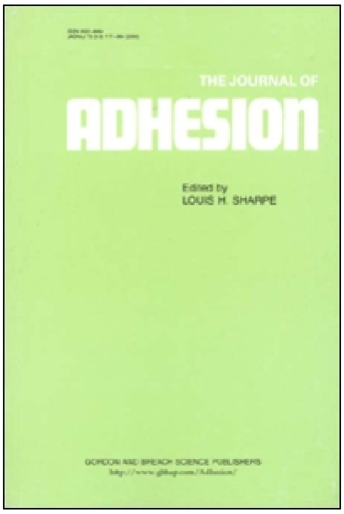

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Blistering as a Form of Degradation in Adhesive Joints*

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Water-filled blisters were observed to form during accelerated aging experiments with aluminum adherends and two structural epoxy adhesives. Both closed adhesive joints and open-face specimens were affected. The blisters grew with time, originated both in the adhesive and at the epoxy-aluminum interface, and were found only at 100% relative humidity at both 65°C and 85°C; blisters were never observed at 85% relative humidity or lower. The same water-soluble ionic species were found in the blister liquid, the two adhesives and water that had been in contact with adhesive samples for an extended period. It is proposed that the blisters grew under the influence of osmosis, originating in water clusters at microscopic voids. Contamination of the aluminum adherends by residual etching solution, although not a necessary precondition for blistering, could facilitate this process by lowering the partial pressure at which water condenses and by creating higher osmotic pressures.

Keywords: Adhesive joint degradation; accelerated aging; water; osmosis; epoxy; durability; delamination; blister

INTRODUCTION

Blistering has been studied as a mechanism of failure in organic coatings [1], and in most instances it has been attributed to osmosis created by water-soluble inorganic salts at the paint-substrate

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*One of a Collection of papers honoring F. James Boerio, the recipient in February 1999 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

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interface. Such contaminants also promote water condensation at the interface by lowering the equilibrium vapor pressure [1]. If it is assumed that such localized water condensation is necessary for degradation, this is consistent with the concept of a critical relative humidity below which certain forms of coating degradation will not occur [2].

Osmotic crack growth has also been reported in fiber-reinforced epoxy and polyester composites immersed in water at elevated temperatures [3]. The epoxy was a model system to which 0.5 wt% ground KCl was added to induce internal cracking.

Photoelastic measurements have been used to monitor the swelling distortion in joints created using commercial epoxy film adhesives and glass adherends [4]. The specimens were immersed in distilled water and in a saturated solution of NaCl or KCl at 60°C. Sub-millimeter sized pressure-filled pockets were observed to form in the joints with one adhesive but not with the other. Adhesive swelling was reduced for both adhesives when immersed in the salt solutions. On this basis it was concluded that osmosis was responsible for the creation of the pressurized pockets, and that the corresponding adhesive must have contained water-soluble inclusions. In a later paper [5], it was suggested that another possible mechanism for pressurization was the swelling of hydrated phosphate deposits resulting from adherend pretreatment.

Similarly, it has been reported that fillers can affect the rate of water uptake in epoxy adhesives, and that osmosis resulting from filler dissolution can influence swelling and the generation of microcavities in the adhesive [6].

The objective of the present work was to investigate the mechanisms of blister formation and growth in aluminum-epoxy adhesive joints subject to accelerated aging at various relative humidities and temperatures.

EXPERIMENTS

Blistering was studied using two commercial epoxy adhesives and aluminum adherends in two specimen configurations: open-face specimens, created by applying the epoxy adhesives as coatings [7], and closed joints of different sizes. The aluminum adherends were pretreated using an FPL etch (ASTM D2651-79), with particular attention paid to ensure complete rinsing with distilled water. The structural epoxy adhesives were a two-part room-temperature curing adhesive (Epoxy 2), and a mineral-filled single-part epoxy having 1 wt% 100 µm glass beads, cured at 150°C (Epoxy 1). The glass transition temperatures, T_g, of the adhesives were measured using differential scanning calorimetry (Dept. of Chemistry, University of Toronto): when cured at 65°C, T_g of Epoxy 2 was 61 ± 0.5°C, while that of Epoxy 1 cured at 150°C was 114 ± 2°C. Environment chambers were established at 65°C and 85°C with three relative humidities (RH), 60%, 85% and 100% (corresponding to equilibrium vapor pressures of aqueous NaOH solutions of 40 wt%, 17 wt% and 0 wt%, respectively). These conditions were monitored regularly using an electronic temperature-humidity probe (Omega HX-94C).

