

Multi-scale Studies of Glass Transition and Uniaxial Tensile Properties of a Commercially Available Epoxy Adhesive Using Experimental Measurements and Molecular Dynamics Simulation

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Abstract In this study, the glass transition and uniaxial tensile properties of a commercially available epoxy adhesive were investigated using experimental measurements and molecular dynamics (MD) simulation. Differential scanning calorimetry (DSC) was used to study the change of glass transition temperature (T_g) with cross-link density (CLD). Uniaxial tensile test was performed to measure the Young's modulus (E), Poisson's ratio (ν) and yielding strength (σ_Y). In MD simulation, the complicated epoxy system was simplified as the mixture of two kinds of simple molecules, with the key information well preserved and the less important details omitted. The molecular model of the cross-linked epoxy network was constructed and its mechanical properties were calculated using MD simulation. Overall, the MD simulation results agreed with experimental ones, which proved the validity of the molecular model and justified the simplification method of the industry-level epoxy system.

Keywords: Epoxy adhesive; Glass transition temperature; Uniaxial tension; Experiment; Molecular dynamics simulation.

INTRODUCTION

Epoxy adhesives have been widely used to joint materials because of strong adhesion and high strength. The mechanical properties of epoxy adhesives have been extensively studied using experimental techniques. Saldanha^[1] conducted dynamic mechanical analysis (DMA) and uniaxial tensile tests to measure the glass transition temperature (T_g), Young's modulus (E) and yield strength (σ_Y) of an epoxy adhesive. Carbas^[2] studied the effect of curing temperature (T_c) on the mechanical properties of an epoxy adhesive and found that with increasing T_c , both T_g and E first increased and then decreased. The phenomenon was attributed to the combined effect of cross-link and oxidation. Researchers have also studied the influence of hygrothermal degradation (HTD) on the mechanical properties of epoxy adhesives. Lettieri^[3] observed that the T_g of an epoxy adhesive reduced after HTD. Zhang^[4, 5] found that the load carrying capability of an epoxy adhesive single lap joint was significantly weakened by HTD. In all these studies, the epoxy adhesives tested were commercially available.

Experiment results are reliable and applicable. But the chemical mechanism behind the phenomenon is not easily understood with experiment alone. For example, when studying the effect of HTD, Zhang^[6] reported recovered yielding strength and reduced tensile toughness of a hygrothermal degraded epoxy adhesive after depleting the water through baking, but this important finding was not followed by elaboration.

Molecular dynamics (MD) simulation is another important method to study the mechanical properties of epoxy adhesives. Wu^[7] constructed the diglycidyl ether bisphenol A (DGEBA)-isophorone diamine (IPD)

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network with Dreiding force field and predicted its E with COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies). Reasonable correlation was found between simulation results and experimental data. Shenogina^[8] studied the change of Young's, shear and bulk moduli and Poisson's ratio (ν) with cross-link density (CLD) in a DGEBA-diethylene toluene diamine (DETDA) network using COMPASS force field. The simulation result produced by dynamic deformation approach agreed well with theoretical prediction. Yang^[9] simulated the uniaxial tension of an epoxy phenol novolac (EPN) with PCFF (polymer consistent force field) and investigated the effect of tensile speed, CLD and temperature. Various methods were applied to acquire T_g and good consistency was achieved. Li^[10] studied yielding behavior of an EPON862-DETDA network under uniaxial tension, and found σ_Y decreased with increasing temperature. Hardening was observed for samples of high CLD. Moreover, Lin^[11] and Chang^[12] studied the moisture diffusion in epoxy systems with MD simulation.

Complementary to phenomenological experiments, MD simulation is able to quantify chemical and physical mechanism by adjusting the nano- or micro-structure of the material. Therefore, once a theoretical explanation was proposed in an attempt to elucidate a phenomenon, such as what has been observed in reference^[6], it can be verified by implementation and reconstruction in MD simulation. Nevertheless, before a molecular model is adopted for mechanism research, it has to be validated by correlating with experiment results. In this sense, the two research methods have to work collaboratively to provide in-depth understanding of the studied material.

In this paper, we investigated the mechanical properties of a commercially available epoxy adhesive using both experimental measurements and MD simulation. Differential scanning calorimetry (DSC) method was employed to study the change of T_g with CLD. Uniaxial tensile test was performed to measure E , ν and σ_Y . The molecular model of the adhesive was constructed and MD simulation was conducted to predict its mechanical properties. By correlating the experiment and simulation results, we examined the validity of the molecular model.

