

# PCCP

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

# Nanoscale crosslinking in thermoset polymers: A molecular dynamics study

Jingtian Kang, Changguo Wang<sup>1</sup>, Defeng Li, Ge He, Huifeng Tan<sup>1</sup>

Center for Composite Materials, Harbin Institute of Technology, Harbin, China, 150001

**Abstract:** In this paper, the nanoscale crosslinking process of thermoset polymer is studied using all-atom molecular dynamics. Based on the crosslinking simulations, the elastic properties of typical E51/593 thermoset polymer are predicted and verified by the tensile experiments within a 10% error. The proposed method shows us a reliable understanding of the nanoscale crosslinking reactions occurring in thermoset polymers. Changes in system energy, and overall density distribution, as well as quantification of bond formation yield a better insight into thermoset crosslinking that would be difficult to obtain through experimentation. The results provide us confidence in realizing virtual design of thermosets leading to tunable properties.

**Keywords:** Thermoset polymer, molecular dynamics simulation, crosslink, mechanical property

## 1. Introduction

Thermoset polymers have important applications in the structural components of spacecraft due to their high stiffness, low weight as well as thermal and creep resistances<sup>[1-3]</sup>. A number of experiments for optimization have to be taken to satisfy the specific demand of material property for space application from its molecular origin such as the length of polymer chain, the type of functional group and so on<sup>[4-5]</sup>. A concept called Materials Genome Initiative for Global Competitiveness (MGI) was first proposed by US government with aim of decreasing the time consumed by development of new materials using powerful computational toolsets and simulation method instead of real experiments<sup>[6]</sup>. Several methods have been used to investigate the relationship between chemistry-structures and polymer properties, including Monte Carlo method<sup>[7-9]</sup>, continuum method<sup>[10-12]</sup>, mesoscale method<sup>[13-15]</sup>, multiscale method<sup>[16-17]</sup>, and molecular dynamics method<sup>[18]</sup>.

The molecular dynamics (MD) simulation has been widely used in the prediction of mechanical property from nanoscale aspects<sup>[19]</sup>. The crosslinking procedure plays a key role in MD simulation of thermoset polymer. Wu and Xu<sup>[20]</sup> proposed a procedure to construct cross-linked polymer networks for DGEBA/IPD epoxy resin

---

<sup>1</sup> Corresponding authors E-mail: wangcg@hit.edu.cn; tanhf@hit.edu.cn.

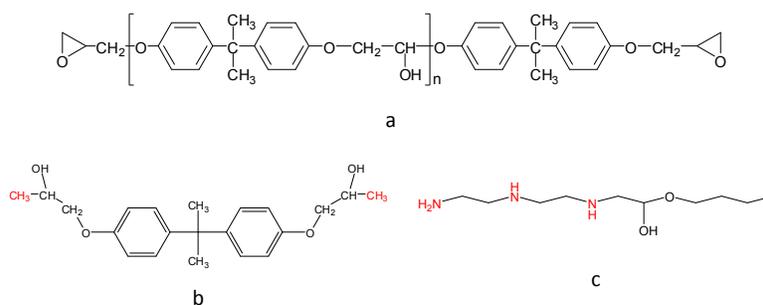
system with DREIDING force field and used COMPASS force field for property predictions. Li and Strachan<sup>[21]</sup> developed a method in which atomic charges evolve significantly only during chemical reactions and simulated the process of polymerization in thermoset polymers with a repeatable manner based on MD simulation. Varshney et al.<sup>[22]</sup> studied cross-linked modeling of thermosetting polymers. They predicted density, glass transition temperature and expansion coefficient of DETDA/EPON-862 epoxy-based polymer.

This paper aims to use the MD method to simulate the nanoscale crosslinking reactions of thermoset polymer. A tensile experiment on the E51/593 thermoset polymer is performed to verify the prediction accuracy of elastic properties obtained from the proposed method. Energy, density, new bond number and some additional parameters are used to reveal and deeply understand the crosslinking procedure of thermoset polymer. Some discussions on the proposed method and crosslinking simulations are summarized and concluded in the end.

