The Effect of Water on the Work of Adhesion at Epoxy Interfaces by Molecular Dynamics Simulation

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Molecular dynamics simulation can be used to explore the detailed effects of chemistry on properties of materials. In this paper, two different epoxies found in aerospace resins are modeled using molecular dynamics. The first material, an amine-cured tetrafunctional epoxy, represents a composite matrix resin, while the second represents a 177°C-cured adhesive. Surface energies are derived for both epoxies and the work of adhesion values calculated for the epoxy/epoxy interfaces agree with experiment. Adding water -- to simulate the effect of moisture exposure -- reduced the work of adhesion in one case, and increased it in the other. To explore the difference, the various energy terms that make up the net work of adhesion were compared and the location of the added water was examined.

Nomenclature

W = work of adhesion
$E_{film,1}$ = configurational energy of thin film of Epoxy 1
$E_{film,2}$ = configurational energy of thin film of Epoxy 2
$E_{interface}$ = configurational energy of the interface
$E_{water\text{-}water}$ = configurational energy of the water-water interaction
$E_{water\text{-}epoxy}$ = configurational energy of the water-epoxy interaction
A = cross-sectional area

I. Introduction

Adhesively-bonded structures in aerospace applications are required to withstand environments that are subject to varying degrees of humidity. It is therefore desirable to know how moisture affects their long term durability. While there are multiple factors that affect the location and uptake of moisture in adhesive bonds, one of the most basic is the chemistry of the adhesive and substrate. Molecular-level, chemically detailed simulation techniques such as molecular dynamics (MD) may be used to model adhesive interfaces. For example the work of adhesion for polyolefin interfaces has been simulated by Clancy and Mattice,[1] and similar methods have been applied to polycarbonate/silane interfaces.[2]

In the present work, these techniques are adapted to model the work of adhesion for two different epoxy interfaces and to shed light on the possible effect of water on adhesive bonds. The epoxies are chosen to represent components used in aerospace composites and adhesives. The first is the tetraglycidyl ether of diaminodiphenylmethane (TGDDM) cross-linked with diaminodiphenylsulfone (DDS). This epoxy is a structural epoxy used in composite matrix resins. The second is diglycidyl ether of bisphenol A (DGEBA) cured with dicyandiamide (DICY) and represents a 177°C-cureable structural adhesive. Interfaces between these components are simulated, and the work of adhesion is calculated for each interface with and without water present.   The paper presents the details of simulations and compares the effect of water on the work of adhesion at the two different epoxy interfaces.

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II. Methods

A. Epoxy Model

The network denoted Epoxy 1 represents TGDDM cross-linked with DDS.   Structures of the monomers are given in Figure 1(a) and (b). A total of 151 TGDDM molecules and 192 DDS molecules were used. The starting molecular structure was comprised of a single epoxy network. Only 342 out of a total of 604 possible TGDDM sites are reacted, so the cross-linking extent of reaction is 57 %. TGDDM repeat units were terminated in unreacted epoxide rings and the DDS repeat units were terminated as amines. Epoxy 1 has 14779 atoms and a density of 1.16 g/cm^3.

Epoxy 2 represents DGEBA (Figure 1(c)) cured with DICY. Products of the DICY curing reaction are quite complicated[3],[4] but are represented here by alternating oxazoline ring linkages (Figure 1(d)), and tri-linkages at amine groups (Figure 1(e)). Of 700 available epoxy groups, 600 are reacted, making the cross-link extent 86%. Epoxy 2 has 15245 atoms and a density of 1.07 g/cm^3. For comparison, density values of 1.12-1.19 g/cm^3 are reported for a bisphenol A type resin cured with a cyclic amine.[5]

B. Molecular Dynamics Simulation

All the simulations were carried out under NVE (constant number of atoms, volume and energy) conditions at 300 K. DL-POLY[6] was used to perform the simulations.