The significance of this study owes to the fact that, to our knowledge, it's the first time that a complicated commercially available epoxy adhesive was simplified for MD simulation. Previous multi-scale studies focused on laboratory synthesized simple epoxy systems^[7, 10, 11]. This paper aims at extending the research scope from laboratory to industry.

EXPERIMENTAL

The epoxy adhesive investigated in this study was Henkel Terokal 5089 (Henkel, Germany). Its general information is available from reference^[13].

Differential Scanning Calorimetry (DSC) Test

DSC was used to measure the CLD and T_g of the epoxy adhesive. 13 un-cross-linked epoxy adhesive samples, each weighing 10–15 mg, were tested by using a TA DSC Q2000 apparatus (TA Instruments, USA). The initial temperature of the samples was 20 °C. The samples went through two stages. In stage 1, the temperature was first raised to 120–180 °C by 15 K/min, then held by 0–20 min, and finally lowered back to 0 °C by 15 K/min. This allowed the samples to partially cross-link. The cross-link temperature and time varied among the 13 samples, so their CLDs were different at the end of stage 1. In stage 2, the temperature was raised to 240 °C by 15 K/min. During this stage, the samples first experienced glass transition and then reached full cross-link. In both stages, the sample's heat flow was monitored by the DSC instrument. The sample's CLD after stage 1 was calculated by Eq. (1),

$$\text{CLD} = \frac{\Delta H_1}{\Delta H_1 + \Delta H_2} \quad (1)$$

where ΔH_1 and ΔH_2 are the sample's cross-link reaction heat in stage 1 and stage 2. The T_g of each sample was also extracted from the heat flow curve.

Uniaxial Tensile Test

The specimen for uniaxial tensile test was in the form of dog-bone (Fig. 1), and its shape and size accorded to American Society for Testing and Materials (ASTM) D 638^[14]. The cross-section of the specimen was a 6 mm × 1 mm rectangle. An adhesive plate was first made, from which the dog-bone shape specimens were cut with a numerical control milling machine. Figure 2 represents the fixture for adhesive plate fabrication. The un-cross-linked epoxy adhesive was heated to 50 °C to increase mobility and improve handling, and was then placed between the two aluminum plates, which had been coated with Teflon films as release agent. Great care was taken in this operation to exclude any air bubble. At both ends, spacers were installed to control thickness and clips were applied to clamp the whole structure. The structure was put in an oven at 180 °C for 30 min and then soaked in 25 °C /50% R.H. (relative humidity) for 24 h before disassembly. In this way, an adhesive plate with smooth surface and dense interior was fabricated.

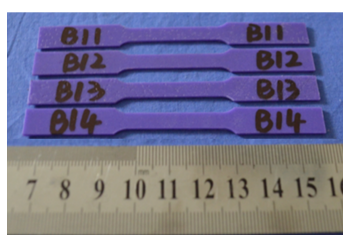


Fig. 1 Dog-bone specimens for uniaxial tensile test

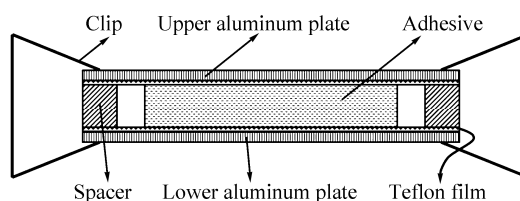


Fig. 2 The fixture for adhesive plate fabrication

The uniaxial tensile test was conducted at 25 °C/50% R.H.. Four dog-bone specimens were tested on the universal tensile test machine CRIMS DDL 50 (Changchun Research Institute for Mechanical Science, China). The specimens were directly clamped by the machine, and were loaded at a cross-head speed of 6 mm/min, which was considered as quasi-static. The specimen load was measured by a load cell mounted on the test machine. Non-contact optical method was used to record specimen strain, which required using specimens with a marked pattern.

MOLECULAR DYNAMICS SIMULATION

Cross-linked Network

The compositions of Henkel Terokal 5089 are listed in Table 1. The adhesive is a complicated epoxy system with 12 kinds of epoxy monomers/oligomers, hardeners and additives. It is not feasible to take into account all the components in MD simulation. To simplify the problem, epichlorohydrin-4,4'-isopropylidene diphenol resin (another name for DGEBA) and modified polyurethane resin (MPUR) were chosen to represent the adhesive because of their largest mass fraction among epoxy monomers/oligomers and hardeners respectively. Although other components also influence the adhesive properties, they are not included in this study.

