Molecular dynamics simulations on adhesion of epoxy-silica interface in salt environment

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ABSTRACT

Epoxy-silica interface exists in various types of newly built as well as aging concrete structures which include flooring and anchoring systems. Sea environment and deicing salt often let the concrete structures be exposed to sodium chloride solution. It is observed from the laboratory evaluation that such exposure often leads to the poor bond durability of epoxy-concrete interface. Yet, there is still a lack of such fundamental understanding as the existing investigations are merely limited to macroscale or mesoscale. Indeed, bond at the interface is governed by the interactions between dissimilar materials lying at the atomistic scale, where atomistic modeling and molecular dynamics simulations can effectively reflect the mechanical behaviors of the bilayer interface. Herein, molecular dynamics simulations together with Bell’s model are employed to evaluate the effect of sodium chloride solution on the adhesion at interface between epoxy and silica. It is shown that sodium chloride solution weakens the adhesion significantly. This finding indicates that the bond deterioration at epoxy-concrete interface is critical in the presence of salt solution, which must be considered in the engineering design strategy for offshore and marine structures.

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1. Introduction

Epoxy-silica interface plays the important adhesion system appearing in concrete, which dominates the construction material in building and infrastructure. Aggregates and gluing cement hydrate which are the component of hardened concrete, all contains silica [1–3]. Meanwhile, epoxy is the polymer with excellent adhesion to concrete. As compared to concrete, epoxy has better mechanical performance and is relatively inert to wide array of chemicals [4–7]. In dry condition, the failure of concrete-epoxy bonded system mostly occurs at concrete [8]. It means that the adhesive force at the interface is higher than the cohesive force of hydrated cement in concrete. Apart from dry condition, there are observed conditions in which the adhesive force at the interface is more critical for the integrity of epoxy-concrete bonded system [9]. One of these conditions is where the sodium chloride (NaCl) solution is present [10,11]. This condition is common exposure to concrete structure based on the numerous existence of marine (i.e. coastal and offshore) structures and the application of salt based deicer [12,13]. The loss of adhesive force at the interface can cause serious issue to the level of catastrophic structural failure leading to fatality. The popular representative case is the failure of concrete strengthened by bonded fiber reinforced polymer (FRP) which can be seen as structural system of multi-layer material consisting of FRP, epoxy and concrete [14–20].

Macroscale mechanical tests were used in many studies to assess the effect of salt environment on the durability characteristic of FRP-bonded concrete system [21]. It is observed that the mechanical properties of such composites are degenerated by the presence of salt with the failure mode mostly observed due to detachment of FRP strengthening system from concrete surface caused by the interfacial debonding between epoxy and concrete [22]. These reported studies confirm the macro- to meso-scale effect of salt to the durability of adhesion at epoxy-concrete interface. However, the effect of salt at atomistic level such as on epoxy-silica interface as the subsystem of epoxy-concrete interface is not yet understood. The investigation at atomistic level can give more
information that is closer to the fundamental origin of debonding at the interface which is governed by adhesion of interatomic interaction. Atomistic simulations have been used as the powerful tool for the investigation at atomistic level to obtain adhesion energy that is well correlated with existing meso-scale experimental data [23,24]. Model has been used to study the adhesion energy between epoxy-silica interface in the presence of moisture implementing molecular dynamics (MD) simulations [25,26]. This example demonstrates that MD simulations can be used to study the durability of epoxy-concrete interface through an understanding of how epoxy-silica interacts with the environment at atomistic level.

The objective of this study is to probe the adhesion energy of silica-epoxy interface in presence of NaCl solution using MD simulations. NaCl is the predominant dissolved salt in sea water and one of commonly used deicers [27]. The model consists of epoxy attached to silica substrate immersed in NaCl solution. Subsequently, steered molecular dynamics (SMD) simulations are performed to apply an external detaching force to epoxy, while keeping silica substrate fixed. Then, modified Bell’s model is used to calculate adhesion energy that can be accomplished by implementing the maximum force obtained from series of SMD simulations at various speeds. The calculated adhesion energy from SMD simulations of NaCl system is compared with those of dry and moist system and the trend is linked with the observation in bond durability at macroscopic level of the three systems reported in existing literature. Our finding reflects the effect from NaCl solution on the deterioration of adhesion energy at epoxy-silica interface, which can further imply the bond durability of epoxy-concrete interface.