Open-face specimens were fabricated for each adhesive from 12.5 mm thick AA6061-T6 plates, 270 × 90 mm, onto which a 0.4 mm thick layer of adhesive was cast between a second aluminum plate that had been treated with a dried mold release agent (see Ref. [7] for details). After curing, the plate treated with mold release was removed and the exposed adhesive surface was cleaned with acetone. Table I shows the numbers of specimens that were manufactured for each adhesive, and placed in each of the six environment chambers. As noted, for each adhesive, 3 open-face specimens were intentionally contaminated prior to bonding with an array of 16 5–7 mm diameter deposits of diluted etching solution (diluted with water to 10% of original concentration), and 16 similar spots of a mold release agent (MS-122N/CO2, Miller-Stephenson Chemical Co.). The

TABLE I Number of open-face specimens tested at each combination of relative humidity (RH) and temperature (*T*) for each adhesive

RH (%)	*T* (°*C*)	*Epoxy* 1	*Epoxy* 2
100	85	5	–
	65	5*	5*
85	85	2	–
	65	5*	4
60	85	3	–
	65	2	–

* Indicates that 1 specimen from this group was artificially contaminated.

TABLE II Number of closed joints of each adhesive tested at 100% RH at 85°C and 65°C

	Epoxy 1		*Epoxy* 2
T (°*C*)	1 *mm*	0.1 *mm*	0.1 *mm*
85	4*	18**	–
65	4*	18**	6***

* Bondline thickness, $h = 1.12\,\mathrm{mm}$; joint width, $w = 6.5$ and 8.5 mm (2 joints for each).
** 2 joints for each combination of $h = 0.24$, 0.56, 1.12 mm; $w = 4.5, 6.5, 8.5\,\mathrm{mm}$.
*** 2 joints for each combination of $h = 0.56\,\mathrm{mm}$; $w = 4.5, 6.5, 8.5\,\mathrm{mm}$.

contamination spots were made by wetting a closed-cell foam cylinder, pressing this lightly against the aluminum surface and drying for 1 hour before application of the adhesives. The open-face Epoxy 1 specimens were prepared on 6 different dates, while those for Epoxy 2 were made on 3 different dates.

For Epoxy 1, a variety of closed joints were prepared on three different dates using 2 different sets of adherends: 1 mm thick AA5454-O and 0.1 mm thick AA 1100-O. Epoxy 2 was used to make joints with 0.1 mm thick AA1100-O adherends on several different preparation dates. Table II gives the dimensions and exposure conditions for these joints, which ranged in length from 119–184 mm. These sandwich-type joints (both adherends of equal size) were fabricated with different bondline thicknesses and widths as part of a related study of water absorption rates. The Epoxy 1 batch used with the 1 mm adherends was different from that used with the 0.1 mm adherends. The joints with the 1 mm thick adherends were cut from larger bonded plates using a diamond saw, and those having 0.1 mm thick adherends were cut from larger bonded plates using a sharp knife.

OBSERVATIONS AND ANALYSIS

Blistering on Open-face Specimens

Blistering on the open-face specimens with both adhesives could be detected by visual inspection after approximately 3 weeks of aging at 100% RH at both 65°C and 85°C. No blisters were ever observed at 85% RH or 60% RH for periods of up to 1 year. Blisters seemed to be randomly distributed over all open-face specimens and varied widely in size. Figure 1 illustrates this for an open-face specimen of Epoxy 2

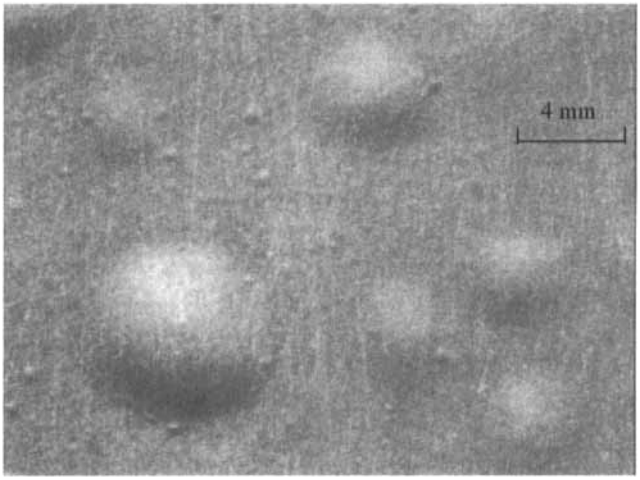


FIGURE 1 A blistered area on an open-face specimen of Epoxy 2 aged for 120 days at 65°C, 100% RH. (See Color Plate I).