The chemical structures of DGEBA and MPUR were not specified in reference^[15], but they had to be determined for MD simulation. Therefore, reasonable simplifications were applied such that the key function groups were preserved while the less important details were omitted (Fig. 3). For DGEBA, the number of repeat unit was set to 1, since the un-cross-linked adhesive was in liquid state, which means lower molecular mass^[16].

$$\begin{aligned}
E_{\text{pot}} = & \sum_b [K_2(b-b_0)^2 + K_3(b-b_0)^3 + K_4(b-b_0)^4] \\
& + \sum_{\theta} [H_2(\theta-\theta_0)^2 + H_3(\theta-\theta_0)^3 + H_4(\theta-\theta_0)^4] \\
& + \sum_{\phi} [V_1(1-\cos\phi) + V_2(1-\cos 2\phi) + V_3(1-\cos 3\phi)] + \sum_{\chi} K_{\chi}\chi^2 \\
& + \sum_b \sum_{b'} F_{bb'}(b-b_0)(b'-b'_0) + \sum_{\theta} \sum_{\theta'} F_{\theta\theta'}(\theta-\theta_0)(\theta'-\theta'_0) \\
& + \sum_b \sum_{\theta} F_{b\theta}(b-b_0)(\theta-\theta_0) + \sum_b \sum_{\phi} (b-b_0)(V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi) \\
& + \sum_{b'} \sum_{\phi} (b'-b'_0)(V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi) \\
& + \sum_{\theta} \sum_{\phi} (\theta-\theta_0)(V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi) \\
& + \sum_{\phi} \sum_{\theta} \sum_{\theta'} K_{\phi\theta\theta'} \cos \phi (\theta-\theta_0)(\theta'-\theta'_0) + \sum_{i>j} \frac{q_i q_j}{\epsilon r_{ij}} + \sum_{i>j} \left[\frac{A_{ij}}{r_{ij}^9} - \frac{B_{ij}}{r_{ij}^6} \right]
\end{aligned} \tag{2}$$

E_{pot}	Potential energy	χ	Improper
K_2, K_3, K_4	Bond coefficients	$F_{bb'}$	Bond-bond coefficient
b, b'	Bond lengths	$F_{\theta\theta'}$	Angle-angle coefficient
b_0, b'_0	Equilibrium bond lengths	$F_{b\theta}$	Bond-angle coefficient
H_2, H_3, H_4	Angle coefficients	$K_{\phi\theta\theta'}$	Dihedral-angle-angle coefficient
θ, θ'	Angles	q_i, q_j	Charge
θ_0, θ'_0	Equilibrium angles	ϵ	Dielectric constant
V_1, V_2, V_3	Dihedral coefficients	r_{ij}	Distance
ϕ	Dihedral	A_{ij}, B_{ij}	Constants
K_{χ}	Improper coefficient		

The molecular model of the epoxy adhesive was built based on the following steps using the Materials Studio 6.0 software package from Accelrys Inc. Literature^[7, 9] has shown that the cross-linked network built in this way mimics the real network very well while the computation cost is acceptable.

1. The DGEBA and MPUR molecules were sketched, and were activated by bond deletion and atom removal. For each DGEBA molecule, the epoxy rings were opened and the H atom on the hydroxyl was removed, creating the $-\text{H}_2\text{C}$ and $-\text{O}$ reactive sites. For each MPUR molecule, the $\text{N}=\text{C}$ double bonds on isocyanates were opened and the H atoms on secondary amines were removed, creating the $-\text{R}_1\text{N}$ and $-\text{R}_2\text{C}$ reactive sites. Energy minimization was conducted to optimize the geometry of the activated molecules.

2. The DGEBA and MPUR molecules were randomly seeded in a cubic cell with 3D periodic boundary conditions using Amorphous Cell. The 64 DGEBA and 32 MPUR molecules occupied a $4.2 \text{ nm} \times 4.2 \text{ nm} \times 4.2 \text{ nm}$ area with a density of 1.12 g/cm^3 . The system was then subjected to energy minimization and 1 ns NVT (canonical ensemble) dynamics at 300 K (with Berendsen thermostat to control temperature) for relaxation.

