Moisture effect on the mechanical and interfacial properties of epoxy-bonded material system: An atomistic and experimental investigation

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This paper uses molecular dynamics simulations and experimental methods to investigate the moisture effect on the mechanical and interfacial properties of epoxy-bonded material systems consisting of SU-8 photoresist and silica substrate. In the simulation, the density (\( \rho \)) and Young’s modulus (\( E \)) of cross-linked SU-8 epoxy network are determined. The \( \rho \) shows a monotonic increase with increasing moisture contents, whereas the \( E \) displays an initial increase followed by a decrease, with the largest deterioration of 5.5% compared with the dry case. Furthermore, a SU-8/silica interface is modeled for the investigation of interfacial integrity. A 77.1% reduction of surface energy at the interface is observed in the presence of moisture. In the experiment, the SU-8 photoresist coated on the silica substrate was conditioned in a water bath under different durations. The SU-8 photoresist after 2-week moisture conditioning became milky and black particle-like material texture was observed under optical microscope, which may imply a change of material structure. The \( E \) of SU-8 photoresist was measured as a function of moisture conditioning duration by using nanoindentation, and it was not deteriorated with pronounced moisture ingress, which agrees well with the simulation observations. Moreover, the fracture energy (\( G_f \)) of the SU-8/silica interface is quantified and the reduction of \( G_f \) under presence of moisture corresponds to the simulation observations. Based on both the computational and experimental approaches, it is found that moisture has insignificant effect on the epoxy mechanical properties, but deteriorates the interfacial adhesion dramatically. The dramatic interfacial deterioration should be carefully considered in epoxy-bonded material systems when subjected to a moisture condition.

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1. Introduction

Epoxy applied to the surface of inorganic/organic materials is a typical form of epoxy-bonded material systems. These material systems have received tremendous attention in both industrial and scientific communities, and can be readily found in applications such as micro-electro-mechanical systems (MEMS), civil infrastructures and aerospace industry [1–3]. The durability of these material systems are mainly determined by the mechanical reliability of the bonded materials and the interfacial integrity. Epoxy possesses a three-dimensional covalent network synthesized chemically by a cross-linking process, which exhibits remarkable material properties, such as high cross-linking degree and stiffness. And thus, epoxy can sustain large degree of deformation, which provides strong mechanical reliability of the cross-linked network. Meanwhile, epoxy has reasonably good adhesion to the bonded materials, which is essential to the functionality and performance of many epoxy-bonded material systems, such as epoxy/silica nanocomposites and concrete/epoxy interface [3,4]. However, as epoxy is sensitive to air humidity, moisture can be absorbed into the epoxy-bonded material systems and interact with the bonded materials [5], which can influence the constituents’ mechanical reliability and the interfacial integrity in the material systems [4,6]. Such moisture affected degradation is a major concern for the engineering applications involving the epoxy-bonded material systems, as it could lead to a structural failure ahead of the expected service life.

In this study, an epoxy-bonded material system typical in MEMS applications is chosen as a representative model, which consists of SU-8 photoresist bonded with silica substrate. A number of preliminary studies have reported that SU-8 photoresist has a higher

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Young’s modulus [7–9] than other commonly used photoresists, such as poly(methyl methacrylate) (PMMA) [10], which makes SU-8 as a favorable photoresist for MEMS applications. But the performance of SU-8 photoresist under moisture condition is not yet fully known at this stage, which can be a major concern to the durability of the entire SU-8/silica bonded system. On the other hand, previous studies have reported the moisture deteriorations in the concrete/epoxy interface and the epoxy chain/silica interface through various experimental and simulation approaches [4,11,12]. Considering a similar bilayer structure of epoxy-bonded material systems, SU-8/silica bonded interface may deteriorate due to moisture ingress. Here, an investigation using both computational and experimental approaches is carried out, which can provide a better understanding of the moisture affected structural behaviors of the epoxy-bonded material system.

Among various computational approaches, molecular dynamics (MD) simulation is a fundamental and versatile tool that enables us to investigate the molecular interaction inside the epoxy structure and at the epoxy-bonded interface. Microscopic information about the molecular structures of the cross-linked network is successfully obtained through the observation of molecular motions [13–32].