## 2. Model and method descriptions

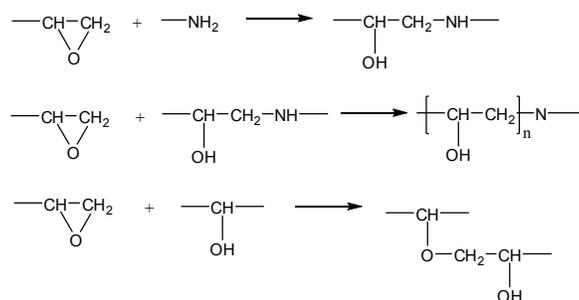
### 2.1 Reaction between amine curing agent and epoxy resin

In this paper, we focus on the bisphenol A glycidyl ether epoxy E51 and the modified amine called 593 because they are common industrial components and easy to prepare specimens for comparison. The molecular structures of the two monomers are shown in Fig. 1. Fig. 1 (a) shows the whole structure of E51, the degree of polymerization  $n$  is chosen as 0. Thus, we simulate the reaction between E51 and 593 shown in Fig. 1 (b) and Fig. 1 (c) respectively. The epoxy resin E51 has to be activated by hydrating the epoxy oxygen atoms at the ends of the molecule for polymerization. However, the curing agent 593 would maintain its original molecular structure. The reaction points of the two components have been marked in red.



**Fig. 1** Molecular formulas (a) origin molecular formulas of E51; (b) E51 used in our simulation; (c) molecular formulas of 593.

There are three principal reactions taking place between amine curing agent and epoxy, as shown in Fig. 2. They are the reaction between epoxy groups and primary amine hydrogens, the reaction between epoxy groups and secondary amine hydrogens, and the etherification reactions between epoxy groups and hydroxy group. The initial reaction of a primary amine can produce a secondary one and the subsequent reaction leads to a tertiary amine. Thus, we assume that the secondary amine hydrogen has the same reactivity as the primary amine hydrogen no matter whether it is newly generated or not, and the etherification reactions can be neglected<sup>[23]</sup>. Based on these assumptions, each amine groups in the curing agent 593 can react with two E51 epoxy molecules. In order to have a perfect stoichiometry, the number of E51 epoxy molecule should be twice as many as that of curing agent 593.



**Fig. 2** Reaction between curing agent and epoxy.

## 2.2 Crosslinking simulation method

In reality, the crosslinking networks are formed by the chemical reaction above. In MD simulation, it is the result of new C-N bonds created in simulation procedure. All the active carbon atoms were analyzed in order to identify if there are active nitrogen atoms within a prescribed distance called cutoff radius. The nearest nitrogen atom within cutoff radius was chosen as the target atom and then a new C-N bond was created. The universal DREIDING force field<sup>[24]</sup> has been employed and the harmonic form of covalent potential is chosen in our MD simulation.

$$E_{total} = E_b + E_a + E_d + E_i + E_{vdw} + E_q \quad (1)$$

The total potential energy of DREIDING for an arbitrary atom system contains energy from bond interaction and non-bond interaction. The bond energy is described as bond stretch ( $E_b$ ), angle bending ( $E_a$ ), torsions of dihedral angles ( $E_d$ ) and improper torsions ( $E_i$ ). The non-bond energy includes electrostatics interaction caused by partial atomic charges and van der Waals interactions between atoms. The van der Waals interactions of DREIDING have been parameterized with either Lennard-Jones (LJ) or exponential-6 form (X6) in the paper.

$$E_{LJ} = D_0 \left[ \left( \frac{1}{\rho^{12}} - \frac{2}{\rho^6} \right) \right] \quad (2)$$

$$E_{X6} = D_0 \left[ \left( \frac{6}{\xi-6} \right) e^{\xi(1-\rho)} - \left( \frac{\xi}{\xi-6} \right) \rho^{-6} \right] \quad (3)$$

Where  $\rho = R/R_0$  is the scaled distance,  $R_0$  is the van der Waals bond length (Å),  $D_0$  is the van der Waals well depth (kcal/mol), and  $\xi$  is a dimensionless scaling parameter. The crosslinking procedure is implemented with LJ function with inner and outer cutoff of 8 Å and 12 Å respectively and the mechanical test is performed with X6 Buckingham functions in this paper.