2. Atomistic simulations

Three systems of models named dry, water and NaCl system are developed to respectively mimic the epoxy-silica bonded system in dry, moist and NaCl condition. In this study, we are focusing on the effect from saturated state of NaCl solution on deterioration of dry, moist and NaCl condition. In this study, we are focusing on the durability at macroscopic level of the three systems reported in existing literature. Our finding reflects the effect from NaCl solution on the deterioration of adhesion energy at epoxy-silica interface, which can further imply the bond durability of epoxy-concrete interface.

2.1. Forcefield

The Consistent Valence Forcefield (CVFF) has been parameterized against a wide range of experimental observations for water, free ions and variety of other functional groups, as well as some inorganic materials including silica [28,29]. Herein, the CVFF potential energy function as shown in Eq. (1) is used with the parameters are presented in Appendix [30].

$$E = \sum_{\text{bond}} K_\text{b}(b - b_0)^2 + \sum_{\text{angle}} K_\phi(\theta - \theta_0)^2 + \sum_{\text{torsion}} K_\psi[1 + \cos(n\phi - \phi_0)]$$

$$\sum_{\text{out-of-plane}} K_\chi[1 + \cos(n\chi - \chi_0)] + \sum_{\text{Coulomb}} \frac{C_{\text{qiqj}}}{|r_{ij}|}$$

where $j$ runs over all the atoms which are bonded to atom $i$ directly. The parameters of CVFF force field are assigned to the component of the simulated system using Forcite tool in BIOVIA Materials Studio software from Accelrys [32].

The density of water and NaCl solution from simulation and experiment is compared to verify the applicability of CVFF governing the interaction between Na$^+$ and Cl$^-$ ion with water molecule. The density is chosen as this value is widely confirmed and its simple measuring procedure minimize the experimental error. The density of simulated water and NaCl solution is obtained from the equilibrated condition of water and NaCl box under NPT 300 K and 1 atm. The water box consists 3000 water molecules. The NaCl solution is in saturated condition with solubility 360 g per 1000 g water [33]. This corresponds to NaCl box solution consisting of 2715 water molecules and 294 Na$^+$ and Cl$^-$ ions. In water and NaCl system, the explicit model of water and spherical Na$^+$ and Cl$^-$ ions are employed. The water and NaCl solution box is generated implementing Packmol package [34]. The molecular dynamics simulations are performed using LAMMPS with the data is generated implementing msi2mp tool [35].

2.2. Model

In the dry, water and NaCl systems, the model of epoxy and silica refers to the model used in study by Büyükoğuturk et al. [25]. Crystalline silica (SiO$_2$) used is α-quartz with structure shown in Fig. 1a with unit cell dimensions $a = 4.916$ Å, $b = 4.916$ Å and $c = 5.405$ Å with $\alpha = \beta = \gamma = 90^\circ$ [36]. This unit cell contains 3 Si and 6 O atoms. A bulk silica substrate is constructed from a unit cell of crystalline silica shown in Fig. 1a by repeating the unit cell in x-, y- and z-directions. The bulk silica is then cut to obtain the silica block with the dimension $a = 50$ Å, $b = 50$ Å and $c = 20$ Å with $\alpha = \beta = \gamma = 90^\circ$. Afterwards the created open bond is terminated by hydrogen atom which means the non-periodic boundary condition is applied to the silica substrate. All the atoms in silica substrate are covalently bond to each other by harmonic bond. The epoxy put in
The model is the chain of diglycidyl ether of bisphenol A (DGBEA) with five repeating units as shown in Fig. 1b, which hereinafter will be stated as epoxy. The model of the silica substrate and the epoxy is developed using BIOVIA Materials Studio.

The developed silica substrate and epoxy then are incorporated into the simulation box of the three systems. The size of simulation box of the three systems is ~58 x 58 x 78 Å with silica substrate and epoxy at the bottom. The size of simulation box is sufficiently large to avoid the interaction between periodic image of silica substrate [37,38]. The amount of H₂O in simulation box of water system is 6541 molecules and that in NaCl system is 5819 molecules. Additionally, there are 630 Na⁺ and Cl⁻ ions in the simulation box of NaCl system. In designing the amount of water molecule and Na⁺ and Cl⁻ ions, density of water used is 0.998 g/cm³ at 300 K and the density of saturated NaCl is 1.1998 g/cm³ [33,39]. The same explicit model of water and spherical Na⁺ and Cl⁻ ions as used in the simulation to obtain the density are employed. The water and NaCl solution box is generated implementing Packmol package. Afterwards, the components of each system are assembled together using BIOVIA Materials Studio.

