Role of Salt on Adhesion of an Epoxy/Aluminum (Oxide) Interface in Aqueous Environments

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INTRODUCTION

In the past two decades, tremendous progress has been made in the characterization of polymer-inorganic interfaces [15–19]. In particular, the development of neutron reflectivity (NR) to characterize the heterogeneous distribution of water within polymer coatings near inorganic substrates by Wu et al. [20] and Kent et al. [21] has enabled correlations to be drawn between environmental driven macroscopic failure of joints and the nanoscale distribution of the environmental agent within the adhesive. Similarly, NR can be used to assess the formation of silane bonds at the substrate in one step coating systems [22]. These measurements of the interfacial structure provide a mechanism to better understand the underlying mechanisms by which interfaces are attacked by environmental factors. We have previously used the combination of NR and fracture mechanics to elucidate a probable mechanism for humidity-induced failure: this is swelling stress driven that is induced by reorganization of adsorbed water at the polymer adhesive-inorganic interface [14]. This explanation, aided by NR measurements to elucidate the distribution of water within the adhesives, is consistent with many of the prior explanations that independently may appear to be contradictory as some have proposed the bulk swelling to be important for humidity failure [23], while others have solely focused on the interface [24]. The success of this approach using NR to examine buried interfaces in adhesives to understand the mechanisms associated with their failure has been limited to the examination of humidity effects to date. However, there are many cases where adhesive joints are exposed to a variety of more aggressive conditions (e.g., rain, general washing, or more severe conditions such as de-icing of an aircraft). In particular, exposure to salt water is particularly egregious as it can also promote corrosion [25], but the influence of salts on the strength of adhesive joints is system dependent, with decrease and increase in adhesive joint strength reported in comparison to the strength in deionized water [26–29]. The origins of this behavior could potentially be related to the partitioning of salt within the adhesive. The aqueous adhesion for one epoxy-aluminum interface [14], which demonstrates the changing role of the interface in determining the durability of the joint. This interfacial sensitivity presents a major challenge in fundamental understanding of environmental impact on adhesive joints.

Joints held by polymeric adhesives are commonplace in many engineered products, but normal service can require exposure to environmental conditions that present a significant challenge for maintaining the structural integrity of the interface. In particular, aqueous environments can wreak havoc on the joint strength. Here, a mechanistic approach is used to understand the difference in the debonding behavior of an epoxy/aluminum (oxide) interface when exposed to deionized (DI) water and aqueous sodium chloride by correlating macroscopic failure with the sorption of salt and water into the adhesive and its nanoscale distribution. For the epoxy-aluminum system examined here, the presence of sodium chloride increases the resistance to crack growth in comparison to DI water. The debonding appears to be controlled by water near the buried interface. Salt water decreases the solubility of water in the epoxy and decreases the concentration of water near the buried interface, but the concentration of salt that enters the epoxy is below the detection limit. Thus, even if ions cannot penetrate or sorb into the adhesive, the presence of salt can significantly alter the water distribution within the adhesive and ultimately the strength of the joint. POLYM. ENG. SCI., 56:18–26, 2016. © 2015 Society of Plastics Engineers

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Contract grant sponsor: NIST (Department of Commerce); contract grant number: 60NANB9D9130; contract grant sponsor: National Research Council (NRC), Research Associateship Programs.

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gradient near the buried epoxy-aluminum that could be associated with the mechanism for failure. However, the potential correlations between salt distribution and adhesive properties have not been investigated.

Here, we begin to investigate the fundamental relationships between sodium chloride distribution within a polymer film and its adhesion performance. In this case, we have selected one of the most commonly utilized interface types for marine applications, where salt water is an ever-present threat: aluminum-epoxy (e.g., shipbuilding, fuel and water tanks). Additionally, aluminum is the most commonly encountered nonferrous metal in commercial applications [15]. The extent of adhesion loss is demonstrated to be dictated by the amount of water present near the buried polymer/substrate interface, which decreases with the addition of salt, for a model interface of oxidized aluminum and amine-cured epoxy. The salt is also excluded from the epoxy film, which provides an osmotic driving force to decrease the water content in the film. Thus, the influence of salt on adhesion appears to be driven by a combination of its solubility in the adhesive and accumulation of water at the joint interface.