The flow chart of crosslinking simulation procedure is shown in Fig. 3. The E51/593 molecules were drawn in Material Studio followed by partial charges using Qeq method<sup>[25]</sup>. The three-dimensional active models for molecules E51 and 593 were constructed corresponding to a predefined density 1.0 g/cm<sup>3</sup> using self-avoiding random walk method<sup>[26-27]</sup> by Amorphous Modules of Material Studio. In order to achieve a perfect stoichiometry, there are one thousand E51 atoms and five hundred 593 atoms in the simulation box. The total number of atoms this simulation system is chosen as 74000 considering the balance between efficiency and accuracy. Periodic boundary conditions are imposed on this cubic unit cell and 1000 steps of energy minimization procedure using the conjugate gradients method was then performed to make these molecules a reasonable configuration and avoid atom overlaps. Then, the total system was equilibrated using an isothermal and isochoric (NVT ensemble) simulation for 100 ps at 600 K followed by an isothermal and isobaric (NPT) MD simulation for 500 ps under atmospheric pressure. After fully equilibrium of the system, the crosslinking procedure was implemented with the fix bond/create command of LAMMPS<sup>[28]</sup>. The chemical reaction was implemented in a stepwise manner with a reaction cutoff distance of 5.64 Å about four times than the C-N equilibrium bond length of 1.41 Å. The newly created C-N bonds, which had been artificially selected to avoid aromatic rings in the initial steps, were relaxed slowly using a 50 ps NPT ensemble with a multi-step relaxation which consists of five 10 ps NPT substeps. Each substep has different C-N bond parameters that can be computed with equation (4),  $K_0$  and  $r_0$  are the normal energy parameter and equilibrium radius of C-N bond. This multi-step relaxation can gradually drag atoms to its normal equilibrium position and avoid instability.

$$K_i = \frac{i}{5} K_0 \quad r_i = i r_0 \quad i = 1, \dots, 5 \quad (4)$$

Once this is accomplished, or if no reactive pairs are found within the cutoff distance, a 50 ps NPT simulation is performed to let the system relax and equilibrate to its new topology before reactive pairs are checked again for possible new reactions. The total number of new C-N bonds was then computed to estimate the degree of curing. We can get into the cooling down process until the desired curing degree is achieved; otherwise, another round of chemical reactions was repeated. In the cooling down process, we used NPT ensemble with a cooling rate of 10 K/60 s followed by another 50 ps NPT ensemble at 300 K. After cooling down, a uniaxial tensile simulation was employed to make a comparison with the actual experiment. We take this mechanical test by stretching one boundary of the simulation cell (fix deform) accompanied by a NVT ensemble at 300 K under atmospheric pressure.

