 Li, K.; Huo, N.; Liu, X.; Cheng, J.; Zhang, J. Effects of the furan ring in epoxy resin on the thermomechanical properties of highly cross-linked epoxy networks: a molecular simulation study. RSC Adv. 2015, 6(1), 769−777.

27 Shokuhfar, A.; Arab, B. The effect of cross linking density on the mechanical properties and structure of the epoxy polymers: molecular dynamics simulation. J. Mol. Model. 2013, 19(9), 3719−3731.

28 Jeyranpour, F.; Alahyarizadeh, G.; Arab, B. Comparative investigation of thermal and mechanical properties of cross-linked epoxy polymers with different curing agents by molecular dynamics simulation. J. Mol. Graph. Model. 2015, 62, 157−164.

29 Wu, C.; Xu, W. J. Atomistic molecular modelling of crosslinked epoxy resin. Polymer 2006, 47(16), 6004−6009.

30 Arab, B.; Shokouhfar, A. Molecular dynamics simulation of

cross-linked urea-formaldehyde polymers for self-healing nanocomposites: prediction of mechanical properties and glass transition temperature. J. Mol. Model. 2013, 19(11), 5053−5062.

31 Zhang, W.; Yang, Q.; Zhong, W.; Sui, G.; Yang, X. Mechanism of modulus improvement for epoxy resin matrices: A molecular dynamics simulation. React. Funct. Polym. 2017, 111, 60−67.

32 Gao, L.; Zhang, Q.; Li, H.; Yu, S.; Zhong, W.; Sui, G.; Yang, X. Effect of epoxy monomer structure on the curing process and thermo-mechanical characteristics of tri-functional epoxy/amine systems: a methodology combining atomistic molecular simulation with experimental analyses. Polym. Chem. 2017, 8, 2016−2027.

33 Shenogina, N. B.; Tsige, M.; Patnaik, S. S.; Mukhopadhyay, S. M. Molecular modeling approach to prediction of thermo-mechanical behavior of thermoset polymer networks. Macromolecules 2012, 45(12), 5307−5315.

34 Yang, Q.; Yang, X.; Li, X.; Shi, L.; Sui, G. The curing and thermal transition behavior of epoxy resin: a molecular simulation and experimental study. RSC Adv. 2013, 3(20), 7452−7459.

35 Wang Z.; Lv, Q.; Chen, S.; Li, C.; Sun, S.; Hu, S. Effect of interfacial bonding on interphase properties in SiO_2/epoxy nanocomposite: a molecular dynamics simulation study. ACS Appl. Mater. Interfaces. 2016, 8(11), 7499−7508.

36 Bhadra, S.; Khastgir, D. Glass-rubber transition temperature of polyaniline: experimental and molecular dynamic simulation. Synth. Met. 2009, 159(12), 1141−1146.

37 Yilmaz, C.; Akalin, C.; Kocaman, E. S.; Suleman, A.; Yildiz, M. Monitoring Poisson's ratio of glass fiber reinforced composites as damage index using biaxial fiber Bragg grating sensors. Polym. Test. 2016, 53, 98−107.

38 Van Paepegem, W.; De Baere, I.; Lamkanfi, E.; Degrieck, J. Poisson's ratio as a sensitive indicator of (fatigue) damage in fibrereinforced plastics. Fatigue & Fract. Eng. Mater. Struct. 2007, 30(4), 269−276.

39 Luo, Z.; Jiang, J. Molecular dynamics and dissipative particle dynamics simulations for the miscibility of poly(ethylene oxide)/poly(vinyl chloride) blends. Polymer 2010, 51(1), 291−299.

40 Fu, Y.; Liao, L.; Lan, Y.; Yang, L.; Mei, L.; Liu, Y.; Hu, S. Molecular dynamics and mesoscopic dynamics simulations for prediction of miscibility in polypropylene/polyamide-11 blends. J. Mol. Struct. 2012, 1012, 113−118.

41 Kim, Y. H.; Webster, O. W. Water soluble hyperbranched polyphenylene: "a unimolecular micelle?" J. Am. Chem. Soc. 1990, 112(11), 4592−4593.

https://doi.org/10.1007/s10118-018-2114-y