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Effect of structural voids on mesoscale mechanics of epoxy-based materials

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Abstract. Changes in chemical structure have profound effects on the physical properties of epoxy-based materials, and eventually affect the durability of the entire system. Microscopic structural voids generally existing in the epoxy cross-linked networks have a detrimental influence on the epoxy mechanical properties, but the relation remains elusive, which is hindered by the complex structure of epoxy-based materials. In this paper, we investigate the effect of structural voids on the epoxy-based materials by using our developed mesoscale model equipped with the concept of multiscale modeling, and SU-8 photoresist is used as a representative of epoxy-based materials. Developed from the results of full atomistic simulations, the mesoscopic model is validated against experimental measurements, which is suitable to describe the elastic deformation of epoxy-based materials over several orders of magnitude in time- and length scales. After that, a certain quantity of the structure voids is incorporated in the mesoscale model. It is found that the existence of structural voids reduces the tensile stiffness of the mesoscale epoxy network, when compared with the case without any voids in the model. In addition, it is noticed that a certain number of the structural voids have an insignificant effect on the epoxy elastic properties, and the mesoscale model containing structural voids is close to those found in real systems.

Keywords: multiscale modeling; molecular dynamics; mesoscale mechanics; epoxy-based materials; structural voids

1. Introduction

Epoxy-based materials are an important family of polymeric materials, which comprise a three-dimensional covalent network formed by a cross-linking process among epoxy monomers. In recent years, these materials have found their applications across a large range of length scales (Browning and Hartness 1972, Adams *et al*. 1997, Conradie and Moore 2002), especially in micro-electromechanical systems (MEMS), where historically silicon or other semiconductor-based compounds are mainly used as the building materials. The increasing usage of epoxy-based materials is due to the fact that they have the potential to yield cheaper fabrication and cheaper devices, and more fundamentally, their remarkable physical properties, such as the strong

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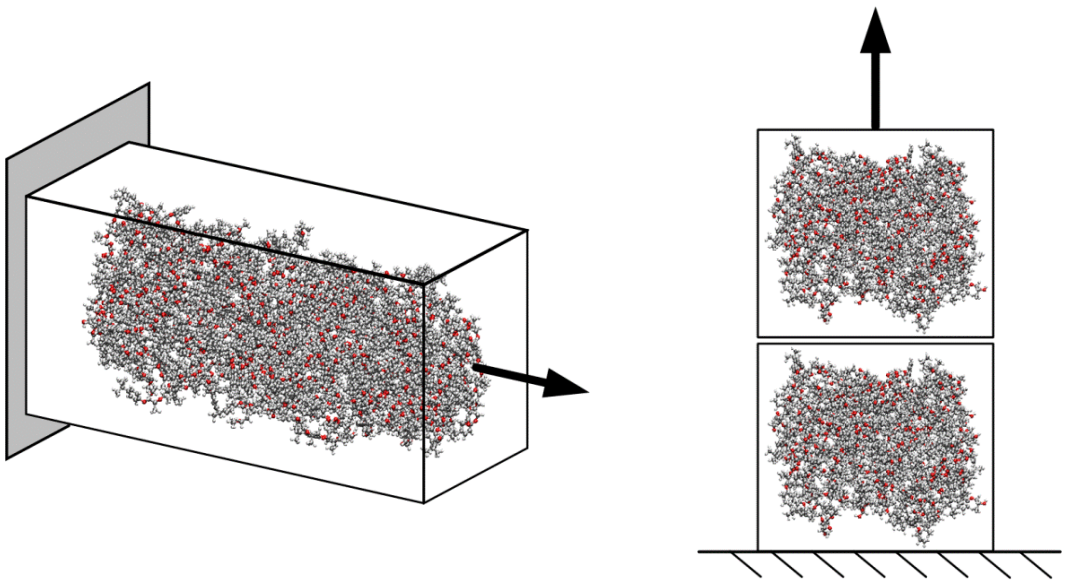
mechanical stability, high thermal and chemical resistance can be put into good use in a variety of devices. As epoxy-based materials are the basis for these various engineering applications, a fundamental understanding of the material structures and mechanical properties is essential, which enables new technologies and to engineer epoxy-based devices. Therefore, considerable scientific and industrial interest has been attracted in investigating the structure-property relationship of the epoxy-based materials. During the curing process, microscopic structural voids, such as free volume can be developed and trapped in the epoxy cross-linked structure (Pethrick 1997, Dlubek *et al*. 2006). Moreover, in the long-term service, voids can be formed in the epoxy structure even for the initially void-free specimens, leading to the changes in material structure (Shibuya *et al*. 1977). Investigations of the microscopic structural voids can provide a basic understanding of the mechanical properties of epoxy-based materials.