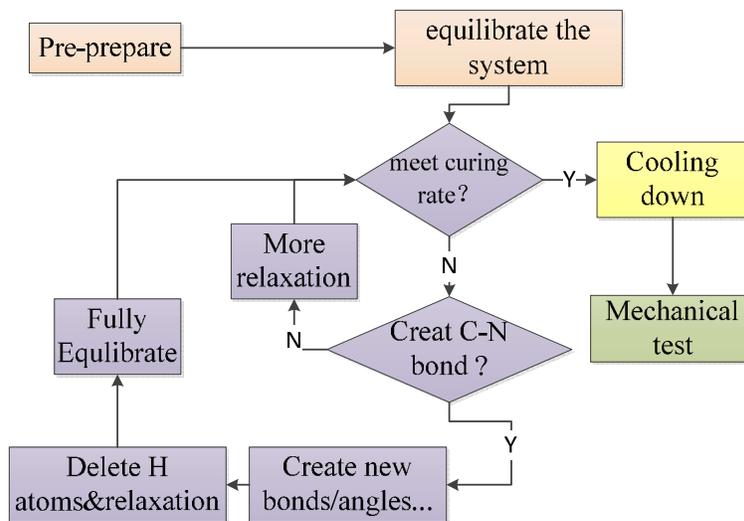


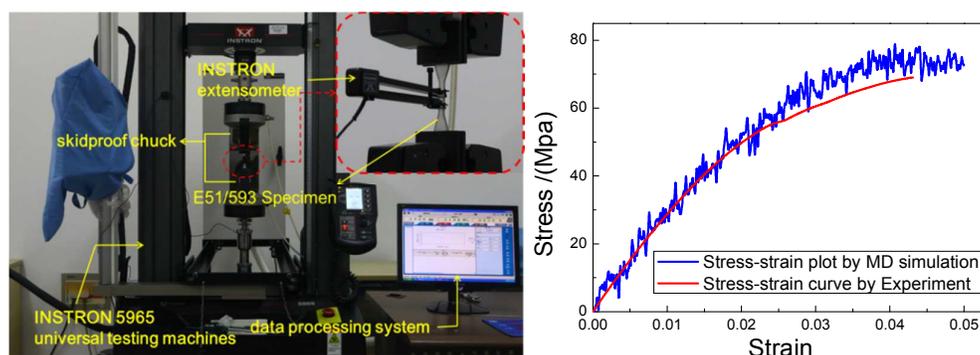
Fig. 3 Flow chart of the simulation procedure.

### 3. Experimental verification

A tensile experiment on E51/593 polymer (as shown in Fig.4) is performed to test its mechanical properties (using INSTRON 5965, US), such as Young's modulus and stress-strain curves, which is used to verify the accuracy of the proposed method. As is shown in Fig. 4(a), the E51/593 specimen (the fabrication details are in the Appendix) was clamped with skidproof chunks and the strain was measured with INSTRON extensometer for accuracy. We conducted this test for five same specimens and made an average for the Young's modulus. Finally, the stress curves and elastic modulus of these specimens had been obtained and compared with simulation results. Fig. 4(b) shows stress-strain curves of the experiment and simulation results. These two curves are closed with each other and have nearly the same trend. In order to

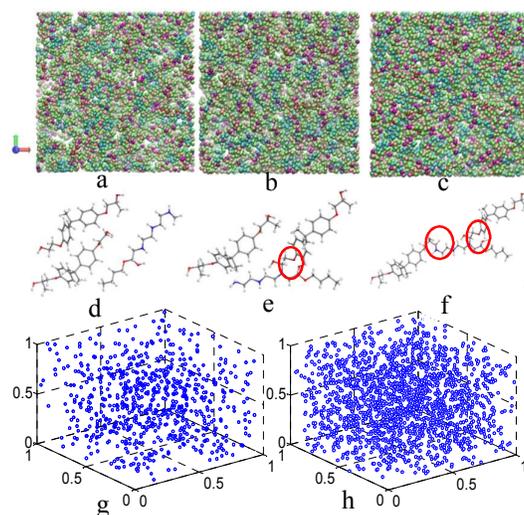
decrease fluctuation of the simulation curves, a regression algorithm was conducted and some additional bond, angle, dihedral and improper brought by these newly created C-N bonds has been considered.

Obtained from Fig. 4 (b), the Young's modulus of E51/593 polymer is 3.125 GPa which is very close to the simulated value (3.361 GPa) corresponding to the 89% curing degree of crosslinking networks considering a balance of efficiency and accuracy. The results show that the proposed method can provide us a reliable understanding of the nanoscale crosslinking reactions occurred in thermoset polymer.



**Fig. 4** Mechanical experiment and results (a) Uniaxial tensile for E51/593; (b) Comparison stress-strain curves between experiment and simulation.