EXPERIMENTAL

Materials

An amine-hardened epoxy using a stoichiometric mixture of diglycidyl ether of bisphenol A (DGEBA) resin (EPON 828, Shell Chemical) and aliphatic polyethertriamine hardener (Jeffamine T403, Huntsman Chemical) was used as the model adhesive. The chemical structures of the amine and epoxide monomers are shown in Fig. 1. The epoxy was adhered to an oxidized aluminum layer that was fabricated by thermal evaporation (Thermonics VE-90) of a 20 nm thick aluminum film on either a silicon wafer (Wafer World, 75 mm diameter, 5 mm thick) with a nominal 10 nm thermal oxide layer for neutron reflectivity (NR), or a 3.2 mm thick borosilicate glass disk with an 8 mm diameter hole (Swiftglass, Elmira, NY) for fracture mechanics measurements. The substrates were cleaned by oxygen plasma prior to evaporation of the aluminum to remove organic contaminants. The thickness of the aluminum film was determined by a quartz crystal microbalance in the evaporator and also confirmed by NR for the aluminum films on the silicon wafers. The aluminum was oxidized by oxygen plasma (SPI supplies plasma prep) for 30 sec at 100 W. The water contact angle determined by the sessile drop method (Ramé-Hart A-100 goniometer, Ramé-Hart, Netcong, NJ, USA) was statistically indistinguishable between the two substrates and agreed with previous measurements for sputtered aluminum oxide [32]. The epoxy layer was applied to the substrates by spin coating the epoxy-amine from toluene (ACS grade, Sigma Aldrich; details are dependent on measurement used as noted below) and then subjecting the specimen to the cure cycle with initial cure at 80°C for 2 h, followed by postcuring at 125°C for 3 h.

Sorption Measurements

Free-standing epoxy films (thicknesses: 200 – 500 μm) were prepared using a drawdown technique, in which the epoxy and hardener mixture was deposited onto release paper. Excess solution was removed by firmly drawing a metal bar across the paper. The obtained films were then cured using the aforementioned schedule. The films were dried extensively in a desiccator until a stable mass was obtained. The films were then immersed in either DI water or salt solutions at room temperature (23 ± 3°C) and periodically removed to determine the film mass using an analytical balance (Mettler Toledo XS) with mass resolution of 10−5 g. The rate of water or aqueous solution sorption was determined from the change in mass with reference to the initial dry mass of the film. The sorption data were reproducible with a standard error of < 5% from multiple measurements.

Fracture Mechanics Tests

Figure 2A illustrates the preparation method used for the multi-layered specimens used in the fracture tests. First, the 8 mm hole in the center of the substrate coated with oxidized aluminum was covered by 9.5 mm diameter, Kapton (Dupont...
Electronic Technologies, Circleville, OH) pressure sensitive adhesive tape (PSAT). This PSAT prevented issues associated with the spin coating of the epoxy layer by filling the hole and also served as a pre-crack. The epoxy-amine in toluene was then spun cast onto the substrate to generate a coating approximately 70 μm thick. A 50 μm thick sheet of polyimide (Kapton E film) on top of the uncured epoxy resin acted as a mechanical backing layer. This multilayer stack was then subjected to the two-step cure cycle previously described. All samples were stored in a desiccator prior to testing.

The joints were tested with a shaft-loaded blister technique (SLBT) performed on a tensile-testing machine (MTS centurion) at a crosshead displacement rate of 5 μm/s. This slow crosshead rate allowed the environmental species to diffuse faster than the crack growth, so the crack front is expected to always be exposed to the same environmental factors. All measurements were performed at room temperature (23 ± 3°C). During the fracture tests, the samples were exposed to (a) deionized (DI) water, (b) aqueous 0.1 mol/L sodium chloride (NaCl), or (c) saturated (6.1 mol/L) NaCl solution. A similar protocol to that reported by O’Brien et al. [33] was used for assessing the impact of environmental factors on adhesion. For comparison, a “control” experiment in air was also conducted. In this case, the specimen was immediately tested after removal from the desiccator to avoid any degradation of the joint strength due to ambient humidity. For the SLBT, a rod with a hemispheric tip (approximately 6.3 mm in diameter) is forced through the center of the 8 mm hole in the substrate to apply a force to the PSAT that covers the opening as illustrated in Fig. 2B. This force produces the growth of a debonded blister. The critical load, \( P \), (determined by the tensile testing machine) and debonded blister radius, \( a \), (determined by optical microscopy, Diagnostic Instruments 11.2 color mosaic with SPOT imaging software) were used to estimate the fracture energy release rate, \( G_C \), assuming linear elastic fracture mechanics [34, 35]:

\[
G_C = \left( \frac{1}{16\pi^2E h} \right)^{\frac{1}{2}} \cdot \left( \frac{P}{a} \right)^{\frac{1}{2}} \tag{1}
\]

where \( h \) and \( E \) are the thickness and the Young’s modulus of the adhesive layer, respectively. The epoxy sorbs less than 3 wt% water for all conditions examined, which is within the uncertainty of the thickness of the epoxy. Therefore the thickness of the adhesive is effectively constant for this calculation. The Young’s modulus will vary more significantly (~20%) [36], but the weak dependence of fracture energy release rate (i.e., \( G_C \propto (Eh)^{-1/2} \)) limits the sensitivity of the fracture energy release rate to film modulus and thickness. Thus, we neglect the change in moduli of the epoxy in the calculation of the fracture energy release rate. Joints were tested in triplicate in each environment.

**XPS Analysis of Joint Failure**

After SLBT, X-ray photoelectron spectroscopy (XPS) (5400 from Physical Electronics) determined the failure path of the fracture surfaces. The XPS used non-monochromated Mg \( K_\alpha \) radiation (1253.6 eV) operating at 300 W. Both the epoxy and substrate of the delaminated surfaces were measured. The clean substrate prior to epoxy coating and the neat epoxy coating were used as controls. All spectra were obtained using small area mode and aperture 4 using an OmniFocus II lens system (Analyzer width = 1 × 3.5 mm²) accepting photoelectrons at 45° from the surface normal. Full surveys were acquired at pass energy of 178.9 eV, while multiplexes were obtained at 44.75 eV. All spectra were adjusted such that the C (1s) peak was located at 284.6 eV [37] and fit with a Shirley baseline using elemental relative sensitivity factor (RSFs) from the manufacturer.

Additional spectra were acquired using Axis Ultra DLD XPS (Kratos Analytical) operating at 150 W, monochromatic Al \( K_\alpha \) radiation (1486.6 eV). This XPS instrument provides significantly improved resolution, especially for low concentrations of nitrogen. Spectra were acquired in hybrid-slot mode (300 × 700 μm²) with photoelectrons accepted into the detector along the surface normal. The spectra of fresh epoxy film and fresh substrates were collected for control purposes. All data analysis was performed using commercially available software (CasaXPS version “2.3.1.16 Pre-rel 1.4”).

**Neutron Reflectivity**

NR measurements required extremely uniform thin epoxy coating. For these measurements, the resin and the hardener mixture were heated at 60°C for 50 min to increase the polymer molecular weight prior to dissolution in toluene and subsequent spin-coating on the aluminum (oxide) coated silicon substrate. The uncured epoxy dewet from the substrate due to capillary forces [38] if the epoxy was not precured. The epoxy-coated substrates were then cured using the same schedule as noted previously. Deuterium oxide, D₂O (Aldrich, 99.9%) was utilized in place of common protonated water to provide significant neutron contrast due to the large difference in scattering cross-section between D and \(^1\)H. NR measurements were performed at the Center for Neutron Research on the NG-7 reflectometer at the National Institute of Standards and Technology (NIST) (Gaithersburg, MD) in the following configuration: wavelength, \( λ = 0.4768 \) nm and wavelength spread, \( Δλ/Δλ = 0.025 \). NR is capable of probing the neutron scattering density at depths of up to several hundred nm, with an effective depth resolution of less than 1 nm. The reflectivity, \( R \), is measured as a function of the momentum transfer normal to the surface of the sensor \( q = \frac{4π}{λ} \sin θ \), where \( λ \) is the neutron wavelength and \( θ \) is the angle of reflection at the specular condition). The reflectivity profiles were fit with a recursive algorithm (reflpack suite developed at NIST) [39] to quantify the change in neutron scattering length density (NSLD) upon exposure to D₂O or aqueous (D₂O based) NaCl solutions. The NSLD is analogous to refractive index for light, but provides a quantitative measure of the volume fraction of atoms present as the neutrons directly interact with the atomic nuclei. This quantitative relationship between NSLD and volume fraction enables the calculation of the concentration within the films. Here, the NSLD is expressed as \( Q_2 \), which is the square of the critical momentum transfer vector for the material below which total external reflection occurs. However with the sorption of both NaCl and D₂O into the epoxy coating, it is not possible to directly isolate their concentrations within the film due to two unknowns for one measurement. In order to characterize the location of NaCl within the epoxy film, the NaCl was dissolved in a mixture of H₂O and D₂O such that the NSLD of the H₂O/D₂O mixture matches that of the epoxy...
film similar to the methodology reported previously for organic salts in polymeric films [40].