3. Covalent bonds were created between close contact reactive sites, *i.e.* $-\text{H}_2\text{C} + -\text{R}_1\text{N}$ and $-\text{O} + -\text{R}_2\text{C}$. The initial close contact cut-off distance was $0.3 \text{ nm}^{[9]}$, meaning that the reactive site pairs within the distance of 0.3 nm would be bonded. The cut-off distance then increased by $0.1 \text{ nm}^{[9]}$ until it reached $1.0 \text{ nm}^{[9]}$. After bond creation at each cut-off distance, the system was subjected to 100 ps NVT dynamics at 300 K for relaxation^[9].

4. After the system reached the prescribed CLD, defined in Eq. (3), the unreacted reactive sites were saturated with H atoms.

$$\text{CLD} = \frac{N}{N_{\text{max}}} \tag{3}$$

where N is the number of created bond, and N_{max} is the maximum number of possible bond creation. For a 64/32 system, $N_{\text{max}} = 192$. The system was fully relaxed after 1 ns NVT dynamics at 300 K. In this way, the molecular model of the epoxy adhesive with prescribed CLD was built (Fig. 5).

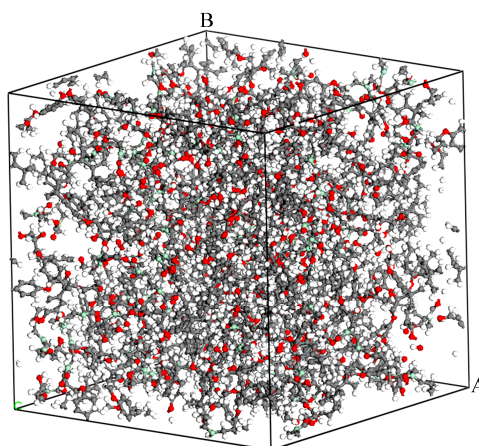


Fig. 5 The molecular model of the epoxy adhesive

Glass Transition Temperature

The glass transition temperature of amorphous and cross-linked polymers can be determined by studying the change of volume with temperature. In either rubbery or glassy state, the coefficient of thermal expansion (CTE) of a polymer is relatively constant. Cooling the polymer from rubbery to glassy state results in a significant reduction in CTE^[22]. In this study, the cross-linked epoxy adhesive was first equilibrated at 500 K with 1 ns NPT (constant temperature and constant pressure ensemble) dynamics (with Berendsen barostat to control pressure) at atmospheric pressure (0.1 MPa)^[9]. The temperature then decreased by 20 K followed by 100 ps NPT dynamics at each time until the temperature reached 160 K. The system volume was recorded and plotted against temperature.

Uniaxial Tension

The uniaxial tensile simulation of the epoxy adhesive was conducted using LAMMPS MD package from Sandia National Labs. 3D periodical boundary condition was applied. The simulation temperature was 300 K. After 1 ns NPT dynamics at 0.1 MPa, the system deformed along the x direction at a nominal strain rate of $1 \times 10^9/s$. Along y and z directions, the boundary pressure was kept as 0.1 MPa to mimic stress-free state. The true stress along x direction, which was converted from system pressure, and the true strain along x, y, z directions was recorded.

RESULTS AND DISCUSSION

Glass Transition Temperature

The DSC thermograms of the epoxy adhesives of different CLD were plotted in Fig. 6. The bending region in each curve corresponds to T_g . For samples with higher CLD, T_g was identified, since the curve bending was more easily captured. This reveals the fact that DSC was not capable of measuring the T_g of this specific epoxy adhesive at lower CLD. Therefore, this study will focus on the CLD larger than 50%. Experimental results show that T_g increased from 25 to 105 °C when CLD increased from 51% to 100%.

T_g was also predicted using MD simulation, by means of investigating the change of volume with temperature. The result (Fig. 7) shows that T_g increased from 310 K to 370 K (37–97 °C) when CLD increased from 50% to 90%. Plotting the results together in Fig. 8 suggests that the MD simulation gave a good prediction of T_g . This means the molecular structure of the epoxy adhesive was valid, which justified the omission of constituents other than DGEBA and MPUR. The T_g -CLD relationship was also well predicted by MD simulation, indicating the definition of CLD in Eq. (3) was correct.