The earlier experimental studies have reported that the voids dimension in epoxy-based materials is normally at the magnitude of nanometer (Pethrick 1997, Dlubek *et al*. 2006). The formation of the voids is shown to be dependent on the epoxy chemistry, which can affect the structural relaxation of the cured products (Dlubek *et al*. 2006). Meanwhile, a recent study on crystalline polymers shows that the specimens with greater free volume possess higher glass transition temperatures, greater damping strength, and lower density (Hsieh *et al*. 2001). Furthermore, the influence of free volume on mechanical properties is reported in a study of epoxy/poly(methyl methacrylate) (PMMA) blends, where a higher weight percentage of PMMA in the blends can increase the relative fractional free volume, but lower the tensile strength (Ravikumar *et al*. 2005). However, despite the abundant investigation of the structural voids, relatively little is known about their effect on the mechanical properties of pure epoxy materials. Molecular dynamics (MD) method can be useful for characterizing the cross-linked structure of epoxy-based materials, and studying the mechanical properties in the consideration of nanoscale structural voids. Microscopic information about the molecular structures of the cross-linked epoxy network has been successfully obtained through the observation of molecular motions (Tam and Lau 2014, Tam and Lau 2015). Notably, an atomistic simulation of an epoxy photoresist has reported a new development of a computational cross-linking algorithm which is capable of constructing a highly cross-linked epoxy network and predicting the physical properties in a close agreement with experimental measurements (Tam and Lau 2014). But it is noted that the epoxy-based materials are generally at sub-micron scale with a large number of cross-links between epoxy monomers. It requires excessive computational power to model the cross-linking process in the epoxy structure, and also calculate the mechanical properties of the three-dimensional molecular structure with structural voids. To overcome these limitations, coarse-grained (CG) molecular dynamics simulations have been performed by using the Kremer-Grest model (bead-spring model) (Kremer and Grest 1990). In the CG molecular models of epoxy-based materials, several monomer units are represented by a single bead. The bead-spring CG model has been used to model the mechanical properties of epoxy-based photoresist and entangled polymer gels (Yagyu *et al*. 2012, Sliozberg *et al*. 2013). Although these studies have successfully used CG molecular dynamics simulations to investigate polymer materials, the modeled bead-spring models are still relatively small in size. More importantly, the earlier atomistic and coarse-grained studies mainly focus on the properties measurements without considering the structural voids, which frequently result in the overestimation of the simulated Young's modulus (Yagyu *et al*. 2012, Tam and Lau 2014). Therefore, the understanding of structural voids effect on the mechanical properties of the epoxy-based materials is also important for achieving a high accuracy in the properties predictions.

In this work, we present the study of the structural voids effect on the epoxy-based materials

based on a developed mesoscale model. The mesoscale model of epoxy-based materials is developed by reducing some of the atomistic degrees of freedom, representing the epoxy structure as a collection of beads connected by spring-like molecular interatomic potentials. These interaction potentials describe the resistance to tensile load, and intramolecular interaction of the epoxy cross-linked structure. Our mesoscale model is capable of treating the deformation physics of giant covalent epoxy network corresponding to systems with millions of atoms. With parameters rigorously derived from full atomistic simulations, our mesoscale model provides a bottom-up description of epoxy-based materials. Because of the increase in the accessible time and length scales, such CG models may significantly contribute to development of a fundamental understanding of multiscale interactions. A certain number of nanoscale structural voids can be easily introduced in the mesoscopic epoxy network according to the experimental data (Dlubek *et al*. 2006). Therefore, it enables studies of epoxy mechanical properties in the consideration of structural voids, which have not been fully understood so far. The focus in this paper is on the SU-8 epoxy-based material, which is designed specifically for the fabrication of high-aspect ratio and three-dimensional MEMS (Campo and Greiner 2007). As the SU-8 photoresist has high functionality, a high cross-linking degree can be obtained, which can permit a high aspect ratio and straight sidewall to be achieved. The highly cross-linked epoxy network makes SU-8 relatively stable in the mechanical domain. Notably, SU-8 has a higher Young's modulus after polymerization process compared with other commonly used photoresists such as PMMA, which is important for achieving a better mechanical reliability of the final products (Lorenz *et al*. 1997, Feng and Farris 2002, Ishiyama and Higo 2002, Feng and Farris 2003, Hammacher *et al*. 2008).

The objective of this paper is to predict the mechanical properties of the epoxy-based materials in consideration of nanoscale structural voids by using our developed mesoscale model. In this paper, a series of full atomistic calculations are firstly discussed to determine the fundamental mechanical parameters of a SU-8 epoxy network, including tensile stiffness and adhesion



(a) Tensile loading (b) Adhesion test

Fig. 1 Mechanical loading cases of the SU-8 to derive parameters for the mesoscopic model

properties. Subsequently, a mesoscopic model of SU-8 and derivation of parameters for this model from full atomistic studies are described. Based on the developed mesoscale model, a certain number of structural voids with a volume of 97 $Å^3$ are introduced into the epoxy structure, and uniaxial elongation is used to investigate the mechanical properties of the mesoscale epoxy models. Finally, the results and implications of the structural voids effect are discussed. This study demonstrates a general mesoscopic coarse-grained technique which can be applicable to different epoxy-based materials involving the cross-linked network structure. Computer models that allow straightforward access to the properties of large-scale epoxy-based materials can provide immediate help in engineering those epoxy-based material systems and devices.