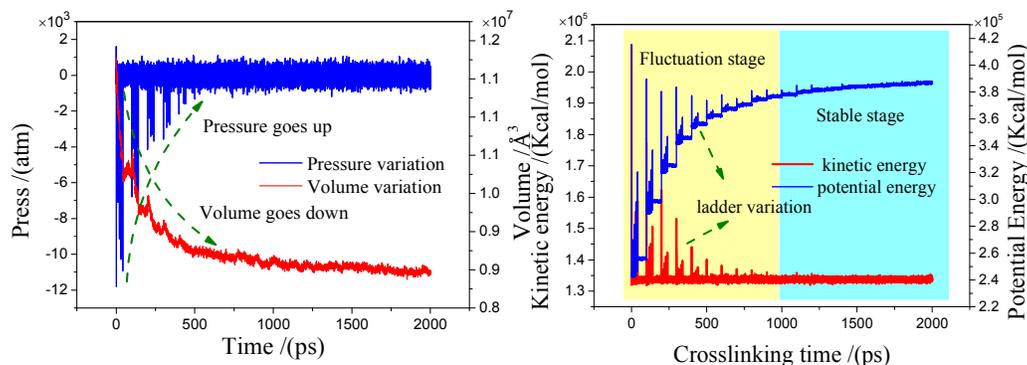
#### 4. Results and discussion



**Fig. 5** Crosslinking results (a) partial crosslinking results with 0% curing degree; (b) with 37% curing degree; (c) with 89% curing degree; (d) crosslinking status with 0% curing degree; (e) crosslinking status with 37% curing degree; (f) crosslinking status with 89% curing degree; (g) scatters of new C-N bonds with 37% curing degree; (h) scatters of new C-N bonds with 89% curing degree;

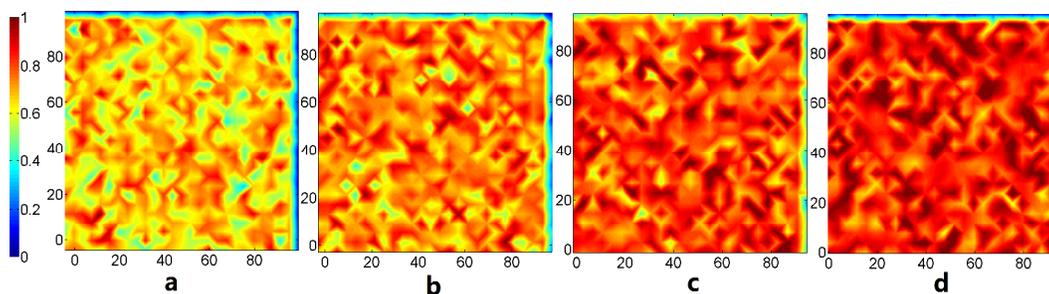
Based on the proposed method, the crosslinking networks under different curing degree have been obtained as shown in Fig. 5 (a-c). The nanoscale crosslinking statuses of different curing degree, which have different crosslinking bonds, are illustrated in Fig. 5 (e-f). The new C-N bonds produced by the crosslinking reaction are shown with 3D scatter images in Fig. 5(d-e), which illustrate a homogeneous distribution within the whole simulation cell.

Some useful parameters, including pressure, volume, energy and density are used to understand and supervise the progress of the crosslinking procedure. There are huge fluctuations for pressure at the beginning which result in a shrinkage effect. This effect will lead a decrease of the cell volume at first, but gradually stable in the last as show in Fig. 6 (a). We can define a curing shrinkage rate,  $\alpha = (V - V_0)/V_0$ , to illustrate the contraction effect in crosslinking procedure, which is 18% in our simulation. Moreover, the potential energy shows us a ladder like increase accompanied by the decrease of kinetic energy. The variation of the energy can be obviously divided into two stages, a fluctuation stage and a stable stage shown in Fig. 6 (b). This is due to the initial instability and the following crosslinking status caused by the new C-N bonds which will be explained later.