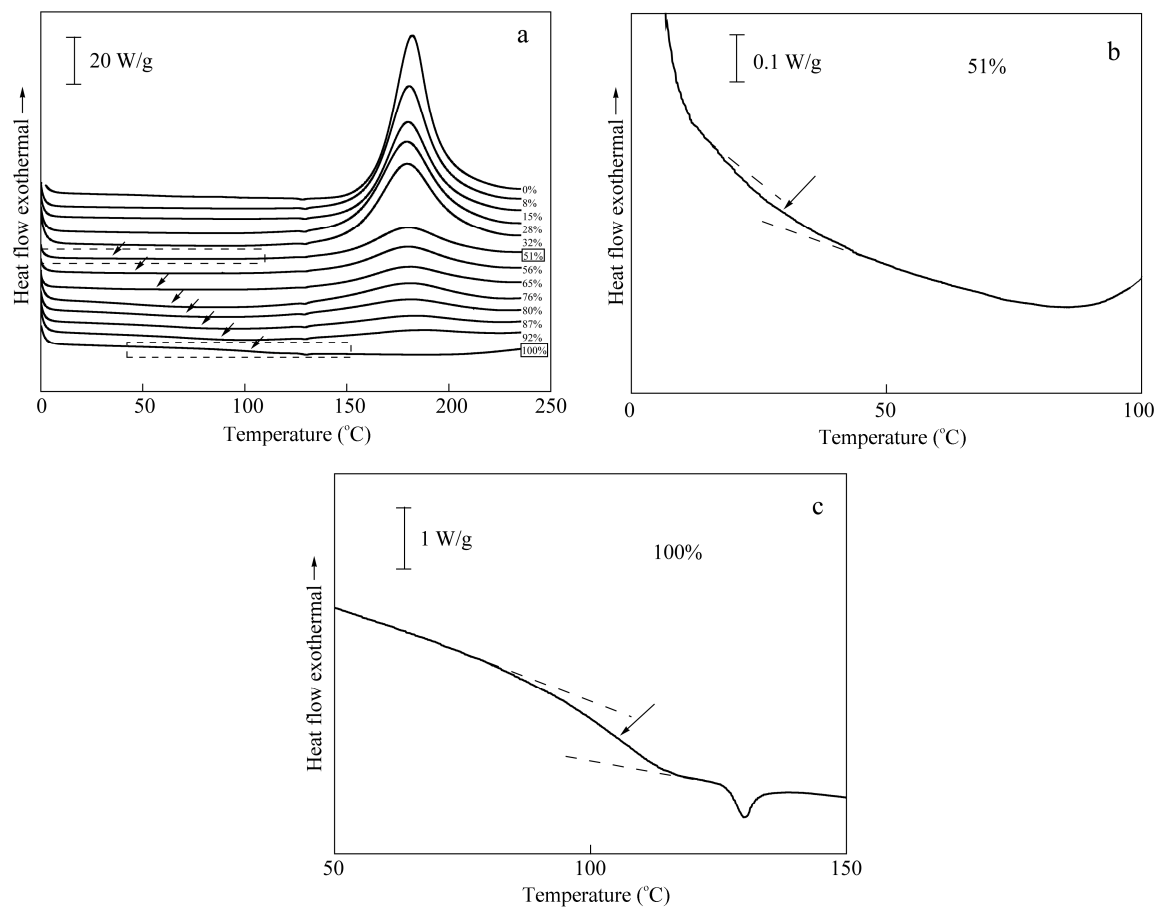


Fig. 6 DSC thermograms of epoxy adhesives of different CLD: (a) full curves for all CLD, (The bending region (indicated by arrows) corresponds to T_g), (b) and (c) show enlarged curves of glass transition region for CLD = 51% and 100%

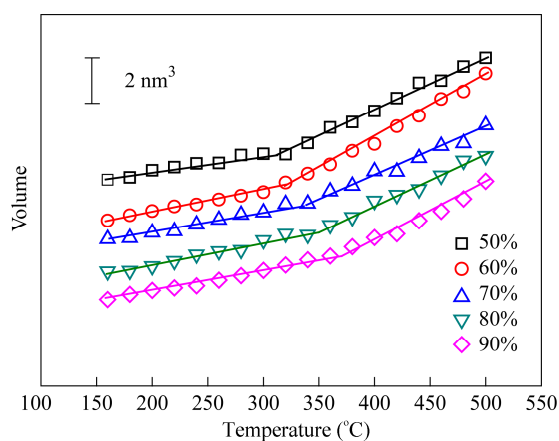


Fig. 7 Change of volume with temperature for epoxy adhesives of different CLD, fitted with bilinear function (The intersection corresponds to T_g .)