2. Methods

2.1 Atomistic simulations

In this section, a series of mechanical loading cases to determine parameters for the mesoscopic epoxy model are described. These studies consist of the following two loading cases: (i) tensile loading, to determine Young's modulus and (ii) an assembly of two epoxy cross-linked molecules to determine their adhesion energy. The different loading cases are shown in Figs. 1(a)-(b). All studies are carried out using the atomistic SU-8 model, which is constructed based on earlier full atomistic study of its microstructure and physical properties (Tam and Lau 2014).

2.1.1 Simulation details

The atomistic simulations are performed by using the classical MD (Allen and Tildesley 1989). During the simulation, MD predicts the evolution of a large number of atoms in time by dealing with a series of Newton's equations of motion governed by interatomic interaction. In general, classical MD is used to simulate model sizes containing a few thousand atoms and time scales on the order of nanoseconds, as such model sizes and time scales are still far beyond the capabilities of quantum mechanics based methods.

The detailed interatomic interactions in the SU-8 molecular structure are described by a forcefield, which is the core of classical MD methods. The forcefield determines the potential energy of all the atoms based on their positions and internal coordinates, including bond lengths, bond angles, torsion angles and improper out-of-plane angles. During recent decades, numerous forcefields describing atomic interaction in various materials with different levels of accuracy have been proposed, each having unique problems and strengths. For covalently bonded materials like the epoxy, several forcefields have been developed, including Consistent Valence ForceField (CVFF) (Dauber-Osguthorpe *et al*. 1988, Maple *et al*. 1988), Dreiding forcefield (Mayo *et al*. 1990) and Polymer Consistent ForceField (PCFF) (Sun 1995). Here the PCFF potential is used to describe the interatomic interactions of atoms in SU-8 structure, which captures not only the pair-wise interactions but also additional cross-coupling terms from the local geometric configuration of the neighboring atoms. The PCFF potential has reported to be reliable for the simulations of epoxy-based materials (Yarovsky and Evans 2002, Yang and Qu 2012, Tam and Lau 2014).

The time step is chosen to be on the order of femtosecond. And the van der Waals (vdW) interaction has a large cut-off of 13.5 Å. The MD simulations are performed using the open source code LAMMPS (Plimpton 1995).

2.1.2 Tensile loading

The computational experiment to model uniaxial tensile deformation of the SU-8 epoxy chain is carried out by keeping one end of the chain fixed, while slowly stretching the other end in the axial direction of the chain. The loading configuration is shown in Fig. 1(a). Three different displacement loading rates are applied in the tensile deformation, including 10, 5 and 2.5 m/s. During the entire tensile deformation, the virial stress tensors are monitored and averaged over the complete chain volume. The stress tensor component in the loading direction is used to extract information about the stress as a function of applied uniaxial strain. The stress-strain curve is then used to calculate Young's modulus E of the SU-8 epoxy network, defined as

$$E = \frac{\partial \sigma}{\partial \varepsilon} \approx \frac{\Delta \sigma}{\Delta \varepsilon}. \tag{1}$$

One representative stress-strain plot corresponding to the displacement loading rate of 5 $m \cdot s^{-1}$ is depicted in Fig. 2. For the small deformation, the results for all the applied loading rates are similar, indicating convergence of the elastic properties. Young's modulus E is determined by performing a regression analysis on the stress-strain data, which is estimated to be 3.21±0.69 GPa, close to the experimental observation of 2.70-+4.02 GPa (Tam and Lau 2014).

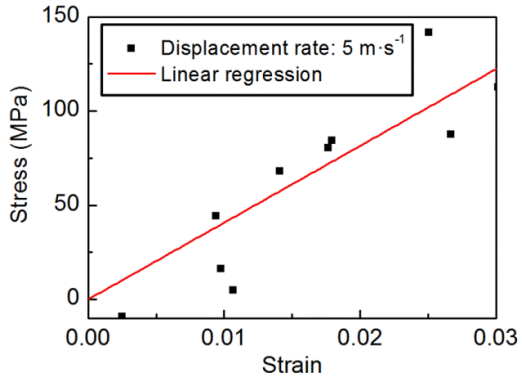


Fig. 2 Stress versus strain data for stretching a SU-8 epoxy chain using the PCFF potential