2.3. Molecular dynamics simulations

The molecular dynamics simulations are performed using LAMMPS with the data is generated implementing msi2lmp tool [35]. The simulation scheme for the three systems are presented in Table 1. The silica substrate and epoxy system is equilibrated for 1 ns in NVT ensemble at 300 K and periodic boundary that within this process the epoxy attach to silica substrate. Afterwards, in case of water and NaCl system, minimization is performed on water molecules and Na⁺ and Cl⁻ ions in NVT ensemble. During this minimization the atom coordinates of silica and epoxy are freezed. Then, the whole systems are equilibrated for 1 ns. Following the minimization and equilibration process, steered molecular dynamics (SMD) are employed in order to pull off the epoxy from silica substrate in dry, water and NaCl system [25]. The basic idea of SMD is to stimulate a filament-substrate system to explore different states, and then free energy difference can be calculated between

<table>
<thead>
<tr>
<th>Step</th>
<th>System</th>
<th>Water</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Eq., NVT, 1 ns</td>
<td>Eq. (silica + epoxy), NVT, 1 ns</td>
<td>Eq. (silica + epoxy), NVT, 1 ns</td>
</tr>
<tr>
<td>2</td>
<td>SMD</td>
<td>Min. (Water), NVE, 50 ps</td>
<td>Min. (Water + NaCl), NVE, 50 ps</td>
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<tr>
<td>3</td>
<td>SMD</td>
<td>Eq., NVT, 1 ns</td>
<td>Eq., NVT, 1 ns</td>
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<td>4</td>
<td>SMD</td>
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these states by using Bell’s model. In our case, the free energy difference between attached and detached states equals the adhesion energy between silica and epoxy. With proper settings and standard manipulations, SMD can measure the adhesion with a high accuracy [40].

As an experimental technique, atomic force microscopy (AFM) also adopts similar concept as illustrated in Fig. 2 and measures the adhesion energy [41]. Therefore, we employ SMD approach and refer to AFM parameterization to evaluate adhesion energy between silica and epoxy. By relating the SMD method with AFM in our study, we can put the parameter of simulation (i.e. spring constant) closer to reality. We employ the spring constant of 65 mN/m, which is the stiffness of AFM cantilever commonly used to study the nano- and non-covalent adhesion force [42]. In this study, the middle carbon atom is tethered and it is vertically moved up to 50 Å that makes the epoxy is pulled off from the silica base. This middle carbon atom is chosen to minimize the height of simulation box for complete detachment of epoxy, which consequently decreases the amount of water molecules and Na\(^+\) and Cl\(^-\) ions included in the simulation hence simulation cost.

2.4. Adhesion energy

The adhesion energy is calculated using modified Bell’s model [43]. Bell’s model provides Eq. (3) wherein \(f\) is the external applied force, \(k_b\) is Boltzmann constant \((\frac{1.38064852 \times 10^{-23}}{}\text{ J K}^{-1})\), \(T\) is the temperature and \(v_0\) is the natural bond breaking speed as defined in Eq. (4) [44]. A natural vibration frequency \(\omega_0 \approx 1 \times 10^{13} \text{ s}^{-1}\) [45].

\[
v = v_0 \exp \left(\frac{f \cdot x_b}{k_b \cdot T}\right)
\]

\[
v_0 = \omega_0 \cdot x_b \cdot \exp \left(\frac{E_b}{k_b \cdot T}\right)
\]

Substitution of Eq. (4) to Eq. (3) with further arrangement results in Eq. (5). It appears from Eq. (5), by employing the slope and y-intercept in linear regression equation of the plot between \(f\) (maximum pulling force) against \(\ln (\frac{v}{v^*})\), the energy barrier \(E_b\) (representing the adhesion energy between epoxy and silica at atomistic scale [25]) and transition state \(x_b\) can be quantified. The \(v^*\) is equal to 1 m/s used for normalization purpose. Various pulling speed ranging from 0.2 m/s to 5000 m/s is applied to obtain the adhesion energy landscape.