With the advancement in atomistic modeling, the interactions of polymer systems in contact with water have been widely studied. Notably, an atomistic simulation of an epoxy-diamine system has shown that with increasing moisture concentration absorbed in the epoxy system, its density shows an initial increase followed by a decrease [33]. The density variations are believed to be resulted from the moisture antiplasticization and plasticization effect, which have also been reported from a simulation study on polyamide 6.6 atomistic model [34]. Another molecular modeling study of the cross-linked network based on diglycidyl ether of bisphenol A (DGEBA) has shown a relatively consistent decrease in Young’s modulus with increasing moisture content, where only the moisture plasticization effect is observed [35]. Moreover, MD simulations have been used in the interface modeling and adhesion measurements in the epoxy-bonded material systems with the consideration of moisture [36,37]. Particularly, a molecular simulation study of a DGEBA/silica interface has revealed the weakening of adhesive energy in the presence of water surrounding the interface [11], which is consistent with the results from experimental studies of the concrete/epoxy specimens [4] and FRP-bonded concrete specimens [38]. These studies have demonstrated the applicability of MD simulations in predicting the moisture effect on the epoxy mechanical properties as well as the interfacial adhesion. But in these constructed networks, the cross-linked bonds can be formed when the potential reactive sites are located at a distance within a reaction radius, which is deviated from the actual situations, where bonds cannot form at the distance as large as the reaction radius in the simulation. Alternatively, real epoxy-bonded materials systems can be synthesized to investigate the moisture effect experimentally [39,40]. The chemical interaction between the absorbed moisture and a DGEBA-based epoxy network is studied by using the experimental and MD simulation approaches, and both results have indicated that three forms of absorbed water exist inside the epoxy structure [39]. In addition, the moisture diffusion in a different DGEBA-based epoxy network is investigated, and the calculated moisture diffusivity from experimental sorption process and MD simulation is consistent [40].

By using the MD and experimental approaches, it can provide a comprehensive picture of how the moisture affects the epoxy-bonded material system. In this study, a SU-8 atomistic model is constructed by employing a cross-linking algorithm, which includes consecutive energy minimization and stress relaxation process. The constructed SU-8 epoxy network is solvated with a successive level of moisture content to investigate the moisture effect on the mechanical properties at nano-scale. Meanwhile, the effect of moisture on the interfacial integrity of the epoxy-bonded material system is quantified by measuring the surface energy of SU-8/silica interface model under both dry and wet scenarios. A close examination on the molecular motions gives an atomistic detail of the interfacial failure mechanism. Furthermore, an experimental investigation on both SU-8 photoresist and silica has been conducted. SU-8 photoresist coated on silica substrate after moisture conditioning is characterized by using microscope and nanoindentation. The material texture and Young’s modulus of the moisture conditioned specimen have been captured to illustrate the moisture effect on the mechanical properties. The interfacial fracture energy of SU-8/silica interface is determined under both dry and wet scenarios experimentally to complement the simulation work.

2. Simulation details

The simulation approaches used here start from the construction of an atomistic cross-linked SU-8 epoxy network. Equilibration and dynamic deformation process are carried out on the solvated SU-8 epoxy networks, and the corresponding density and Young’s modulus are computed to investigate the moisture effect on SU-8 mechanical properties. Meanwhile, the moisture affected interfacial integrity is investigated based on a molecular model representing the SU-8/silica interface. The free energy profile of the interface is constructed and used to compute the surface energy of the concerned interface under dry and wet scenarios, respectively. We give more details into the methods used here in the following sections.

2.1. Atomic models

The cross-linking of SU-8 photoresist is initiated by the UV irradiation, which activates the epoxide groups of the SU-8 monomers. The reaction between the activated epoxy monomers results in a highly cross-linked network, and it is noted that this cross-linking reaction does not require external liquid curing agent. The chemical structure of SU-8 monomer is shown in Fig. 1(a), which comprises eight epoxide groups. In this work, cross-linked SU-8 photoresist is modeled three-dimensionally by cross-linking reactions of SU-8 monomers using Materials Studio software [41]. This cross-linked epoxy system is simulated previously in an investigation of its cross-linking process and physical properties [32].

An atomistic model of SU-8 epoxy monomer is first built by using the Sketch tool [41], as shown in Fig. 1(b). The initial SU-8 uncross-linked structure is constructed at the temperature of 300 K by using the Amorphous Cell module [41], which uses a Monte Carlo packing algorithm according to the rotational isomeric states model [42]. A total of forty SU-8 monomers (7960 atoms) are packed into a 3D periodic simulation box with a density of 1.07 g/cm³, the value of which is adopted from the commercially available data by MicroChem. The size of SU-8 epoxy network is determined by investigating the size effect on SU-8 mechanical properties in dry condition, as described in the electronic supplementary information in our previous study [32]. The amorphous SU-8 structure is equilibrated for 10 ps in the isothermal and isochoric ensemble (NVT) at 300 K, followed by another 10 ps equilibration in the isothermal and isobaric ensemble (NPT) at 300 K and 1 atm, and the integration time step is 1 fs. During the entire relaxation process, the Nose thermostat [43,44] is used for the temperature control and Andersen barostat [45] is used for the pressure control. As the cross-linking reaction of SU-8 photoresist is usually carried out at elevated temperature higher than room temperature, same relaxation process is used to equilibrate the structure at that.
temperature before cross-linking reaction. A temperature of 368 K (95 °C) is chosen, as it is the cross-linking temperature of SU-8 sample in the experimental program. After the initial relaxation, the cross-linking process of SU-8 photoresist is carried out by using a cross-linking algorithm developed in previous study [32], which allows the SU-8 structure to achieve high cross-linking degree and get rid of geometrical distortion. Here, the steps involved in this algorithm are described briefly: (1) the reactive atoms located inside the current reaction radius are recognized; (2) the epoxide groups comprising those recognized reactive atoms are open; (3) the recognized reactive atoms are connected to form cross-links; (4) the unreacted atoms at the open epoxide groups are saturated with hydrogen atoms; (5) the cross-linked structure is relaxed using a combined relaxation process. The reaction radius during the cross-linking process is set to be 3—10 Å, with an increment of 0.5 Å. Within each reaction radius, the cross-linking reaction is performed at most three times or it stops if no reactive atoms are identified. After each cross-linking reaction, the structural information is updated by introducing new bonds, angles, torsional angles, and improper angles into the cross-linked structure. The cross-linking process of SU-8 model is completed when the maximum reaction radius (10 Å) is achieved or all available potential reactive atoms are reacted.