RESULTS AND DISCUSSION

Figure 3 illustrates the fracture energy release rate of epoxy-aluminum (oxide) joints as measured using the SLBT. In ambient air (control), the joint exhibits the greatest fracture energy release rate ($\approx 400$ J/m$^2$). DI water yields a substantial (50%) decrease in fracture energy as expected based on prior reports [9, 41, 42]. However, the addition of small concentration of NaCl (0.1 mol/L) increases the fracture energy release rate slightly relative to that in DI water on average, but this difference is not statistically significant. At high salt concentration (saturated NaCl), fracture energy release rate increases substantially to greater than 300 J/m$^2$, but this is still weakened relative to the control specimens at ambient conditions. These aqueous environmental factors increase the susceptibility of the joint to failure, but addition of salt improves the adhesive strength.

In order to identify the fundamental origin of the improved adhesive strength with the addition of salts, first, the loci of failure in each case needs to be known to understand if the failure is adhesive or cohesive. Figure 4 illustrates the XPS spectra associated with the substrate and epoxy side of the joint after failure in each environment. The thermally evaporated Al$_2$O$_3$/Al thin film on the borosilicate substrate provides a simple route to understand if the failure occurs near the substrate interfaces through examination of the Al (2p) peak as shown in Fig. 4a; two clear peaks are observed for the substrate, while the epoxy control yielded no measureable Al signal. Examination of the epoxy side of the failure surface illustrates no distinguishable Al (2p) signal, so the failure is not within the aluminum oxide layer. However, the substrate side of the failure always exhibits a detectable Al peak. Therefore, the locus of failure must be within approximately 10 nm of the interface due to the sampling depth associated with XPS. Examination of the intensity of the Al (2p) peaks suggests that the failure is further into the epoxy when fractured at room temperature (RT) without any environmental conditioning due to the weaker signal as shown in Table 1. The Al (2p) signal is slightly stronger for the fracture when conditioned with DI water (H$_2$O) in comparison to the saturated NaCl solution (NaCl), which suggests that the failure moves closer to the interface as the joint strength decreases.

Similarly, the nitrogen associated with the amine should enable identification of the epoxy as shown in Fig. 4b. Both failure surfaces show a significant N content, which is consistent with the conclusion from the Al (2p) spectra that the failure is within the epoxy. As expected there is no detectable N (1s) in the substrate prior to attachment to the epoxy, but the N (1s) signal for
TABLE 1. Relative elemental compositions of all measured/detected elements.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Surface</th>
<th>Al (2p)</th>
<th>C (1s)</th>
<th>Cl (2p)</th>
<th>N (1s)</th>
<th>Na (1s)</th>
<th>O (1s)</th>
<th>Si (2p)</th>
<th>X-ray</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ctrl Substrate</td>
<td>26.1 29.2 0.1 ND ND 44.4 0.3 Mg</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ctrl Epoxy</td>
<td>ND 84.6 ND 0.8 ND 14.4 0.2 Mg</td>
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</tr>
<tr>
<td>RT Substrate</td>
<td>7.9 64.6 0.5 2.2 0.9 22.9 1.0 Mg</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>RT Epoxy</td>
<td>ND 79.4 0.1 2.1 0.8 17.5 0.1 Mg</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>H2O Substrate</td>
<td>16.2 47.7 0.2 1.3 0.7 33.3 0.6 Mg</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>H2O Epoxy</td>
<td>ND 82.2 0.1 2.1 0.6 14.1 0.9 Mg</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>NaCl Substrate</td>
<td>15.0 44.4 2.4 1.5 2.6 33.8 0.4 Mg</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>NaCl Epoxy</td>
<td>ND 79.8 0.3 2.7 1.1 15.5 0.6 Mg</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Ctrl Epoxy</td>
<td>ND 68.9 ND 1.4 ND 20.1 9.5 Al</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>NaCl Epoxy</td>
<td>ND 79.4 ND 6.4 ND 13.6 0.6 Al</td>
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</table>

All values are in elemental percentages. Conditions correspond with those in Figure 4.