\[
f = \left(\frac{k_b \cdot T}{x_b}\right) \ln v - \frac{k_b \cdot T \cdot \ln v_0}{x_b} = A \cdot \ln v + B \tag{5}
\]

It is noted that the spring constant influences the calculated adhesion energy from Bell’s model [46]. Bell’s model accounts for the frequency of forming and breaking the non-covalent bonds, which means the bonds are reversible [47]. Specifically, the lower spring constant tends to increase the calculated adhesion energy. This is because the lower spring constant leads to slower increment in pulling force (symbolized by \(F\) in Fig. 2). In this case, more time is available for the formation of the reversible bonds, leading to a higher occurrence of these bonds. Consequently, a higher adhesion energy is measured. However, this effect is not investigated further here. Instead, we use a same spring constant in the study of dry, water, and NaCl system to make the calculated adhesion energy of the three systems is comparable.

3. Results and discussions

This section presents the result from the atomistic simulations described in previous section and the discussion regarding the adhesion energy at epoxy-silica interface in NaCl system as compared to dry and water system.

Fig. 3 shows the density of water and saturated NaCl simulation box equilibrated under NPT 300 K and 1 atm. The obtained density for water and saturated NaCl respectively is 0.971 g/cm\(^3\) and 1.179 g/cm\(^3\), which is close with the respective values (0.998 g/cm\(^3\) and 1.200 g/cm\(^3\)) from experiment [33,39].

The equilibrated simulation box of the three systems is shown in Fig. 4. In NaCl system, the ions tend to be attracted to the silica surface that this observation complies to the physical phenomena.

Fig. 3. Density of water and NaCl from simulation and experiment.

Fig. 4. Equilibrated states of (a) dry system, (b) water system and (c) NaCl system. Yellow, white, grey, red, blue and green represents silicon, hydrogen, carbon, oxygen, Na\(^+\) and Cl\(^-\) ions, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
that the object tends to attract ions in ionic solution.

The plot between the movement of tethered atom and its respective SMD pulling force is presented in Fig. 5. The influence from the associated surrounding environment (i.e., water and NaCl) can be recognized from the different in evolution of the slope of the graph toward the complete detachment of epoxy from silica substrate among the three systems. The slope is the ratio on the change between SMD pulling force and the movement of tethered atom. Its deviation is the manifestation from the variation in adhesion force (non-covalent bond to silica) and harmonic covalent force characteristic along the epoxy. Such deviation can also be interpreted as the equality between the pulling force and the total force from the adhesion and harmonic covalent force exerted by epoxy interacting with silica substrate. In the following discussion, the latter mentioned total force is called epoxy-silica force. The helical-shape slope is related to the dynamic movement of the atom. The vertical slope means that the generated pulling force and epoxy-silica force is equal. The horizontal slope can be resulted from the consecutive similar epoxy-silica force (its value equal to pulling force) is achieved simultaneously. Similarly, the slope with positive tangent can be due to the consecutive epoxy-silica force that is relatively different is achieved successively. The pulling force overpasses the epoxy-silica force is indicated by the slope with negative tangent. The complete detachment of epoxy from silica substrate is indicated by sudden vertically downward drop of the slope or pulling force closing null.

The recorded maximum forces then are plotted against ln (v/v*) in Fig. 6. The parameters of linear regression equation are analyzed to obtain the adhesion energy $E_b$. The linear relationship can be observed between the natural logarithmic speed of pulling speed and the associated maximum pulling force as proposed to follow Eq. (5). In all three systems, two distinct regimes is observed, each of which follows a linear logarithmic dependence of the maximum SMD pulling force with respect to the pulling speed. The first regime is in the range of pulling speed 0.2–100 m/s and the second regime is in the range 100–5000 m/s. The calculated adhesion energy from the linear function in the first regime for dry, water and NaCl system is 12.00, 7.09 and 5.11 Kcal/mole-Å and that obtained from the function in the second regime is 0.55, 0.08 and 0.08 Kcal/mole-Å, respectively. The adhesion energy for dry and water system corresponding to the first regime is similar to that previously reported [25]. In fact, the lower pulling speed as captured in the first regime gives a more detailed dynamic evolution of the system (e.g., reversible bond) to occur in response to the applied SMD pulling force. As the result, a more accurate intrinsic adhesion energy can be obtained. Theoretically, the intrinsic properties should be independent from the pulling speed.