The epoxies were simulated as thin films (Figure 2 (a)), in interfacial systems (Figure 2(b)), and as interfacial systems with water. The thin films of each epoxy are simulated with open boundaries in the z-direction and periodic boundaries in the x- and y- directions. Interfacial systems consisted of two adjacent thin films. The interfacial systems simulated here differ from those in Ref. 1 in that all the boundaries are periodic. The most extensive calculations were for Interface System 1 (Epoxy1-Epoxy 2), for which three separate simulations were performed. A standard deviation for the energy within a simulation was derived by comparing nine subsections of the total 450,000-step trajectory. Interface System 2 used the same two films in a different orientation (head-to-head vs. head-to-tail). Its one simulation was similarly divided into nine sections of 50000 steps per section. For Systems 3 and 4 (Epoxy 1-Epoxy1), a similar procedure was used, but with seven sections of 50000 steps. To study the epoxy-epoxy interface with water, 196 water molecules were equally divided between the two interfaces within the simulation cell which is equivalent to 1.6 wt % water. Altogether, six simulations were performed with the water molecules starting in different initial configurations near the interface. Potential energies from each simulation were calculated every 1000 time steps then averaged for the simulation. The Epoxy 1/Epoxy 2 interface was carried to a total of 450000 time steps; the Epoxy 1/Epoxy 1 interface to 50000 steps.

C. Force Fields

The AMBER force field was used and the parameters were taken from Ref [7]. Sulfur parameters for the AMBER force field were also taken from the literature.[8],[9] The water is simulated as a TIP3P water molecule.[10],[11] In this model the water has 3 sites co-located with the atomic position, fixed bond lengths, and partial atomic charges at each atomic site. The electrostatic interactions were calculated out to 1.3 nm, and no Ewald summation[12] was used. Atomic charges were obtained using the RESP method in the NWCHEM program.[13] Geometries of the monomers in Figure 1 were optimized at the Hartree-Fock (HF) level using the STO-3G basis set and electrostatic potentials were calculated using HF with the 6-31G* basis set.

The force field was validated by calculating the surface energy. It was found that reducing all Lennard-Jones epsilon parameters and partial charges by 25 % gave surface energies in agreement with experiment,[14] so this reduction was used in the present calculations. Changing Lennard-Jones and Coulombic parameters for potential refinement has precedent in the literature.[15]

D. Work of Adhesion

The work of adhesion of the epoxy interface is determined from MD simulation of the epoxy interface and the simulation of each epoxy thin film. The work of adhesion *W* is calculated as

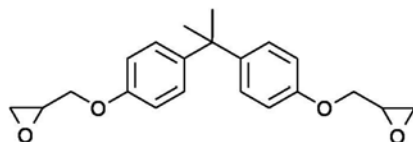$$W = (E_{film,1} + E_{film,2} - E_{interface})/4A \qquad (1)$$

where $E_{interface}$ is the total potential energy of the interface simulation cell (Figure 2(b)) and 1 and 2 refer to the two films that were combined to make up the interface cell. Eq. (2) is updated from Reference 1 to account for the two interfaces. In all the present simulations the cross-sectional area, *A*, is 30.76 nm^2.
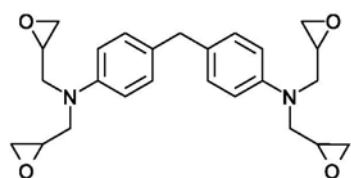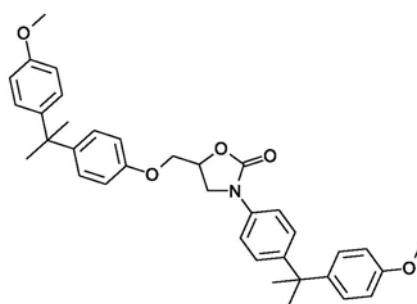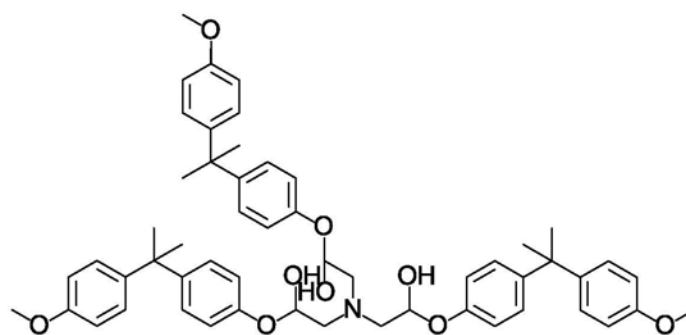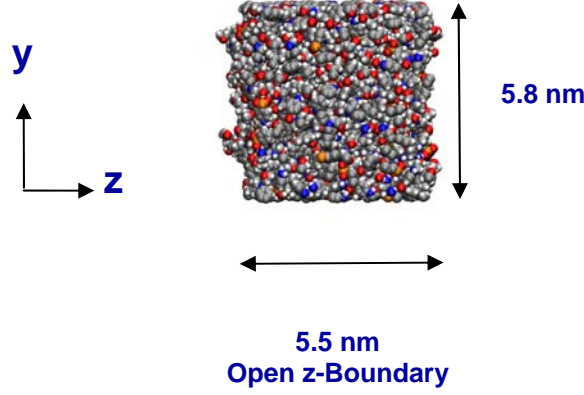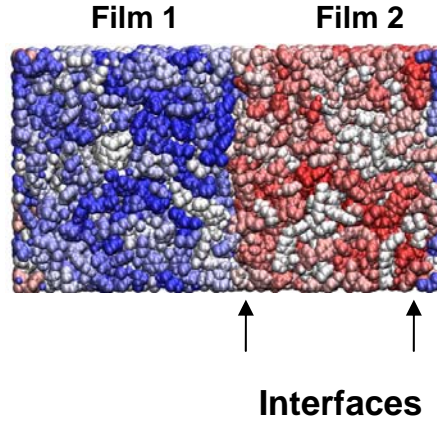
(a) TGDDM
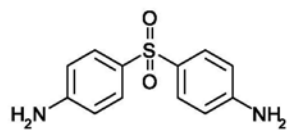
(b) DDS