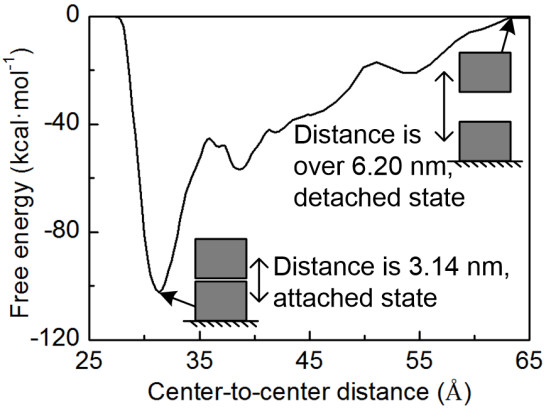


Fig. 3 The plot of the free energy against the center-to-center distance from metadynamics simulation

2.1.3 Interaction of two epoxy molecules: Adhesion properties

In the three-dimensional covalent epoxy network, there are molecules that are not directly connected, where no direct covalent interactions form between these epoxy molecules. The primary interaction forces of these epoxy molecules are weak dispersive interactions. The adhesion energy of epoxy molecules is calculated using the metadynamics method (Laio and Gervasio 2008, Lau *et al*. 2012, Lau *et al*. 2014, Tam and Lau 2015). The metadynamics simulations are performed using the LAMMPS and PLUMED packages coupled with PCFF potential. The geometry of the two epoxy molecules is depicted schematically in Fig. 1(b). The system is first equilibrated without application of any external mechanical load. The equilibrated state of the system is affirmed by examining the root-mean-square displacement (RMSD) of the atoms in the epoxy molecules, which becomes stable at the end of the equilibration. After that, metadynamics simulation is performed using the PLUMED package. The free energy is measured as a function of the center-to-center distance between two epoxy molecules. The metadynamics simulation converges after a 17 ns time span, permitting a full exploration of all possible states. The plot of the free energy against the center-to-center distance is shown in Fig. 3. The equilibrium distance between two epoxy molecules is found to be $\Delta D \approx 31.4$ Å, which approximates to the thickness h_0 of the epoxy molecule. And a relationship between ΔD and h_0 that depends on the dimension of the epoxy molecules can be arrived

$$\frac{\Delta D}{h_0} \approx 1. \tag{2}$$

For same size of the epoxy molecules in the weak dispersive interactions, the equilibrium distance ΔD can be approximated as equal to their thickness. The free energy difference between the attached state and the separated state is 102.36 kcal·mol^{-1}. With the surface area being 14.00 nm^2, the normalized adhesion energy E_s of two epoxy molecules is approximately equal to 50.8 mJ·m^{-2}.

2.2 Mesoscopic model development: Training from pure atomistic results using energy and force matching

From the atomistic simulation results carried out on the epoxy chain and molecules, it can develop a better understanding of the mechanisms and forces during the deformation of epoxy at a microscopic level. The information is used to develop a mesoscopic model, in which beads are connected by springs to represent the epoxy covalent network, whereas all parameters are completely derived from atomistic calculations. With the reduction of degrees of freedom in the mesoscopic model, it can model the epoxy structure with lengths on the order of few tens of nanometers. Therefore, this approach enables one to study the nanoscale structural voids.

2.2.1 Potential energy

The goal here is to develop a mesoscopic model possible to perform large-scale studies of the mechanics of epoxy-based materials, eventually leading to understanding of structural voids effect on the behavior of these materials. The total energy of the system can be expressed as

$$E = E_T + E_{weak}, \tag{3}$$

where E_T is the energy stored in chemical bonds due to stretching along the axial direction, and

E_{weak} constitutes weak, dispersive interactions between different parts of epoxy structure. Similar techniques have been used effectively to model the behavior of carbon nanotubes, collagen molecules, wood cell walls and silica nanocomposites (Buehler 2006a, Buehler 2006b, Sen and Buehler 2010, Adler and Buehler 2013).

The axial strain energy is simulated through harmonic potential of the form

$$\phi_T(r) = \sum_{bonds} \frac{1}{2} K_T \left(r - r_0\right)^2, \tag{4}$$

where r is the distance between bonded beads, with the "0" subscript that refers to the equilibrium distance. Meanwhile, the weak, dispersive interactions are modeled by a 12:6 Lennard-Jones (LJ) potential of the form

$$\phi_{weak}(r) = \sum_{pairs} 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{5}$$

with ε as the energy at equilibrium and σ as the distance parameter for each pairwise interaction.