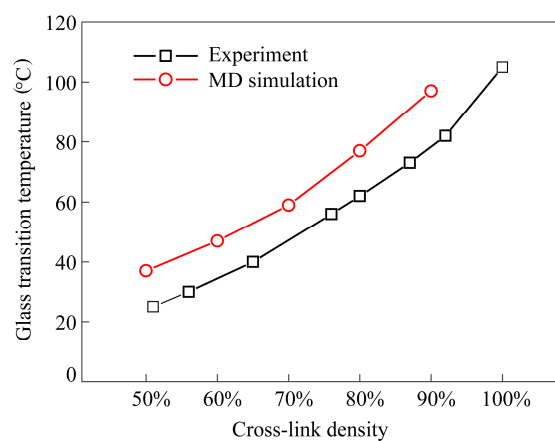


Fig. 8 Change of T_g with CLD

Uniaxial Tension

The experiment result of the true stress-strain (σ - ε) curve of the epoxy adhesive under uniaxial tensile quasi-

static loading is shown in Fig. 9. The given curve is the average curve of the four specimens. The curve shows that σ increased linearly with ε when $\varepsilon < 0.020$, and E was equal to 1.3 GPa. Further increase of ε led to the yielding of the adhesive, with σ increasing at a slower pace and stabilized at $\sigma_Y = 37$ MPa. Finally, the epoxy adhesive failed at $\varepsilon_f = 0.080$. The measured strain rate was $3.0 \times 10^{-3}/s$.

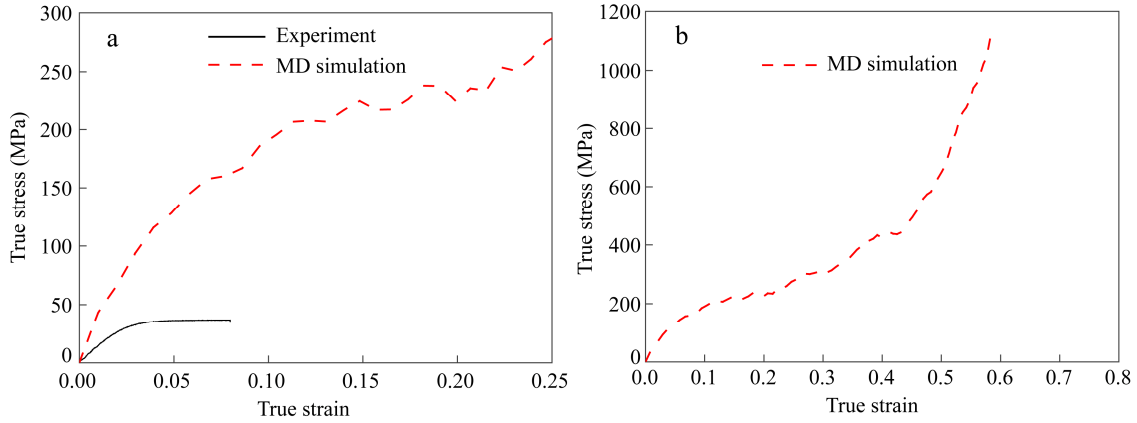


Fig. 9 σ - ε curve of the epoxy adhesive under uniaxial tensile loading: (a) experiment compared to simulation and (b) the whole curve for simulation

The MD simulation result of the σ - ε curve is shown in Fig. 9(b). The curve shows that σ increased linearly with ε when $\varepsilon < 0.10$, and E was equal to 1.8 GPa. The adhesive yielded at $\sigma_Y = 210$ MPa. σ continued to grow to 420 MPa when ε reached 0.40. After that, it increased at a faster pace and exceeded 1 GPa. Failure was not predicted in the simulation.

The elastic lateral strain-tensile strain curves for both experiment and simulation are plotted together in Fig. 10. Both curves show an elastic Poisson's ratio (ν) of 0.42. The above experiment and simulation results are summarized in Table 2.