ND = Not detectable.

the control epoxy is only slightly above the noise. This result is reproducible and attributed to the preferential segregation of the Epon 828 to the surface over the Jeffamine hardner on adhesive curing. The N signal increases for the failure substrate surface from DI water to saturated NaCl solution to the ambient environment; this is consistent with the relative thickness of residual epoxy on the substrate after failure determined from analysis of the Al (2p) spectra. Additionally, carbon (Fig. 4c) should also provide an easy route to assess the presence of the epoxy on the two failure surfaces, but there is significant carbon contamination (likely from the environment where the SLBT are performed) on the substrate control. Despite this limitation, there is a significant increase in the carbon signal for the substrate failure surfaces. Consistent with the decrease in Al (2p) signal intensity and increase in N (1s) signal, the substrate failure surface exhibits the largest C (1s) signal for the ambient control (Table 1). These data provides a consistent picture for the failure occurring near the substrate with the failure locus approaching the interface as the adhesive strength of the joint is weakened by environmental factors.

One simple explanation for the differences in the failure strength of the joints would be the bulk absorption of water or salt water. Figure 5 shows these sorption isotherms for the three environments examined. Despite the difference in the substrate failure surfaces determined by XPS, the isotherms for DI water and 0.1 mol/L NaCl exhibit nearly identical equilibrium sorption and uptake kinetics. Thus, the fluid uptake into the bulk epoxy does not likely completely explain the differences in adhesive strength in aqueous solution dependent on the salt concentration. Significantly increasing the NaCl concentration (saturated NaCl) decreases the equilibrium sorption by a factor of approximately 1.5 and also the water uptake rate. One simple explanation for this behavior is the change in the driving force for water adsorption as the chemical potential of water is decreased in salt solution, but this assumes the salt is at least partially excluded from the epoxy. This would effectively generate an osmotic pressure that inhibits the water uptake. Conversely, from a kinetics perspective, the bulkiness of ionic clusters and the interplay between the molecular pore size of the epoxy network and the radii of the hydrated ions could also control the uptake as size of the hydrated ions have been reported to be similar to the mesh size of crosslinked epoxy [31]. Nonetheless for all environments examined, the equilibrium uptake is less than 3 wt%, but more than 50% reduction in adhesion strength is observed from the SLBT. Combined with the XPS data, this suggests that the local environment near the failed epoxy-substrate interface may be significantly different from the environment of the bulk adhesive. It has been established that the concentration of water near a solid interface may differ significantly from that in the bulk of the polymer [20, 21, 43].

To understand the role of the interface, NR is applied to elucidate how water (and salt ions) is distributed near the epoxy-aluminum (oxide) interface. First, the structure of the stack obtained from the deposition of the aluminum on the silicon wafer with a thermal oxide must be understood, especially as the aluminum was oxidized. For the timeframes measured here, it is important to note that we find no evidence of further oxidation of the aluminum during the exposure to the aqueous solutions. However, for real world applications, such as a ship component exposed to seawater, one would expect long term exposure to lead to corrosion of the aluminum due to unavoidable pin hole defects in the epoxy that provide local nucleation sites for corrosion. Figure 6 illustrates the reflectivity from the aluminum coated silicon wafer (substrate) and then shows a second curve after spin-coating of an epoxy film on the substrate. In order to fit the data for the substrate, a diffuse surface oxide in the aluminum is required. The thickness of the oxidized aluminum is approximately 5 nm. The solid line in Fig. 6a (substrate) shows the excellent fit obtained for the aluminum coated silicon wafer when a surface oxide is included. After spin coating, the NSLD curve (Fig. 6b) can be fit very well with the substrate results and the addition of an epoxy layer that is 81 nm thick. With these preliminary fits in place, how and where water and salt is situated in the epoxy-aluminum (oxide) can be assessed qualitatively using NR.