Fig. 7 presents the comparison of the calculated adhesion energy from the three systems. The adhesion energy of water system is lower than that of dry system, which confirm the finding in the previous reported study [25]. As compared to the other two systems, NaCl system has the lowest adhesion energy. The adhesion energy in NaCl system is 5.11 Kcal/mole-Å, which is 57% and 28% lower from that in dry (12.00 Kcal/mole-Å) and water (7.09 Kcal/mole-Å) system, respectively. This trend in decreasing adhesion energy from dry to NaCl system is consistent with macroscale experimental result that indicates the more severe effect of NaCl solution than water only on the performance of FRP-bonded concrete system [48]. Therefore, the finding in deterioration of adhesion energy from MD simulations explains the general observed behavior that salt condition leads to failure mode in the delamination at epoxy-concrete interface with load carrying capacity lower than that in dry and moisture condition [49,50]. This behavior has been observed in wide range of epoxy based adhesive. It is suggested that the decline in the macroscale performance of such system is a manifestation of deterioration at its subsystem at lower scale (e.g., adhesion energy of epoxy-silica interface).

Furthermore, this finding suggests the more detailed consideration upon engineering design process towards the improved bond durability of epoxy-silica interface in salt environment. When it is
applied as strengthening system in concrete structure, such improvement is expected to give the significant impact to service life that is vulnerable to salt environment. The severe influence of salt observed at nano- (adhesion energy of epoxy-silica interface) to macro- (epoxy delamination) scale implies the potential for improved durability through the multiscale design approach. Within the molecular level, the adhesion energy can be used as a parameter to indicate bond durability at the interface. In this case, MD simulations can be employed as the powerful tool to design the molecular structure of epoxy that is suitable for salt environment. At macroscale level, it is entailed that the design approach developed for the specific condition (i.e. dry and moisture condition) may need further modification to account the weakening effect of salt. The design tool such as finite element method should be able to include the information from MD simulations to give the more complete influencing parameters in designing epoxy-bonded system for concrete structure in salt environment. The application of this engineering design process for improved bond durability of epoxy-silica interface in salt environment can benefit the design strategy to lengthen the service life of concrete offshore structure through the following recommendation.

The source of salt influencing the adhesion of epoxy-silica interface may come not only from the surrounding offshore environment but also from inside the concrete. The latter source may happen largely due to the nature diffusion of salt solution through the pore of concrete. Based on the existence of salt influencing the adhesion of epoxy-silica interface, the refurbishment strategy to lengthen the offshore concrete structure implementing FRP-concrete bonded system where epoxy is used as bonding agent can be grouped as follows:

1. The case for concrete is free from salt solution. This condition can be achieved by the application of concrete protective coating/insulation system since the initial stage of construction to prevent salt diffusion into the concrete. The engineering design of FRP-bonded concrete system following the guidance for dry and moisture condition should be sufficient if the protective coating/insulation system is reapplied appropriately after refurbishment.

2. The case for concrete contains salt solution. In this condition, the engineering design of FRP-bonded concrete system should

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**Fig. 6.** Maximum detaching pulling force as a function of speed variation for (a) dry, (b) water and (c) NaCl system. The slow pulling mode (SPM) and the fast pulling mode (FPM) correspond to the pulling speed ranging from 0.2 to 100 m/s and from 100 to 5000 m/s respectively.

**Fig. 7.** Adhesion energy of epoxy-silica interface in dry, water and NaCl condition. The adhesion energy in NaCl condition is lower than that in dry and water condition.
account for deterioration of adhesion at epoxy-silica interface as previously mentioned. In this case the decrement in load carrying capacity of FRP-bonded concrete system due to the deterioration at epoxy-silica interface should be considered. It is also recommended to apply the pretreatment on the surface of concrete substrate prior to the application of epoxy.

4. Conclusion

In this study, the effect of NaCl solution on the adhesion of epoxy-silica interface has been evaluated using molecular dynamics simulations. Our finding indicates that NaCl solution weakens the adhesion energy of epoxy-silica interface. This result complies with experimental observation on epoxy-concrete interface at macroscale level that also shows the weakening performance of concrete-FRP bonded system in the presence of NaCl solution. This multiscale observation suggests that the durability at macroscale is the manifestation from the degeneration at atomistic level. This finding provides the piece of information that can be used in synthesis and design practice towards the more durable interface from severe influence in salt environment.

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References