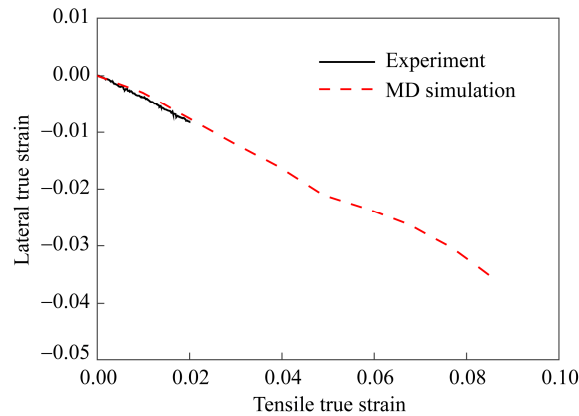


Fig. 10 The experiment and simulation elastic lateral strain-tensile strain curves of the epoxy adhesive under uniaxial tensile loading

Table 2. Uniaxial tensile properties of the epoxy adhesive, experiment and simulation

	Experiment	Simulation	Difference (%)
E	1.3 GPa	1.8 GPa	38
ν	0.42	0.42	0
σ_Y	37 MPa	210 MPa	468
ε_f	0.080	Not predicted	

The E predicted by MD simulation was 38% larger than the experiment value, mainly owing to strain rate effect. Polymers are strain rate dependent materials. Dynamic mechanical analysis (DMA) results show that the storage modulus (E') of a polymer increases with frequency (f). Moreover, if the polymer is in glassy state, its E' changes slightly with f when f is high^[22]. In this study, the epoxy adhesive was stretched at a strain rate of $1 \times 10^9/\text{s}$ in MD simulation, and $3.0 \times 10^{-3}/\text{s}$ in experiment. In both cases, the epoxy adhesive was in glassy state. So the difference in E was reasonable. The elastic ν predicted by MD simulation was exactly the same with experiment result, because ν is a geometric property of a polymer and is not influenced by strain rate.

MD simulation and experiment gave considerably different values of σ_Y . The reasons are twofold. On one hand, strain rate played a role. Zhang reported a 50% increase in σ_Y of an epoxy adhesive when the tensile strain rate increased from $5.0 \times 10^{-3}/\text{s}$ to $1.0 \times 10^2/\text{s}$ ^[6]. It is reasonable to believe that the difference in σ_Y could become even larger when the strain rates are more dissimilar, as is in this study. On the other hand, the yielding mechanisms were different for the two cases. The molecular model of the epoxy adhesive in MD simulation described a 3D periodic network that extended to infinity. The network was perfectly cross-linked with no flaw. It kept integrity when stretched, so the molecular chains had very limited mobility when non-bond interaction was dominating in the yielding stage, resulting in a higher σ_Y . In experiment, the specimen was hardly perfect. The fillers, air bubbles and other inclusions caused weaker interaction in the adhesive. When it was stretched, local debonding occurred and led to crazing^[22]. In these regions, the molecular chains were not constrained laterally and thus had higher mobility. Consequently, the adhesive yielded at a lower σ_Y .

The failure of adhesive was observed at $\varepsilon_f = 0.080$, while failure did not occur in MD simulation even when ε exceeded 0.60. One of the reasons was that the flaws in the adhesive led to earlier failure in experiment than in MD simulation. Another more intrinsic reason lied in the fact that the PCFF adopted in MD simulation was not able to predict bond break. For a cross-linked structure with sufficiently high CLD, it was very hard to create failure with pure non-bond interaction. So σ continued to grow without dropping in MD simulation.

In general, reasonable correlation of uniaxial tensile properties has been achieved between experiment and MD simulation. Again, this indicated that the simplified molecular model of the epoxy adhesive was reliable.

Limitations and Prospects

An important limitation of this study was the disparities of time and length scales between experiment and MD simulation. The time scale difference, being a minor concern, triggered the strain rate effect and led to quantitative inconsistency. The major concern was length scale, which resulted in different yielding and failure mechanisms. In future work, we would narrow these gaps by resorting to coarse grain (CG) techniques^[23]. The CG method allows larger system size to mimic micrometer-scale structure as well as lower loading speed. CG molecular dynamics also features bond breaking^[24], which provides great help in failure analysis. In this way, the uniaxial tensile properties can be better predicted. Furthermore, the molecular model will be employed for multi-scale study of the effect of HTD on the mechanical properties of the epoxy adhesive.