Once the cross-linking process is completed, a short relaxation process is used to cool down the cross-linked structure until the room temperature (300 K) is reached. During the cooling process, the SU-8 model is first equilibrated in an NVT ensemble for 10 ps, and then in an NPT ensemble for another 10 ps. The relaxation process is performed at temperatures of 368 K, 334 K and 300 K, respectively (i.e. a gradual change of temperature from elevated temperature to room temperature). Using the cross-linking algorithm, a SU-8 epoxy network comprising 8222 atoms is built and used in the simulation to investigate its mechanical properties with different moisture contents. As a highly hydrophobic material, SU-8 photoresist is only slightly moisture-permeable. The equilibrium moisture concentration is found to be 3.3 wt% in SU-8 [46], and is less than 4 wt% of DGEBA-based epoxy [5,6,47], where DGEBA is the basic component of SU-8 monomer. In this study, different amount of water molecules are added to the cross-linked SU-8 epoxy network using the Sorption module [41], which vary from 1, 2, 3, 4 wt% of the SU-8 epoxy network molar mass. The added water molecules are located at the lowest energy sites in the cross-linked SU-8 structure. The epoxy network solvated with 4 wt% moisture content is considered as the moisture saturated case.

Though the cross-linked structure is equilibrated during the cross-linking process, the relatively short time frames used in the above relaxation processes are not sufficient for the epoxy network to reach the true equilibrium state. In order to achieve a fully relaxed molecular structure, the cross-linked SU-8 model is further equilibrated using an equilibration scheme as described in previous study [32]. The equilibration scheme consists of seven equilibration cycles under both NVT and NPT ensembles at 300 K. The pressure applied at the NPT equilibration is gradually increased from atmospheric pressure to 50,000 atm in the first three equilibration cycles with a longer time frame (50—150 ps each) that allows an adequate relaxation of the structure. In these processes, the SU-8 epoxy network is compressed efficiently with a large pressure applied on the cross-linked structure. Then, the pressure is steadily reduced to 1 atm in the last four cycles in a shorter time frame (5—15 ps each) in order to control the large pressure jumps. Along with the decrease of applied pressure, the cross-linked structure is decompressed accordingly. These compression and decompression steps can greatly improve the accuracy of the achieved densities [32,48,49]. Finally, a 5 ns molecular equilibration under a constant temperature of 300 K and a constant pressure of 1 atm is carried out such that a fully equilibrated state can be achieved. By examining the root-mean-square displacement (RMSD) of the atoms, which keeps at a constant level before the equilibration run is completed, it implies that the SU-8 epoxy network is equilibrated. The constant temperature and pressure are controlled by Nose-Hoover thermostat and barostat [50], respectively. The equilibration process of the cross-linked SU-8 epoxy network is performed in the open source code LAMMPS [51].
During the cross-linking and equilibration process, the consistent valence force field (CVFF) [52,53] is used to describe the inter- and intra-molecular interactions. Partial charges of atoms are estimated by using a bond incremental method [54]. The applicability of CVFF in the investigation of epoxy mechanical properties has been validated in our previous study [32]. Water molecules employ the parameters of the TIP3P model with a cutoff distance of 10 Å [55]. During the MD equilibration, the bond lengths and angles of water molecules are kept constant by using the SHAKE algorithm [56]. Van der Waals (vdW) and Coulombic interactions are truncated at a distance of 10 Å. The velocity-Verlet integrator is used in the integration of the equations of motion using a time step of 1 fs. Periodic boundary conditions are applied in all three directions.