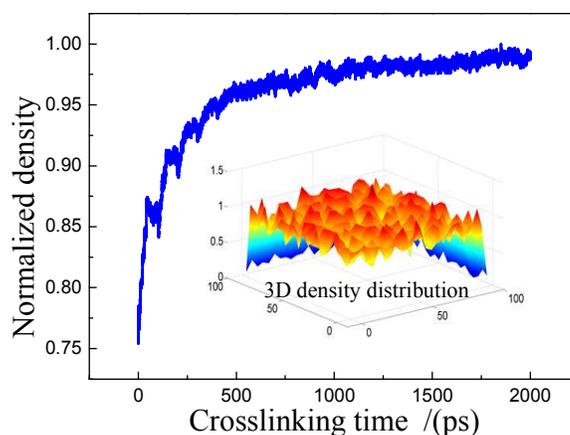
**Fig. 6** The variation of parameters in Crosslinking procedure (a) pressure and volume variation; (b) variation of kinetic energy and potential energy

The density distribution contours under different curing degree are shown in Fig. 7, which is used to study the variation of system caused by the crosslinking reaction. These density contours provide us a clear and visual understand of the density distribution which is generally homogenous and gradually increasing in the crosslinking procedure.



**Fig. 7** Density distribution contours under different curing degree (a) 0% ; (b)37%; (c)46%; (d)89%

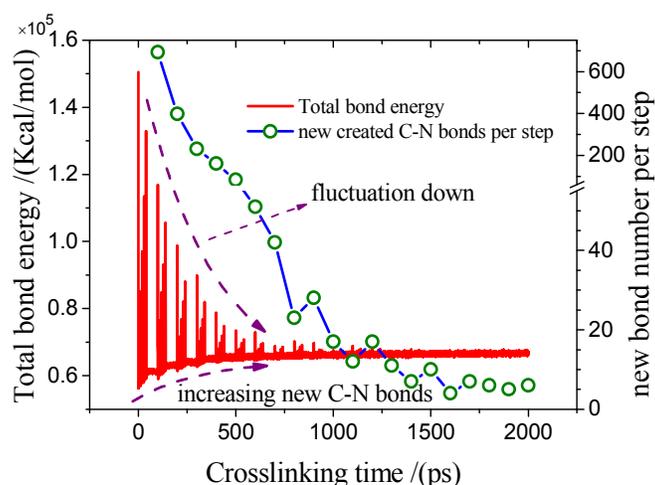
In addition, the local inhomogeneity and variation of the density indicate the formation of the crosslinking networks. A more quantitative understanding for the increasing of density is illustrated in Fig. 8.



**Fig. 8** Density curve in crosslinking procedure

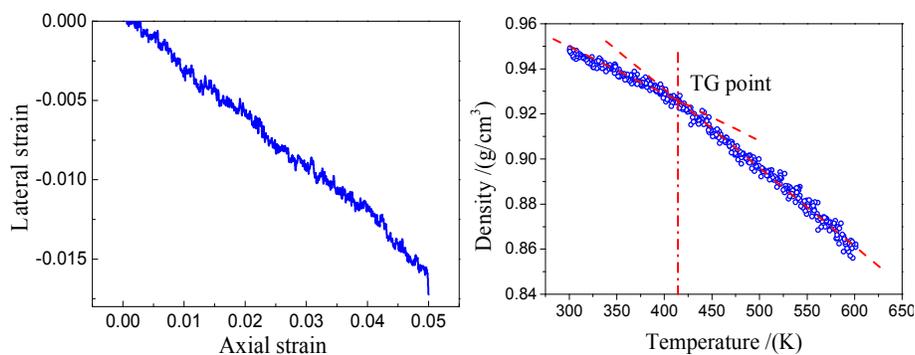
The number of new C-N bonds is large at the beginning of crosslinking procedure, which results in an increasing of bond energy, but reduces rapidly with the time goes by. The large number of new bonds created in one step will inevitably cause fluctuations of bond energy (as shown in Fig. 9) and other energy mentioned above (Fig. 6 (b)). The numerical instability and fluctuation brought by the new bonds in the initial steps had been avoided by the multi-step relaxation method mentioned above. Moreover, there are only small amount of new C-N bonds at one step in the last stage of crosslinking but it will take a relative long relaxation time shown in Fig. 9 . This will make a relative stability for these parameters in the last (as shown in Fig. 6). As our experience, the cutoff radius should not be less than the equilibrium distance of C-N bond to make it physical. A small cutoff radius would consume a relative long time for the system to achieve a desired curing degree due to the mini number of new bonds created in the last based on the results from Fig. 9; A long cutoff radius would create more C-N bonds in a single step but result in a computational instability during

the MD process.