CONCLUSIONS

In this study, we examined the glass transition and uniaxial tensile properties of a commercially available epoxy adhesive using both experimental measurements and MD simulation. DSC and uniaxial tensile tests were performed. For MD simulation, DGEBA and MPUR were selected to represent the adhesive and its mechanical properties were predicted. Reasonable correlation has been achieved between experiment and MD simulation. The conclusions are as follows.

1. For MD simulation, representing the commercially available epoxy adhesive with two main compositions simplifies the problem but does not sacrifice accuracy in the prediction of T_g , E and ν .
2. The T_g of the epoxy adhesive increases when the CLD increases, which was observed in both experiment and MD simulation.
3. MD simulation gives a 38% higher E than experiment, mainly owing to an increase of strain rate from $3.0 \times 10^{-3}/\text{s}$ to $1.0 \times 10^9/\text{s}$.

4. Experiment and MD simulation produced same value of ν , a geometric parameter insensitive to strain rate and size.

5. MD simulation gives a 468% larger prediction of σ_Y and no prediction of failure, because of incapability of reconstructing correct yielding and failure mechanism.

REFERENCES

- 1 Saldanha, D.F.S., Canto, C. and da Silva, L.F.M., *Int. J. Adhes. Adhes.*, 2013, 47: 91
- 2 Carbas, R.J.C., Marques, E.A.S. and da Silva, L.F.M., *J. Adhes.*, 2014, 90(1): 104
- 3 Lettieri, M. and Frigione, M., *Constr. Build. Mater.*, 2012, 30: 753
- 4 Zhang, F., Wang, H.P. and Hicks, C., *Int. J. Adhes. Adhes.*, 2013, 43: 14
- 5 Zhang, F., Yang, X. and Wang, H.P., *Int. J. Adhes. Adhes.*, 2013, 44: 130
- 6 Zhang, F., "Effect of hygrothermal degradation on the dynamic response and cohesive zone model of adhesively-bonded structure", Thesis, Tsinghua University, 2013
- 7 Wu, C. and Xu, W., *Polymer*, 2006, 47(16): 6004
- 8 Shenogina, N.B., Tsige, M. and Patnaik, S.S., *Polymer*, 2013, 54(13): 3370
- 9 Yang, S. and Qu, J., *Polymer*, 2012, 53(21): 4806
- 10 Li, C. and Strachan, A., *Polymer*, 2011, 52(13): 2920
- 11 Lin, Y.C. and Chen, X., *Chem. Phys. Lett.*, 2005, 412(4): 322
- 12 Chang, S.H. and Kim, H.S., *Polymer*, 2011, 52(15): 3437
- 13 URL: [https://tds.us.henkel.com/NA/UT/HNAUTTDS.nsf/web/BF63884582D6A89F852575610048CCF6/\\$File/Terokal%205089-EN.pdf](https://tds.us.henkel.com/NA/UT/HNAUTTDS.nsf/web/BF63884582D6A89F852575610048CCF6/$File/Terokal%205089-EN.pdf) [22 July 2014]
- 14 ASTM Standard D638 - 10, "Standard test method for tensile properties of plastics", ASTM International, West Conshohocken, PA, 2003
- 15 URL: <http://hybris.cms.henkel.com/henkel/msdspdf?country=US&language=EN&matnr=1182757> [22 July 2014]
- 16 Petrie, E.M., "Epoxy adhesive formulation", McGraw-Hill, 2006, p. 59
- 17 Chen, P., Liu, S. and Wang, D., "Epoxy resin and its application" (in Chinese), Chemical Industry Press, Beijing, 2011, p. 78
- 18 Sun, H., *J. Comput. Chem.*, 1994, 15(7): 752
- 19 Sun, H., Mumby, S.J. and Maple, J.R., *J. Am. Chem. Soc.*, 1994, 116(7): 2978
- 20 Sun, H., *Macromolecules*, 1995, 28(3): 701
- 21 Hill, J.R. and Sauer, J., *J. Phys. Chem.*, 1994, 98(4): 1238
- 22 Halary, J.L., Laupretre, F. and Monnerie, L., "Polymer Materials: Macroscopic Properties and Molecular Interpretations", Wiley, 2011, p. 183
- 23 Marrink, S.J., Risselada, H.J. and Yefimov, S., *J. Phys. Chem. B*, 2007, 111(27): 7812
- 24 Lorenz, C.D., Stevens, M.J. and Wool, R.P., *J. Polym. Sci., Part B: Polym. Phys.*, 2004, 42(18): 3333