2.2.2 Equilibrium distances of beads and corresponding masses

The mass of each bead can be determined by assuming a homogeneous distribution of mass in the molecular model, which is an excellent assumption for the homogeneous structure of epoxy-based materials. The beads are connected through springs to form a network model of a primitive cubic system, which is considered as a representative of the epoxy cross-linked structure. Such three-dimensional bead-spring network is analogous to the mesoscopic crystalline silica, of which one bead is connected with six neighboring beads by springs (Sen and Buehler 2010). In the epoxy network with structural voids, the beads at the void locations can be removed to create the structural voids. Previous studies have shown that the void volume is 87-111 $Å^3$ for the diglycidyl ether of bisphenol A (DGEBA) epoxy resin, and 97±33 $Å^3$ for the uncured DGEBA (Jeffrey and Pethrick 1994, 1997, Dlubek *et al*. 2006). In this study, it is designated that one bead has the same mean volume of the voids, i.e., 97 $Å^3$. The equilibrium distance r_0 of two beads is calculated to be 4.6 Å. As the SU-8 has a density of 1.2 g·cm^{-3}, it is determined that the mass of one bead with a volume of 97 $Å^3$ is around 70 amu. Therefore, each bead has a weight of 70 amu.

2.2.3 Dispersive and nonbonding interactions

The LJ parameters are chosen to reproduce the adhesion energy determined from full atomistic simulations. In all these considerations, it is assumed that a pair-wise interaction between different particles is sufficient and that there are no multi-body contributions (Buehler 2006a, Buehler 2006b). Based on these assumptions, the interaction between different molecules is modeled using a LJ 12:6 potential.

The equilibrium bond distance is related to the distance ΔD between two epoxy molecules in contact by weak, dispersive interactions. With

$$\phi = \tan^{-1}\left(\frac{r_0}{2\Delta D}\right), \tag{6}$$

a relationship between ΔD and the angle ϕ that depends on the geometry of the mesoscopic system can be arrived,

$$D = \frac{\Delta D}{\cos\phi}, \tag{7}$$

where ΔD can be approximated to the thickness h_0 of the epoxy molecule, i.e., $\Delta D \approx 4.6$ Å. The distance parameter in the LJ potential is then given by

$$\sigma = \frac{D}{\sqrt[6]{2}} \approx 4.6 \text{ Å}, \tag{8}$$

where D is the equilibrium bond distance.

The LJ potential minimum is at $r=D$ and is given by $-\varepsilon$. Per unit cell of bonds in this setup, the energy per unit area is given by

$$E_S = \frac{2}{S_0}\left[\phi_{weak}(D) + \phi_{weak}\left(\tilde{D}\right) + ...\right], \tag{9}$$

where

$$\phi_{weak}(D) = -\varepsilon. \tag{10}$$

The distance to second nearest neighbors is

$$\tilde{D} = \frac{\Delta D}{\cos\left(\tilde{\phi}\right)}, \tag{11}$$

where

$$\tilde{\phi} = \tan^{-1}\left(\frac{3r_0}{2\Delta D}\right). \tag{12}$$

Similar calculations can be done for the third, fourth, etc. nearest neighbors.

The numerical value for adhesion strength of two epoxy molecules from MD simulation is E_S=50.8 mJ·m^{-2}. The parameter ε in the mesoscopic model is chosen so that the atomistic and mesoscopic model feature the same adhesion energy per unit area. For nearest neighbors only, we find

$$\varepsilon = \frac{E_1 S_0}{2}. \tag{13}$$

For more than one nearest neighbors in the case of larger cut-off radius

$$\varepsilon = \frac{E_S S_0}{2}\left[\left(1 + \pi^{(2)} + \pi^{(3)} + ...\right)^{-1}\right], \tag{14}$$

where $\pi=\phi_{weak}(\tilde{D})/\phi_{weak}(D)$. We define term $(1+\pi^{(2)}+\pi^{(3)}+...+\pi^{(N)})=\beta^{(N)}$ and find that $\beta^{(6)}\approx 1.0988$, which leads to $\varepsilon \approx 0.7$ kcal·mol^{-1}, with a cut-off distance at r_{cut}=30 Å.

2.2.4 Tensile spring parameter

The tensile spring constant is determined from previous tensile loading deformation, where various calculations of stretch versus deformation are carried out in the regime of small loads and

consequently small displacements. The stress-strain response of SU-8 epoxy obtained in full atomistic calculations is used to develop the interaction of bonded beads. The spring constant k_T is then defined as

$$k_T = \frac{A_c}{r_0} E \tag{15}$$

with A_c being the cross-sectional area of the SU-8 epoxy chain with a value of 20 nm^2, and r_0 the equilibrium distance of two beads. Based on the low-strain rate tensile testing data discussed in previous section, k_T is found to be around 201.82 kcal·mol^{-1}·Å^{-2}.

2.3 Mesoscopic simulations

The parameters used in the mesoscopic simulations of SU-8 epoxy are summarized in Table 1. A series of samples are modeled to describe the mesoscale mechanics and structural voids effect of epoxy-based materials. Two cases are investigated: (i) a simple validation calculation to compare the mesoscale model to the experimental results; and (ii) a study of structural voids effect on mesoscale epoxy structure.