To investigate the interface integrity of SU-8/silica interface under moisture effect, an epoxy-bonded material system consisting of cross-linked SU-8 in contact with a crystalline silica substrate is constructed. Previous studies suggest that a small-scale model of epoxy-bonded material system is capable of characterizing the interfacial adhesion properties [11,37]. Using the same cross-linking algorithm as aforementioned, a smaller scale of SU-8 epoxy model originating from four monomers is built. Before bonded with the silica substrate, the SU-8 epoxy model is cleaved in such a manner that the normal vector of the cleaved surface (to be contact with silica substrate) is at the [1 0 0] direction. For the silica substrate, hydrogen atoms are used as termination atoms at its upper and bottom surface. By using Build Layers tool [41], an atomistic model of SU-8/silica interface comprising 4889 atoms is constructed as shown in Fig. 2. In the case describing the saturated moisture condition, the SU-8/silica interface is fully immersed in a water box using the TIP3P water model [55]. Periodic boundary conditions are applied in all directions of the interface model. The dimensions of the silica substrate are large enough to prevent the interactions between the imaged SU-8 models, and the vertical dimension of simulation box is sufficient to ensure no interactions between the mirrored images of the interface model. Partial charges of all the atoms in this system are calculated by charge equilibrium (QEq) method, as it is reported that the charge distributions of QEq result in a good agreement with experimental measurements and ab initio calculations [57]. Previous studies on water slabs with finite thickness demonstrate that due to the high polarization of water molecules, the truncation method of Coulombic force can lead to the ordered orientation of water molecules at the cutoff distance [58,59]. Consequently, a cutoff distance of 10 Å is used for the vdW and short-range Coulombic interactions during the MD simulations, whereas the long-range Coulombic interaction is calculated with the particle–particle particle-mesh (PPPM) solver [60]. During the equilibration process, the SU-8/silica interface is first equilibrated at 300 K for 500 ps in the NVT ensemble. After that, the interface is further equilibrated at 300 K and 1 atm for 500 ps in the NPT ensemble. And a final 500 ps NVT equilibration is carried out on the SU-8/silica interface before the production simulation. The equilibrated state of the interface is affirmed by examining the RMSD of the atoms in the SU-8 epoxy model. The equilibration process is carried out in LAMMPS [51].

2.2. Uniaxial tensile deformation of cross-linked SU-8 epoxy network

The mechanical properties of equilibrated SU-8 epoxy networks, in terms of Young’s modulus ($E$) are determined by the uniaxial tensile deformation at 300 K. Due to the time scale limitation of MD simulations, high strain rates are typically used in order to obtain the system response within a reasonable timespan. The strain rate effect on SU-8 mechanical properties is studied in our previous study, where five different strain rates were examined in the tensile deformations of SU-8 epoxy network in dry condition, ranging from $1 \times 10^7$ s$^{-1}$ to $1 \times 10^9$ s$^{-1}$ [32]. The simulation results are in good accord with experimental observations measured at much slower time scales, which indicates that $E$ of SU-8 epoxy network is not sensitive to the high strain rate. Here, the deformation is applied in a step-wise manner at a strain rate of $1 \times 10^3$ s$^{-1}$, and the atmospheric pressure is maintained in the two transverse directions. At each deformation step, the SU-8 epoxy network is deformed by 0.1% in strain followed by a 10 ps equilibration process before next deformation step. For all deformation processes, the SU-8 epoxy network is deformed by 3% in total. The virial stress tensors are monitored during the entire tensile deformation. After the deformation, $E$ of the SU-8 epoxy networks is calculated as the initial slope of the stress-strain curve obtained at the loading direction.

2.3. Metadynamics analysis of SU-8/silica interface

In the present study, the interface integrity between SU-8 photoresist and silica substrate is examined and quantified by the determination of surface energy under dry and wet scenario, respectively. The surface energy is a material property that describes the energy required to create new surface, which is characterized by deriving the free energy profile (FEP) between the attached and detached states of SU-8/silica interface. It should be mentioned that free energy is regarded as the internal energy which can be converted to work. Here, an attached state refers to the lowest free energy stage and a detached state corresponds to the separation between the mass center (CM) of SU-8 and silica surface larger than half of the vertical box dimension (i.e. 60 Å). The free energy barrier ($E_b$) between the attached and detached states is divided by an associated area ($S_0$) of molecular attachment (computed as the contact area of cross-linked SU-8 epoxy network projected onto the silica substrate), and the result yields an estimate of the upper bound of the surface energy between SU-8 photoresist and silica substrate, i.e.:

$$\gamma_s = \frac{E_b}{S_0} \quad (1)$$

The FEP of the epoxy-bonded material system from an attached stage to a detached stage is reconstructed by the metadynamics approach [37,61], which is a powerful method for accelerating rate
events and reconstructing the free energy in the system. This method is used to reconstruct the FEP as a function of a collective variable (CV), which is able to describe the detachment process of the SU-8 photoresist from the silica substrate. In this study, the CV is chosen as the distance between the SU-8 photoresist’s CM and silica surface in the vertical direction [61]. The dynamics in the space of the chosen CV is enhanced by a history-dependent potential constructed as a sum of Gaussians centered along the trajectory followed by the CV. In metadynamics, the actual FEP is filled by a series of Gaussians, and the sum of Gaussians is exploited to reconstruct iteratively an estimator of the free energy. The meta-dynamics calculations are performed by using the PLUMED plug-in package [62], which can be integrated with LAMMPS [51]. A series of external energy is added to the SU-8/silica interface every 100 fs as the form of a Gaussian with a height of 0.005 kcal/mol and a width 0.35 Å. The parameters of the Gaussians have been adjusted carefully to achieve high sampling accuracy and reasonable computational cost. The calculated FEP as a function of simulation time can be derived by summing up all these Gaussians.