(c) DGEBA

(d) Di-linkage

(e) Tri-linkage

Figure 1. Molecular structures of (a) TGDDM, (b) DDS, and (c) DGEBA, and the (d) di- and (e) tri-linkages caused by DICY in the DICY cured DGEBA.

(a) Thin film simulation of TGDDM/DDS. Colors: C=dark grey, H=light grey; O=red; N=blue; S=orange.

(b) Interfacial system. Film 1 is shaded blue and Film 2 is shaded red.

Figure 2. Molecular structures of (a) epoxy as a thin film and (b) the Epoxy 1/Epoxy1 interface

The work of adhesion in the presence of water has been defined in previous work[14] as

$$W = (E_{film,1} + E_{film,2} + E_{water-water} + E_{water-epoxy} - E_{interface})/4A \qquad (2)$$

When water is included, contributions to W from the water-water ($E_{water-water}$) and the water-epoxy ($E_{water-epoxy}$) interaction energies need to be accounted for. $E_{water-water}$ is calculated as the total non-bonded water-water interaction including Lennard-Jones and Coulombic contributions. $E_{water-epoxy}$ includes the non-bonded interaction between the epoxy and the water (also calculated from the Lennard-Jones and Coulombic contributions).

III.   Results and Discussion

Table 1 includes the total energies of the simulation cells with no water. Absolute energies from MD are not comparable with experiment, but they are included here to indicate the level of precision needed when subtracting to get W. The uncertainties reflect the statistical fluctuations both within simulations and among different simulations. The W values obtained are in reasonable agreement with available experimental results which are given as 50-90 mJ/m^2 for epoxy against various other polymer surfaces and 88-99 mJ/m^2 for epoxy against carbon fiber reinforced plastics (CFRP).[16] The CFRP surfaces are likely to be resin (epoxy) rich, perhaps with some contribution from the carbon fiber. Table 2 shows the work of adhesion obtained when water molecules had been inserted during the