**Fig. 9** number of newly created C-N bonds and variation of bond energy

In addition, some additional results have been investigated by our simulation. The Poisson ratio can be calculated by the method mentioned above in the mechanical test. The value of Poisson ratio is the slope of lateral and axial displacement of different cell edges shown in Fig. 10 (a) which is 0.317 in our simulation. The glass transformation temperature ( $T_g$ ) has an important influence on the performance of polymer material. The physical properties of thermoset polymer will show great differences when temperature crosses the glass transition point.  $T_g$  was measured by the slope change of this curve obtained by cooling down procedure which had been processed by the linear fitting for accuracy as shown in Fig. 10 (b). In our simulation, The value of  $T_g$  for E51/593 polymer was 412 K.  $T_g$  is a kinetic quantity which depend on cooling down rate. It is generally accepted that per order of magnitude increase in cooling rate will cause an increase of about 3-5 K in  $T_g$  [29]. With this relation, we can infer the actual  $T_g$  from the simulation results. A cooling down rate of 10 K/min is usually adopted by real experiment. In our simulation, the cooling down rate is 10 K/60 ps about 13 orders of magnitude higher than that of experiment which will lead to about 65 K higher than experiment results. Besides, there are two key issues related to the cooling down procedure. The first one is cooling rate. A too high cooling down rate will bring internal stress into the simulation cell. Second, the system should be fully equilibrated and this can reduce the fluctuation of pressure in the following step.



**Fig. 10** Additional results gained by simulation (a) Tensile strain and transverse strain; (b) glass transformation temperature plot.

## Conclusion

In this paper, the nanoscale crosslinking reaction of thermoset polymer is modeled based on the molecular dynamics method. According to the proposed method, the simulation procedure to form crosslinking networks is determined, and the elastic properties of thermoset polymer are also predicted. The simulated Young's modulus of E51/595 thermoset polymer is close to the experimental result within a 10% error, which indicates that the proposed method is reliable to predict the mechanical properties of thermoset polymer with the considerations of nanoscale crosslinking.

Based on the results, the number of new C-N bond has a close relationship with the crosslinking procedure, which not only affects the tendency and equilibration of the energy, but also brings volume contraction and density variation. Therefore, more cautions should be paid on the determinations of new C-N bond in order to obtain a reasonable crosslinking networks. These results also help us deeply understand the crosslinking procedure and control the crosslinking reaction of thermoset polymer in the simulation. Additionally, the property definition of angles and dihedrals brought by the new C-N bonds has important effects on the mechanical response of the networks. A full equilibrium of the system and an appropriate cooling rate has a great influence on decreasing the fluctuation.

The proposed method and the results obtained in this paper will give references to the calculation of crosslinking polymer as well as the virtual design and optimization of new polymer material.

## Appendix: Fabrication details of the tensile specimen

The epoxy resin in our paper, which was purchased from Wuxi Resin Factory of Bluestar New Chemical Materials Co. Ltd in Jiangsu, China, is bisphenol A glycidyl

ether epoxy E51. Its epoxy value is  $0.5 \pm 0.01$  (epoxy equivalent weight = 184-195 g/equiv, degree of polymerization in the chemical structure is about 0.18). The curing agent, which was purchased from Shanghai Resin Factory Co. Ltd in Shanghai, China, is a modified amine called 593. It is a transparent liquid with long-chain structure and its viscosity is 80-100 mPa.s at 298.15K.