3. Experimental program

The cross-linking process in MD simulation is achieved by creating new bonds between the potential reactive atoms, which simplifies the actual chemical reaction happened in the experimental curing process. In order to demonstrate the applicability of MD simulation approach used in this study, experimental study has been carried out for validation. The mechanical property of SU-8 photoresist, in terms of Young’s modulus, was chosen as an indicator in the experimental study of the moisture effect on the mechanical property of epoxy-bonded material system. And the interfacial fracture energy of SU-8/silica interface is characterized under both dry and wet scenarios to illustrate the moisture effect on the interfacial properties. The experimental procedures for the fracture energy characterizations are described in our previous study [12].

3.1. Materials and sample preparation

SU-8 2000 was used in the experimental program of mechanical property measurements. As the new generation of SU-8 photoresist, SU-8 2000 has improved coating and adhesion properties after curing process [63]. The SU-8 photoresist was coated onto the fused silica surface through spin coater. In order to generate a 20 µm thick film in this work, the spin coater was rotated with a speed of 2500 rpm for 30 s after the uncured and unbaked SU-8 (liquid state) was placed onto the silica substrate. After spinning, the specimen was placed in vacuum for 1 h to get rid of the solvent in SU-8. Then, the sample was treated under UV for 90 s so that the SU-8 can cross-link under the stage. And then the sample surfaces were focused and the calibrations, the samples were mounted on a magnetic sub-base for testing, such as a one-inch square magnetic stainless steel piece. The mounted locations were chose where three magnets under the stage. And then the sample surfaces were focused and their boundaries were traced using the focused image.

In this work, the Hysitron Tribolindenter was used for conducting the nanoindentation. The load range for this machine is between 10 µN and 10 mN, and the depth range is between 20 nm and 5 µm. Before getting started, the chamber door was closed, while the optical light and the software controlling the indenter were turned off. The three control units below the chamber, namely, the power for the piezo tube attached to the transducer, the transducer to which the tip is attached, and the X–Y stage on which the sample sits, were kept on during the experiments. In the process of nanoindentation, the software and the optics light were first turned on. Then the indentation axis calibration was conducted. When making the calibration indents with blunt tips, 10,000 µN was used for the one dimensional force transducer. After the calibration, the samples were mounted on a magnetic substrate for testing, such as a one-inch square magnetic stainless steel piece. The mounted locations were chose where three magnets under the stage. And then the sample surfaces were focused and their boundaries were traced using the focused image.

The fused silica sample was first indented under a 7 × 3 grid (i.e. 21 indents in total), and the computed Young’s modulus was used for comparison with existing literature data to determine the correctness of the experiment. After that, the 20 µm thick SU-8 thin film deposited on the fused silica substrate was indented under two 7 × 7 grids (i.e. 98 indents in total). Each 7 × 7 grid corresponded to a single load rate. In this experiment, two different loading rates were considered, namely 20 µN/s and 2000 µN/s, to get rid of the loading rate effect on the calculated parameter.

4. Results and discussions

The results obtained from the methods described in Sections 2 and 3 are presented here, which include the discussions about the moisture effect on SU-8 mechanical properties and SU-8/silica interfacial integrity from the simulation perspective, followed by the experimental verification of the moisture affected SU-8 mechanical properties and SU-8/silica interfacial integrity.

Two atomistic structures of SU-8 photoresist with high degrees of cross-linking are built. The SU-8 epoxy network used in the investigation of its mechanical properties achieves conversion degree of 82%, while the smaller scale model for the SU-8/silica interface reaches 81%. Both atomistic models are obtained from one successive cross-linking reaction by using the cross-linking algorithm. The cross-linking degree of the smaller scale SU-8 model is shown in Fig. 3, which is obtained at different reaction radius values. A sharp rise can be seen when the cross-linking degree nearly reaches 70% over a span of the reaction radius between 3 and 6 Å. After that, the cross-linking process evolves slowly and becomes saturated with the reaction radius larger than 9 Å. This phenomenon corresponds to our previous finding, where a relatively larger reaction radius has an insignificant enhancement in the cross-linking degree [32]. The high cross-linking degree of SU-8 epoxy network indicates that the cross-linking algorithm is capable of constructing highly cross-linked epoxy network close to those synthesized polymer materials through various experimental approaches [65,66].
For the mechanical characterization of SU-8 epoxy network, density ($\rho$) is a critical parameter which should be consistent with the experimental value. During the 5 ns NPT MD equilibration run in LAMMPS, the three orthogonal directions of the simulation cell are adjusted independently corresponding to the atmospheric pressure, and the $\rho$ of SU-8 epoxy network is sampled every 5 ps. In order to minimize the statistical error, only the recorded $\rho$ from the final 1 ns equilibration run is accounted for the density calculation. The average $\rho$ of SU-8 epoxy network is shown in Fig. 4, with respect to moisture content ranging from 0 to 4 wt%. The error bars shown in the figure are obtained from the standard derivations of the averages. A $\rho$ of $1.04 \pm 0.002$ g/cm³ is obtained for the SU-8 epoxy network under dry scenario, which shows a good agreement with the available value in the range of $1.07-1.20$ g/cm³ by MicroChem. Therefore, the generated model of cross-linked SU-8 epoxy network is considered as a suitable structure model for investigating the moisture effect on epoxy mechanical properties. For the solvated SU-8 epoxy networks, the $\rho$ shows a steady increase with increasing moisture absorption, and reaches $1.06 \pm 0.001$ g/cm³ at 4 wt% moisture content. For SU-8 photoresist, no related experimental data are available for a direct comparison with the moisture affected $\rho$. It is believed that the monotonic increase of $\rho$ is due to the weight gain from the absorbed moisture. In view of the small variation of the $\rho$ between dry and wet scenarios, it is inferred that the absorbed moisture does not make a large difference to the SU-8 cross-linked structure. Further investigation on the moisture affected SU-8 mechanical properties can consolidate this finding.