2.3.1 Validation: Tensile test of a mesoscale SU-8 network

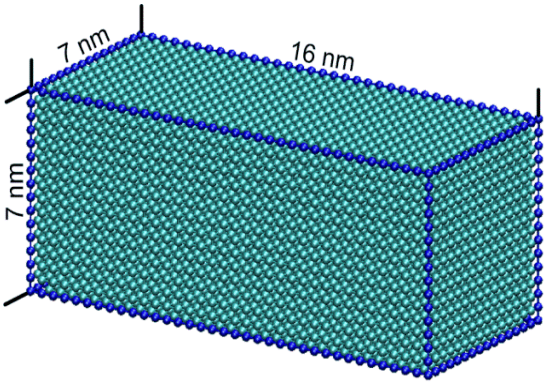
The initial mesoscopic model is set up by distributing the 9,216 (36×16×16) beads in the 16×7×7 nm^3 simulation box. These beads are equally separated by 0.46 nm, and connected with springs to form a covalent network, as shown in Fig. 4(a). Several springs are removed averagely in the epoxy network, to achieve the experimental cross-linking degree of around 83% (Tam and Lau 2014). A large time step of 5 fs can be used for integration of the equations of motion, as each bead has a large mass of few tens of atomic mass units (Buehler 2006a). Non-periodic and shrink-wrapped boundary conditions are used in all three dimensions during the simulations. The system is equilibrated for 12.5 ns to reach an energy-minimized state. And then the mesoscopic epoxy chain is subjected to the tensile loading as similar to the loading case shown in Fig. 1(a). The stress versus strain is recorded during the deformation of the mesoscopic model.

2.3.2 Effect of structural voids on a mesoscale SU-8 network

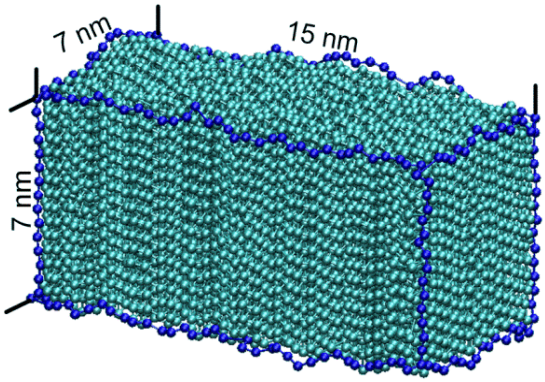
Based on the previous defined mesoscopic model, structural voids are introduced to quantify the effect on the mechanical properties. It is reported that the mean number of structural voids per mass unit is 0.65 nm^{-3} (Dlubek *et al*. 2006). For the initial mesoscopic model, its volume is around 770 nm^3, and thus the number of structural voids in the model is 500. In this study, it is designated that one bead has the same mean volume of one void. To create the structural voids, 500

Table 1 Summary of mesoscopic parameters derived from atomistic modeling

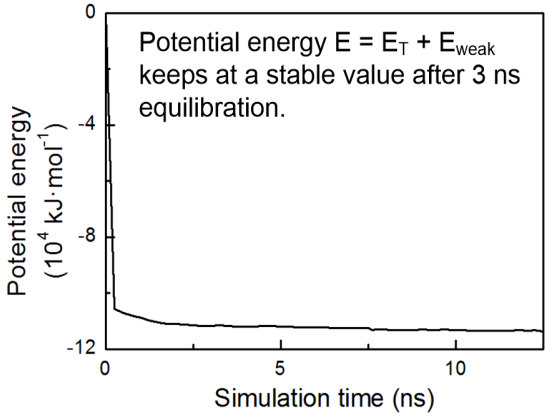
Parameter	Numerical value
Equilibrium bead distance r_0 (Å)	4.6
Tensile stiffness parameter k_T (kcal·mol^{-1}·Å^{-2})	201.82
Dispersive parameter ε (kcal·mol^{-1})	0.7
Dispersive parameter σ (Å)	4.6



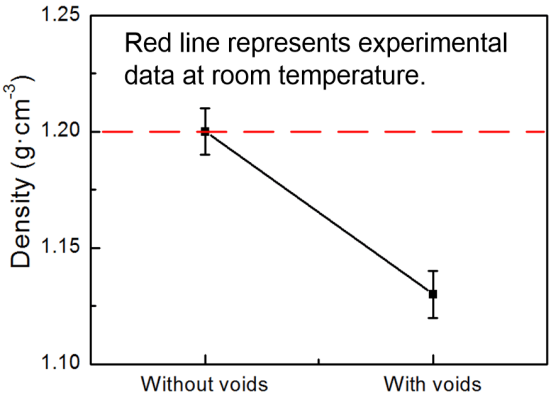
(a) The initial configuration



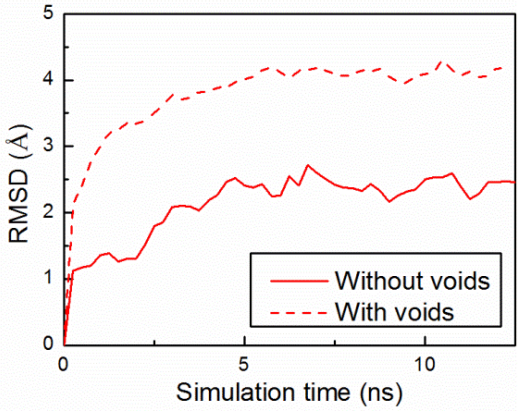
(b) The equilibrium configuration



(c) Potential energy evolution



(d) Density of equilibrated mesoscopic models



(e) Root-mean-square displacement of the beads

Fig. 4 Snapshots of initial and equilibrium configurations, plot of potential energy evolution, density and root-mean-square displacement (RMSD) of the beads of mesoscopic SU-8 model