4

construction of the interface cells. The average work of adhesion for the Epoxy 1/Epoxy 2 interface when water is present is calculated as 148 ± 12 mJ/m^2, a significant *increase* compared to the case without water (Table 1). For the Epoxy 1/Epoxy 1 interface with water, 53 ± 16 mJ/m^2 is obtained, a *decrease* relative to the case without water. The latter matches the experimental trend, given as a decrease (from 90 or so to 22-44 mJ/m^2) for epoxy/CFRP[16]. Unfortunately, little is known about the resin chemistry, method of introducing the water, or test procedure in those experiments.
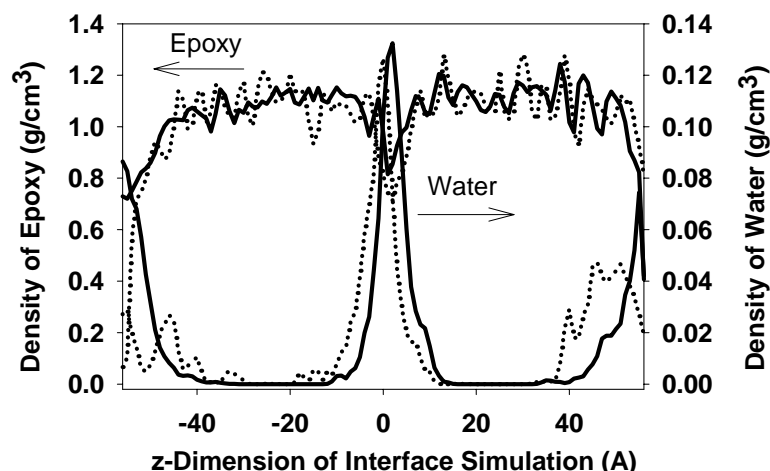
Comparing the various terms in equation (2), we find that the contributions due to the respective films and the total interface system are fairly similar for Epoxy 1/Epoxy 2 (152 mJ/m^2) and Epoxy 1/Epoxy 1 (175 mJ/m^2). On the other hand, the water-water and water-epoxy terms are vastly different for the two cases. Those terms contribute a total of -4 mJ/m^2 for Epoxy 1/Epoxy 2 and -122 mJ/m^2 for Epoxy 1/Epoxy 1, so they dominate the change in work of adhesion when water is added. Thus it appears the location and/or interactions of the water control the net energetic effect. As illustrated in Figure 3, water penetrates further into the Epoxy 1/Epoxy 1 system during the simulation than it does in the Epoxy 1/ Epoxy 2 system. At first glance, this is a little surprising, given that Epoxy 1 is denser, but Epoxy 1 is also less-highly crosslinked and its polar DDS molecule is thought to have an affinity for water. More work on varying the details of epoxy network structures is clearly needed.

Table 1. Potential Energies of the Epoxy Interfaces

Interfacial System	Energy of Film 1 (kJ/mol)	Energy of Film 2 (kJ/mol)	Energy of Interfacial System (kJ/mol)	Work of Adhesion (mJ/m^2)
	Epoxy 1	Epoxy 2		
1	83500 ± 600	84900 ± 1000	165800 ± 600	35 ± 18
2	83500 ± 600	84900 ± 1000	164000 ± 600	59 ± 18
	Epoxy 1	Epoxy 1		
3	83500 ± 600	83500 ± 600	160500 ± 400	87 ± 13
4	83500 ± 600	83500 ± 600	160200 ± 300	91 ± 12

Table 2. Work of Adhesion in the Presence of Water

Simulation Trial	Work of Adhesion at Interface of Epoxy1 and Epoxy2 (mJ/m^2)	Work of Adhesion at Interface of Epoxy 1 and Epoxy 1 (mJ/m^2)
1	144	76
2	134	73
3	167	37
4	161	40
5	144	45
6	139	47

Figure 3. Density profile of the epoxy for the Epoxy 1/Epoxy 2 (solid lines) and Epoxy 1/Epoxy 1 interfacial systems (dotted lines), and the density of water across the respective systems.

IV. Summary

Molecular dynamics simulations of two different epoxy/epoxy interfaces have been performed with and without water, and the work of adhesion has been calculated. Epoxy 1 represents the matrix resin of a carbon fiber reinforced epoxy composite, and is modeled as DDS cured TGDDM epoxy. Epoxy 2 represents the epoxy part of a structural adhesive, and is modeled as DICY cured DGEBA. Both interfaces have work of adhesion values when water is not present that are in reasonable agreement with experimental predictions in the literature. However, for the case of Epoxy 1/Epoxy 1 interface, water reduces the work of adhesion, while for the Epoxy 1/Epoxy 2 interface the water increases the work of adhesion. Experimentally, water reduces the work of adhesion, so the behavior of the Epoxy 1/Epoxy 2 interface is unexpected. The exact cause of the different behavior has not been identified in this study, but the difference can be generally attributed to molecular interactions with water. Two specific clues to the reasons for the difference have emerged. In calculating the work of adhesion for each interface, there is a large difference between the interface systems in the magnitude of the work of adhesion contributed by the terms associated with the water interactions. Also, more water migrated into the epoxy in the case of the Epoxy 1/Epoxy 1 interface than in the case of the Epoxy 1/Epoxy 2 interface. These two observations point to underlying mechanical and/or chemical explanations for the difference in interface behavior.

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