During the uniaxial tensile deformation, the stress of SU-8 epoxy network along the loading direction shows a linear response to the applied strain, which indicates that SU-8 epoxy network is elongated elastically within the 3% deformation. Based on the obtained stress-strain curves, $E$ is calculated by performing a linear regression analysis on the stress-strain data ranging within 3% deformation. The calculated $E$ is shown in Fig. 5, 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 cross-linked SU-8 in dry condition is $4.43 \pm 0.23$ GPa, which is in accord with the experimental tensile test measurements in the range of $2.70-4.02$ GPa [7–9]. 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 could result in the higher moduli observed. Therefore, MD simulation result could be in closer agreement with that from high strain rate or low temperature pulling experiment. In addition, the slight overestimation of $E$ is common with MD simulation, as the constructed model is free of structural defects and voids, which are normally existed in the macroscopic samples. For the solvated SU-8 epoxy networks, the $E$ reaches the peak of $5.03 \pm 0.15$ GPa at 1 wt% moisture content, and then decreased steadily to $4.18 \pm 0.23$ GPa at moisture content of 3 wt%, with another small increase to $4.37 \pm 0.19$ GPa at moisture content of 4 wt%. Our results show that at low moisture content, the absorbed moisture may have a beneficial effect towards the SU-8 Young’s modulus, which has been reported in various polymeric materials [33–35,64]. The explanation of this phenomenon can be made from a viewpoint of moisture antiplasticization effect. As SU-8 epoxy network is highly cross-linked after cross-linking process, the absorbed moisture starts to fill in the free volume of epoxy
structure, and thus, enhances the stiffness of the SU-8 photoresist. As the moisture absorption in the SU-8 structure continues to increase during its long-term service life, the absorbed moisture decreases the epoxy elastic modulus and SU-8 photoresist becomes softened. This moisture effect is called plasticization. But our results indicate that even with large amount of moisture absorption, the largest decline of $E$ is only 5.5% at 3 wt% moisture content. Independently, SU-8 epoxy network solvated with larger moisture content (i.e. 5, 6 wt%) are simulated to see if any change of modulus can be observed with the moisture content beyond the limit of 4 wt%. The results show that the downturn in $E$ is not obvious in these epoxy networks with a larger moisture content. Equipped with the relationship between the SU-8 Young's modulus and the absorbed moisture content, it can be concluded that moisture has no severe impact on the SU-8 mechanical properties, which further demonstrates that SU-8 is able to provide a strong mechanical reliability for the epoxy-bonded material system during their whole life-circle.

With the quantitative mechanical property characterization of SU-8 epoxy network, the interface integrity of SU-8/silica interface under moisture effect can now be quantified. The equilibrated conformations of the SU-8/silica interface under dry and wet scenarios are shown in Fig. 6. The SU-8 epoxy network is well attached to the silica substrate in dry condition, as shown in Fig. 6(a) and (b). This phenomenon indicates the good affinity between the SU-8 photoresist and the silica substrate. On the contrary, from the equilibrated conformation under wet scenario as shown in Fig. 6(c) and (d), it is noted that the SU-8 epoxy network is slightly detached from the silica substrate, and some water molecules diffuse into the gap between the epoxy network and silica substrate. The situation observed in wet condition reflects that the good connection between these two dissimilar materials is interfered by the surrounding water molecules. The different conformations of epoxy network in dry and wet conditions signify different interfacial adhesion between SU-8 photoresist and silica substrate.

During the simulation using the metadynamics method [61], the FEPs of the SU-8/silica interface at successive simulation time frames are constructed under dry and wet scenarios and plotted in Fig. 7. Meanwhile, simulation snapshots are captured, which present the behaviors of epoxy network in the detaching process. Fig. 8(a)–(d) are snapshots showing the detachment of epoxy in dry condition and these graphs correspond to the FEP plotted in