Table 2 Weight of mesoscopic SU-8 model

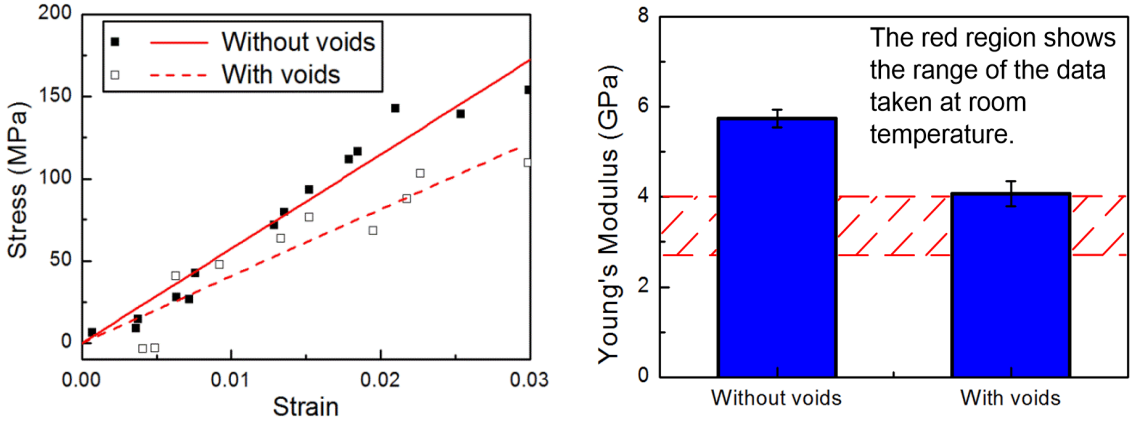
	Without voids	With voids	Loss of weight
Weight (amu)	641,620	610,120	~5.5%

beads are removed from the initial mesoscopic model, and the springs connected to the removed beads are deleted accordingly. These 500 beads for structural voids are selected randomly and distributed averagely across the mesoscopic model. To determine the variation from different random models, two independent models with structural voids have been constructed. Same as the original model, 500 beads are selected randomly and removed accordingly, but the distributions of the removed beads are different from each other. The weight of the mesoscopic models is summarized in Table 2. The mesoscopic SU-8 model is equilibrated adequately using the equilibration conditions corresponding to previous case. And then the computational tensile deformation is carried out to investigate the mechanical response of the model with structural voids.

3. Result and discussion

3.1 Properties of the mesoscale SU-8 network

In equilibrium state, the epoxy network is relaxed to the potential energy minimum, as shown in Fig. 4(b). The evolution of the potential energy is plotted in Fig. 4(c), where the potential energy decreases to a stable value at 3 ns. For the validation of the developed mesoscopic model, density (ρ) is a critical parameter which shall be consistent with the experimental value. During the last 5 ns MD equilibration run, the ρ of SU-8 epoxy network is sampled every 100 ps. The average ρ of mesoscopic SU-8 network without structural voids is shown in Fig. 4(d). The error bars shown in the figure are obtained from the standard derivations of the averages. A ρ of 1.20±0.01 $g \cdot cm^{-3}$ is obtained for the SU-8 epoxy network with no structural voids, which shows an excellent agreement with the experimental value of 1.20 $g \cdot cm^{-3}$ by MicroChem. Meanwhile, Young's modulus (E) of the mesoscopic SU-8 model is another important material parameter for validation. During the uniaxial tensile deformation, the stress versus strain as obtained using the mesoscopic model is recorded and shown in Fig. 5(a). The stress along the loading direction shows a linear response to the applied strain, which indicates that mesoscopic epoxy network is elongated elastically within the small strain deformation. The E is calculated by performing a linear regression analysis based on the obtained stress-strain curve. The result is shown in Fig. 5(b), and the error bars presented in the plots refer to the standard deviations of the calculated results. The data reported is from a single run, and the standard deviation comes from the linear regression of the stress-strain curve obtained from that simulation run. The E of the mesoscopic SU-8 network is 5.74±0.19 GPa, which is larger than the experimental tensile test measurements in the range of 2.70-4.02 GPa (Lorenz *et al*. 1997, Feng and Farris 2002, Hammacher *et al*. 2008). Realistically, MD probes the modulus in the athermal limit. Compared with the experiment, the strain rate in MD simulation is several orders of magnitude higher, and the contribution of thermal motions to the mechanical response of the material is less. Both factors can result in the higher moduli observed. Therefore, MD simulation result can be in closer agreement with that from high strain rate or low temperature pulling experiment. Meanwhile, the overestimation of E is consistent with our previous study of full atomistic epoxy network, which might be due to the fact that the constructed mesoscopic model is free of structural voids, as they normally exist in the experimental samples (Tam and Lau 2015). Nonetheless, in view of the good agreement of ρ with experimental data, the developed mesoscopic SU-8 network is considered as a suitable model for investigating the effect of structural voids on epoxy mechanical properties.