Figure 7a illustrates the reflectivity profiles as $R \times q^4$ for the dry state, exposure to pure D$_2$O, and in saturated NaCl solution (in D$_2$O). This data representation corrects for the $q^{-4}$ decay in reflection according to Fresnel expressions [44] and provides an

FIG. 5. Water absorption isotherms of freestanding epoxy immersed in deionized water (○), 0.1 mol/L NaCl (+) and the saturated NaCl (●). The sorption data were highly reproducible with standard error of <.5%.

FIG. 7a illustrates the reflectivity profiles as $R \times q^4$ for the dry state, exposure to pure D$_2$O, and in saturated NaCl solution (in D$_2$O). This data representation corrects for the $q^{-4}$ decay in reflection according to Fresnel expressions [44] and provides an
improved sensitivity to high $q$ data in the fits. The fit of each data set provides the NSLD profiles as illustrated in Fig. 7b. There are a number of distinct features that provide insight into what is occurring in the epoxy film and at the interface. First, the NSLD for the epoxy film increases substantially more than expected from linear swelling; the change in NSLD corresponds to nearly 14 vol% water, while the linear swelling of epoxy is only 1.3% based on the neutron reflectivity measurements. This difference can be attributed to the D-H exchange within the epoxy as this phenomenon has been observed previously for polymers with exchangeable hydrogen moieties such as pendant hydroxyl groups [45]. It should be noted that the linear swelling is less than expected based on the mass uptake of water in bulk samples (2.2 wt%, Fig. 5). There are two reasons for this discrepancy: first, the swelling of networks is constrained in thin films to 1D swelling, where the thin film swelling should be the square root of the bulk swelling based on Flory–Rehner theory [46]. Second, D$_2$O and H$_2$O are slightly different thermodynamically, so a slight increase in solubility for H$_2$O over D$_2$O might be expected.

In comparison to the swelling in pure D$_2$O, the change in the NSLD for the epoxy film upon exposure to nearly saturated NaCl in D$_2$O is significantly less. This is consistent with the decreased sorption in the bulk epoxy determined gravimetrically, but there is also a significant decrease in the NSLD for the bulk solution; thus, incorporation of NaCl into the film would also lead to a decrease in the NSLD for the epoxy film. In addition to the changes in the epoxy film, the NSLD of the aluminum oxide increases upon exposure to either solution; this change indicates that voids are present in the oxide, which enables transport of water within the oxide. The inclusion of water into this layer is likely responsible for the corrosion typically observed in epoxy-aluminum joints [47]. It is also interesting to note that we did not previously observe water permeation into a sputtered aluminum oxide coating using neutron reflectivity [32]. Thus, the specimen preparation appears critical to the permeability of aluminum oxide to moisture. This water may be detrimental for the adherence of the aluminum oxide layer to the metal layer [47]. However, the XPS data (Fig. 4a)
the joint strength between water and saturated salt solution. D2O
neutron reflectivity could provide insight into the differences in
num oxide and epoxy, careful examination of this interface with
joints.
num oxide to the metal layer is not the weakest link in the
ated epoxy surfaces suggesting that the adherence of the alumi-
demonstrates no measurable Al (2p) signal in any of the delami-
ated epoxy surfaces suggesting that the adherence of the aluminum oxide to the metal layer is not the weakest link in the joints.
As the failure occurs near the interface between the aluminum oxide and epoxy, careful examination of this interface with neutron reflectivity could provide insight into the differences in the joint strength between water and saturated salt solution. D2O (3.3 × 10^{-4} and Å^{-2}) and NaCl have larger NSLD than the epoxy, so accumulation of D2O near the interface would act to locally increase the NSLD. A significant difference in the shape of the NSLD near this interface can be observed between immersion in D2O and saturated NaCl solution. The width of the epoxy-aluminum oxide interface is very similar for the dry and salt cases, but immersion in D2O leads to a significant broadening of this interface, which has been attributed to water accumulation [13]. Additionally prior studies on the role of humidity on adhesion illustrated a decrease in adhesion as the width of this interface increases [14]. However, the ambiguity associated with two possible absorbing species (D2O and NaCl) does not allow for the concentration profiles to be elucidated from these experiments without additional information.
In order to better understand the differences in the NSLD profiles, an additional experiment where the NSLD for the water is matched to the epoxy by using a H2O/D2O mixture; a similar contrast match methodology has been used to calculate the distribution of an organic salt in a polymer film [40]. The NSLD for NaCl is larger than epoxy and thus the reflectivity profile will be altered if NaCl is present in the epoxy film. Figure 8a illustrates no statistical change in the reflectivity with the addition of salt to the contrast match solution. This result suggests that the salt does not significantly accumulate at the interfaces, nor within the epoxy film itself. Previously, the difference in NSLD between epoxy and NaCl was used to identify accumulation of NaCl at an epoxy (EPON resin SU-8)-silicon interface ex-situ after removing the sample and drying [31]. In this case, it was inferred that the accumulation of NaCl at the interface would be analogous to that of an epoxy-aluminum interface, but this is not true for water where a significant decrease in interfacial water is observed at aluminum oxide interface [32] relative to that at the silicon wafer interface [43]. In order to confirm the lack of NaCl within the epoxy films (including at the interface), an ex-situ experiment analogous to that used to identify accumulation of salt [31] is utilized. As illustrated in Fig. 8b, the reflectivity profile is not altered by exposure to saturated NaCl in D2O. The film was soaked for approximately 10 h prior to removal from solution. The film was not rinsed with water, but the excess solution was allowed to drain off the surface prior to drying. This result is consistent with no NaCl adsorbed within the epoxy coating. The maximum concentration of NaCl is <1 vol% based on the sensitivity to the NSLD of the epoxy layer. Moreover, the aluminum oxide cannot be significantly (<5 Å) altered by the exposure to the saturated salt solution for 10 h despite the thin epoxy coating (79 nm) as the reflectivity profile is invariant. For epoxies, the influence of salt on adhesion has been shown to vary depending on the formulation and substrate examined [26–28]. These differences are likely due to the dependence of the salt distribution on the epoxy chemistry and its processing, which will be the focus of future work.
Denoting a factor x as the fractional increase in effective crack length increase associated with water uptake and neglecting changes in the adhesive modulus and thickness to the aqueous environment, the ratio of fracture energy release rate of a joint exposed to an aqueous environment to fracture energy release rate at ambient conditions for a given load obeys the following proportionality:

\[ \frac{G_i}{G_0} \approx \left(1 + \frac{x}{a} \right)^{−\frac{1}{2}} \]

(2)

where the index i represents the different aqueous environments, and \(G_0\) is the fracture energy release rate recorded for ambient conditions. Substituting the measured \(G_{i,D2O}\) and \(G_{i,NaCl}\) and \(G_0\) (Fig. 3), the factor x for DI water and the saturated NaCl are found to be 0.85 and 0.28, respectively. Thus, the competitive attack of water molecules on the interface in pure water relative to that in the saturated salt can be illuminated
by the ratio of these two $x$ values (3.04). If the failure mechanism is simply dictated by water adsorption, the ratio of equilibrium interfacial water content of DI water to the saturated NaCl is expected to follow the similar scaling relationship for fracture energy. The equilibrium water adsorption ratio for the bulk epoxy between pure water and saturated salt determined from the gravimetric measurements is found to be 2.2, which is significantly less than the 3.04 predicted by this scaling. However as the moisture at the interface is likely driving the crack growth, the increased water concentration at the interface is the more relevant factor.

These simple scaling arguments for the fracture energy and interfacial water adsorption provide insight into how interfacial adhesion decreases upon water ingress. There appears to be little if any contribution from aluminum oxide hydration to the failure mechanism. While there is significant water uptake in the epoxy-aluminum oxide interface as determined by NR.

CONCLUSIONS

We have conducted studies of the debonding mechanisms of an epoxy/aluminum oxide interface upon exposure to liquid water and aqueous sodium chloride. Substantial decrease in measured fracture energy release rate is observed when the interfaces are exposed to aqueous environments. The inclusion of salt leads to an increased fraction energy release rate in comparison to DI water due to the reduction in water uptake because of the osmotic pressure associated with the salt and the exclusion of salts from the epoxy. A quantitative assessment for the role of water molecules on adhesive debonding was made using scaling relationships. The fracture energy is observed to scale with water concentration near the epoxy-aluminum oxide interface as determined by NR.

ACKNOWLEDGMENTS

We thank Drs. Edwin Chan and Gordon Christopher for their assistance with the deposition of aluminum on silicon wafers and plasma treatment, respectively. The authors would also like to acknowledge Johns Hopkins University for the use of their surface analysis laboratory.

REFERENCES