![Fig. 6. Two side views demonstrating the attachment between SU-8 photoresist and silica substrate under (a), (b) dry and (c), (d) wet scenarios. Red lines represent the water molecules. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
shown in Fig. 8(a), it can be observed that the hydrogen and oxygen atoms in the epoxy structure closely interact with the hydroxyl groups of the silica surface, which is believed to result in the large well depth of the resulted FEP. After that, there are two intermediate stages before the complete detachment as shown in Fig. 8(b) and (c). From these two figures, it can be seen that the detachment of SU-8 epoxy network appears after certain amounts of energy are added into the SU-8/silica interface. But the interfacial adhesion remains at a high level due to the interactions of the functional groups as aforementioned, so that the CM of SU-8 epoxy network keeps relatively constant, which leads to the second large well depth in the FEP. From Fig. 8(a)–(c), it can be seen that the epoxy network continuously moves away from the silica substrate. Eventually, the SU-8 epoxy network fully detaches from the silica substrate, which implies that the vdW and Coulombic interactions between these two dissimilar materials almost disappear and the detachment is therefore achieved, as shown in Fig. 8(d). Furthermore, the snapshots of detachment process show that the bonded system loses adhesion sequentially, which demonstrates that the system is forced to escape from the local free energy minimum in a non-collective manner. The sampling time is long enough to let the actual FEP being filled up by the Gaussians and the system can explore the entire domain of the defined CV with equal probability before complete detachment. Therefore, it is clear that the sampling in metadynamics approach is reasonable and thus the adhesion measurements could be obtained properly. Based on the FEP shown in Fig. 7(a), the energy barrier $E_b$ between the attached (peak a) and detached (point d) stages is obtained as 61.11 kcal/mol. The projected contact area $S_0$ of the cross-linked SU-8 epoxy network is 675.47 Å². According to Eq. (1), the surface energy of SU-8/silica interface under dry scenario is calculated as 62.86 mJ/m². Independently, a SU-8 epoxy network with 970 atoms is constructed, which has atoms approximately double of the original SU-8 model (425 atoms), and can demonstrate stronger cohesive interactions. The simulation result confirms that there is no significant difference in the surface energy if a much larger number of chains are employed to mimic a SU-8 film. This finding coincides with recent observations that in wet well bonded interatomic regime, the adhesion energy of the polymer to the substrate is nearly independent of cohesive interaction variations [67]. Therefore, current strategy is believed to be sufficient for obtaining the adhesion properties which is close to the real state of the SU-8/silica interface. The closest point of comparison is the interfacial energy on a different epoxy/silica interface of 147–188 mJ/m² [36], and the work of adhesion on a SU-8/nickel substrate [68], with experimental results of 40–60 mJ/m² and simulation results of 200–220 mJ/m². As our calculated surface energy of SU-8/silica interface is at a magnitude close to the simulated work of adhesion of SU-8/nickel interface, it is inferred that the nature of the interfacial bonding of these two systems is similar, which is dominated by the non-bonded and non-directional vdW forces and Coulombic interaction.

Under wet scenario, the detachment of SU-8 epoxy network undergoes similar process, i.e., starting from attachment, going through intermediate stages and finally accomplishing the detachment. Fig. 8(e)–(h) are snapshots under wet scenario corresponding to the FEP shown in Fig. 7(b). The minimum free energy of SU-8/silica interface occurs at the distance of 7.09 Å with a well depth of 13.97 kcal/mol. By observing the corresponding interface conformation as shown in Fig. 8(e), it is evidenced that water molecules enter the gaps between the SU-8 epoxy network and silica substrate which interrupts the interaction of these two materials, and thus, results in a smaller well depth of the FEP in wet condition. The energy barrier $E_b$ and the projected contact area $S_0$ are computed as 13.97 kcal/mol and 533.43 Å² under wet scenario. And the surface energy of SU-8/silica interface is calculated as 14.37 mJ/m². A 77.1% reduction in the surface energy of SU-8/silica interface is determined in the presence of moisture, which further reveals that the moisture around the SU-8/silica interface is a major factor towards the structural failure of the epoxy-bonded material system. The trend of moisture deterioration is in agreement with the results from fracture based study [4] and molecular dynamics approach [11] of the concrete/epoxy material system in structural mechanics applications. In these investigations, it is reported that there is a substantial decrease in the interfacial fracture toughness of epoxy-bonded material system under prolonged moisture, which is accompanied with a shift of failure mode from material decohesion to interface separation. The MD results in this study provides the molecular details of the interactions between the bonded interface and water molecules, which can deteriorate the
interface integrity of SU-8/silica interface and finally result in the structural failure of the epoxy-bonded material system.

Experimental results are presented here to verify the moisture effect on SU-8 bulk mechanical properties and SU-8/silica interfacial properties. After 2-week moisture conditioning, the SU-8 photoresist is first characterized under optical microscope, as shown in Fig. 9. Compared with the dry sample, it is observed that there is a change in the material texture of the moisture conditioned SU-8 photoresist. In dry condition, it is noticed that SU-8 photoresist is highly transparent. However, the SU-8 photoresist became milky and black particle-like material texture was observed after 2-week moisture conditioning. This difference in material texture may result from the water molecules absorbed in the bulk SU-8 thin film layer. Water molecules are very dipolar as oxygen atoms have a higher electronegativity than hydrogen atoms. Partial charges caused by the difference in electronegativity can lead to strong interactions of water and functional groups and between water molecules in the cross-linked epoxy structure [69]. Both types of interaction can lead to the formation of water clusters. On the other hand, it is expected that hydrolysis of epoxy occurs when water molecules interact with the cross-linked network, which may involve the
release of oxygen resulting in the formation of bubbles. The changed material texture under the effect of moisture can be related to the formation of water clusters or bubbles. From this observation under optical microscope, it further consolidates the importance of our study of the moisture effect on the mechanical properties of SU-8 photoresist, as well as the interfacial integrity of the SU-8/silica interface.