(a) Stress versus strain data from tensile test (b) Histograms showing the Young's modulus

Fig. 5 Tensile test of the mesoscale SU-8 network

3.2 Effect of structural voids

To investigate the role of structural voids on epoxy properties, the mesoscopic model with a certain number of voids is constructed. During the equilibration process, the ρ of the SU-8 epoxy network with structural voids is measured and compared with the model with no voids, as shown in Fig. 4(d). The computed SU-8 ρ with voids is 1.13±0.01 g·cm^{-3}, which is slightly smaller than the model without voids. Meanwhile, the density ρ of the two independent models with different distributions of structural voids is found to be in good accord with the original model. The reason for a relatively smaller density is that the existence of structural voids in the epoxy network causes a loss of weight in comparison with the sample without voids, and more essentially, it weakens the covalent interactions in the cross-linked network, where the monomers near the structural voids can flow more freely, which can lead to the expansion of the network before the curing process is completed. The movement of the monomers in the epoxy cross-linked structure, i.e., the beads in the mesoscopic model, can be quantified by using the root-mean-square displacement (RMSD) of the beads during the equilibration run. By comparing the RMSD shown in Fig. 4(e), it is observed that the RMSD of the beads in the model with structural voids keeps at a higher level than that of the model without voids, which demonstrates the larger movements of beads, i.e., the beads flow more freely in the model with voids. Further investigation on the structural voids affected epoxy mechanical properties focuses on the analysis of the Young's modulus. The stress-strain data of epoxy network with voids is shown in Fig. 5(a). The E is calculated to be 4.07±0.28 GPa, which agrees very well with the experimental results of 2.70-4.02 GPa (Lorenz *et al*. 1997, Feng and Farris 2002, Hammacher *et al*. 2008). In the meanwhile, the measured E of the two independent models is also close to the original model. In view of the computed ρ and E of the three models with structural voids, no significant variation is observed from different random models. Furthermore, our results show that with the existence of structural voids, the mesoscopic model possesses the Young's modulus identical to experimental samples, in comparison with the larger variation of the model without voids. Therefore, the developed mesoscopic model of epoxy-based materials with structural voids can be regarded as a reasonable structure close to those found in the real systems, which can be used as basis in the various investigations involving the cross-linked

network at mesoscale. Equipped with the relationship between the SU-8 Young's modulus and the structural voids, it can be concluded that the structural voids are intrinsic to the epoxy-based materials, and a certain number of the voids with a volume of 97 $Å^3$ have no severe impact on the epoxy elastic properties.

4. Conclusions

In this study, molecular dynamics simulations are used to investigate the effect of structural voids on the mechanical properties of epoxy-based materials by using SU-8 photoresists as a representative model. Full atomistic simulations are carried out to study the deformation behavior of epoxy-based materials, where the constructed models are subjected to different mechanical loadings to measure the elastic and adhesion properties of the epoxy-based materials. From the results of full atomistic modeling, we have derived parameters of the mesoscopic epoxy model, which can be used to describe the mechanical response of epoxy-based materials. The developed mesoscale epoxy model possesses a density identical to the reality. Meanwhile, the Young's modulus of the mesoscopic model is close to the experimental data obtained from tensile loading cases. Further investigations shed light on structural changes due to the influence of structural voids. With the existence of structural voids, the mesoscopic epoxy structure has a relatively lower density. Moreover, it is shown that the structural voids reduce the elastic performance of the epoxy-based materials. By incorporation of structural voids, it enables the prediction of the epoxy mechanical properties with a high accuracy. This can lead to a more realistic mesoscale modeling of the epoxy-based materials.

The mesoscale model reported here can open up several possibilities for future studies, particularly at the sub-micron scale, as well as mesoscale applications, which focus on integrated epoxy structures. Results from the current mesoscopic modeling can be used in the investigation on the epoxy-bonded interfaces consisting of different dissimilar materials, which have been increasingly seen in daily applications. It is envisioned that our work will be beneficial to the design, synthesis and applications of epoxy-based materials, so as to engineer the performance of epoxy-based material systems and devices.

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