The epoxy resin E51 was poured into a beaker at room temperature. Then the curing agent 593 was added into this beaker with vigorous stirring until the system became homogeneous. The mass ratio between E51 and 593 is 1: 0.2768. The binary mixture was poured into prepared molds of standard tensile specimen. It was then crushed with two steel plates, and cured at  $60^\circ\text{C}$  for 2 hours. The degree of curing of these specimens was about 92%

### Acknowledgements

Authors gratefully acknowledge supports from National Natural Science Foundation of China, 1172079; Program for New Century Excellent Talents in University, NCET-11-0807; the Fundamental Research Funds for the Central Universities, HIT.BRETHIII.201209.

### References

1. Liu C, Qin H and Mather P T, *J. Mater. Chem.*, 2007, 17, 1543.
2. Tupper M, Munshi N and Beavers F, *Aerosp. Conf. Proc.*, 2001, 5, 2541.
3. Hussain F, Hojjati M and Okamoto M, *J. Compos. Mater.*, 2006, 40, 1511.
4. Keledi G, Hári J and Pukánszky B, *Nanoscale*, 2012, 4, 1919.
5. Sun H, Liu Y, Tan H, et al. *J. Poly. Sc.*, 2014, DOI: 10.1002/APP.39882.
6. Materials Genome Initiative for Global Competitiveness, website: [http://www.whitehouse.gov/sites/default/files/microsites/ostp/materials\\_genome\\_initiative-final.pdf](http://www.whitehouse.gov/sites/default/files/microsites/ostp/materials_genome_initiative-final.pdf)
7. Binder K and Paul W, *Macromolecules*, 2008, 41, 4537.
8. Detcherry F A, Pike D Q and Nealey P F, *PRL*, 2009, 102, 197801.
9. Ozmusul M S, Picu C R and Sternstein S S, *Macromolecules*, 2005, 38, 4495.
10. Wernik J M and Meguid S A. *Int. J. Solids Struct.*, 2014, 51, 2575.
11. Valavala P K and Odegard G M, *Rev. Adv. Mater. Sci.*, 2005, 9, 34.
12. Grest G S, Lacasse M D and Kremer K, *J. Chem. Phys.*, 1996, 105, 10583
13. Groot R D and Warren P B, *J. Chem. Phys.*, 1997, 107, 4423.
14. Müller - Plathe F, *CHEMPHYSCHEM*, 2002, 3, 754.
15. He Y D, Qian H J and Lu Z Y, *Polymer*, 2007, 48, 3601.

16. Zeng Q H, Yu A B and Lu G Q, *Prog. Polym. Sci.*, 2008, 33, 191
17. Kacar G, Atilgan C and Ozen A S., *J. Phys. Chem. C*, 2010, 114, 370.
18. Ajori S, Ansari R. *Physica B*, 2015, 459, 58.
19. Wang C, Liu Y, Lan L and Tan H, *Nanoscale*, 2013, 5, 4454.
20. Wu C and Xu W, *Polymer*, 2006, 47, 6004.
21. Li, C.Y. and Strachan, A, *Polymer*, 2010, 51, 6058.
22. Varshney V, Patnaik S S and Roy A K, *Macromolecules*, 2008, 41, 6837.
23. Girard-Reydet E, Riccardi C C and Sautereau H, *Macromolecules*, 1995, 28, 7599
24. Mayo S L, Olafson B D, Goddard W, *J. Phys. Chem.*, 1990, 94, 8897.
25. A. K. Rappe, W. A. Goddard III., *J. Phys. Chem. A*, 1991, 95, 3358.
26. Theodorou D. N. and Suter U.W. , *Macromolecules*, 1985, **18**, 1467.
27. Theodorou D. N. and Suter U.W. , *Macromolecules*, 1986, **19**, 139.
28. Plimpton S, Crozier P and Thompson A. *Sandia National Laboratories*, 2007, 18.
29. Ferry, J. D., *Viscoelastic properties of polymers*, *John Wiley & Sons*, 1980