In the nanoindentation experiments of the silica samples, it is noticed that there is no observable change in the measured mechanical properties under different moisture conditionings. The calculated Young’s modulus of silica is 69.58 ± 0.42 GPa, which is very close to the existing data. The small variation between our experimental measurement and the existing literature value, as well as the small standard deviation of the experimental measurement, implies that the experiment is correctly conducted. Accordingly, the 20 μm thick SU-8 film deposited on the silica substrate is indented in every 2-week moisture conditioning. The measured E for both dry and wet SU-8 samples is shown in Fig. 10. In dry condition, the E are measured as 4.80 ± 0.15 GPa and 5.00 ± 0.06 GPa for loading rate of 20 μN/s and 2000 μN/s, respectively, which are in good agreements with the existing nanoindentation results ranging from 4.50 to 6.21 GPa [70,71]. After conditioned in the water bath for 2 weeks, SU-8 photoresist becomes more rigid. With continuous moisture ingress, SU-8 photoresist softens and its E shows a slight decrease after 8-week moisture conditioning, but is still comparable in value to the dry case. The variations in E agree well with the simulation results, where the SU-8 photoresist stiffness does not change significantly under the moisture effect. From both the MD simulation and nanoindentation results of SU-8 photoresist, it can be concluded that moisture has minimal effect on the mechanical properties of the cross-linked epoxy in the epoxy-bonded material systems.

To complement the simulation work, the fracture energy of SU-8/silica interface is determined under both dry and wet scenarios experimentally, as described in our previous study [12]. For the dry samples, the interfacial fracture energy (Γf) is measured as in the range of 12.0–24.5 J/m², as presented in Table 1. For the wet samples after 4-week moisture conditioning, the results show that Γf has an upper bound of 12.7 J/m², which is about half of that under dry scenario. This result is in reasonable agreement with the simulation results using the metadynamics approach, which validates the deleterious effect of moisture on the SU-8/silica interfacial adhesion.

<table>
<thead>
<tr>
<th>Week</th>
<th>Young’s modulus (GPa)</th>
<th>Loading rates (μN/s):</th>
<th>20</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4.5</td>
<td>2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 9. SU-8 photoresist under optical microscope.

Fig. 10. Histograms showing the relationship of Young’s modulus of SU-8 photoresist with respect to the duration of moisture conditioning, under two different loading rates: 20 μN/s and 2000 μN/s.

<table>
<thead>
<tr>
<th>Fracture energy (J/m²)</th>
<th>Dry</th>
<th>Wet</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.0 ≤ Γf ≤ 24.5</td>
<td></td>
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<tr>
<td>Γf ≤ 12.7</td>
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</table>

Table 1 Fracture energy of SU-8/silica interface under both dry and wet scenarios [12].
5. Conclusions

In this study, a fundamental investigation of moisture effect on the mechanical properties and interface integrity of SU-8/silica material system is performed. The MD simulation results show that the density of SU-8 photore sist displays a monotonic increase with increasing moisture contents in the cross-linked structure, whereas its Young’s modulus is not deteriorated even under excessive moisture absorption. Moreover, the adhesion of SU-8/silica interface is quantified using the concept of surface energy through metadynamics approach, and a 77.1% reduction in the surface energy demonstrates that moisture deteriorates the SU-8/silica interface severely. The simulation snapshots reveal that water molecules interact with the bonded interface closely, which can be a major factor in the interfacial deterioration, and thus, result in the structural failure of the epoxy-bonded material system. On the other hand, experimental results of moisture conditioned SU-8 photore sist show that the absorbed moisture can cause a change in the material texture, but have no severe influence on the Young’s modulus, which correspond to the simulation observations. Furthermore, by considering upper and lower bounds of the fracture energy for both dry and wet samples, it is hypothesized that the fracture energy of the bonded system can reduce down to 50% of its original value in the presence of moisture, which validates the deleterious effect of moisture on the SU-8/silica interfacial adhesion as observed in the simulation.

The detrimental effect of moisture on the epoxy-bonded material system found in this work is in accord with the investigations on concrete/epoxy interface in structural applications. The fundamental knowledge obtained in this study demonstrates that the local interface deterioration degrades the global behavior of epoxy-bonded material system, and shortens its service life. For this reason, the surrounding humidity should be controlled to prevent excess moisture penetration to the material system. Our work further confirms that the interfacial degradation cannot be overlooked (i.e., a huge deterioration under the effect of moisture) and cannot be hinted from the variation of the individual bulk material properties (e.g., variation of E). It is envisioned that our work will be beneficial to the design, synthesis and applications of various epoxy-bonded material systems, especially the durability under moisture effect of particular concerns.

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