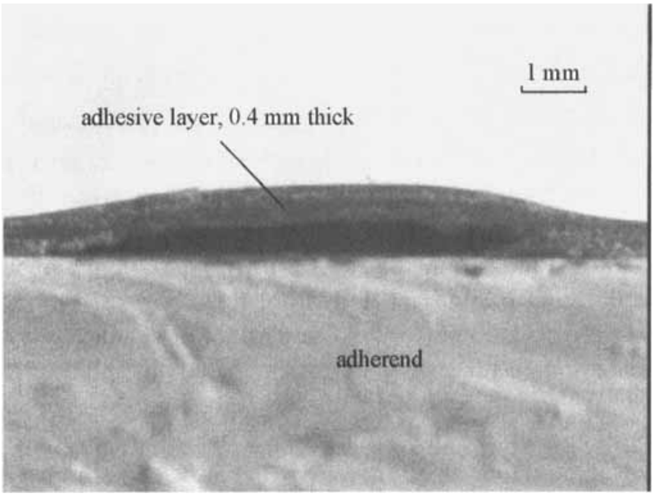


FIGURE 2 A cross-section of a blister on the specimen shown in Figure 1. (See Color Plate II).

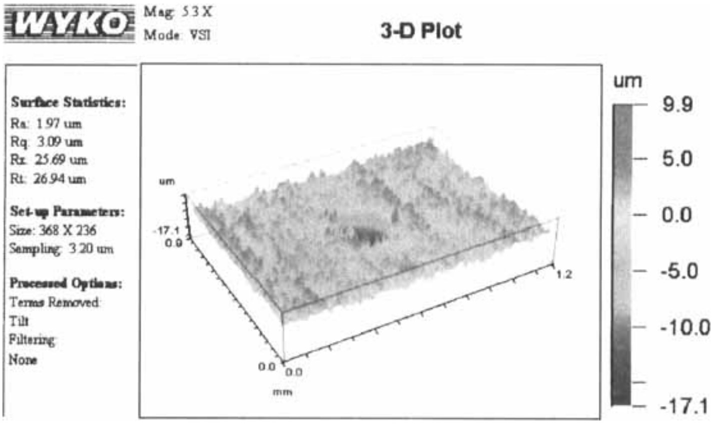
aged for 120 days at 65°C, 100% RH. As aging time increased, they grew in height (up to a maximum of approximately 3 mm) and diameter (up to about 6.5 mm), and increased in number. Figure 2 shows a cross-section of a single blister on the specimen shown in Figure 1. A detailed examination of 20 Epoxy 1 blisters and 14 on

Epoxy 2 specimens, showed that the blisters on open-face specimens represented an interfacial delamination of the 0.4 mm thick adhesive layer from the aluminum adherend. Visual inspection and scanning electron microscopy (see below) showed that there was no residual adhesive on the aluminum plate under the blisters. All blisters were full of liquid water that had a neutral pH. In some cases there were as many as 27 blisters in an 8 cm^2 survey area. Blisters could burst open and collapse; for example, at 85°C, 100% RH a blister under Epoxy 1 grew in height from 0.5 mm to 0.7 mm (approximately 6.5 mm diameter) over the period from 43 to 82 days, and had collapsed by day 97. As a further example, with Epoxy 2, a blister was observed to grow in height from 1.4 to 2.4 mm (diameter approximately 6 mm) during the period from 105 to 159 days, collapsing soon thereafter.

On the deliberately-contaminated open-face specimens, blisters appeared after three weeks of aging at all spots where diluted, residual etching solution had been deposited under the adhesive. This occurred for both adhesives aged at 100% RH (65°C), but no blisters were ever observed during 120 days of testing at 85% RH, nor on the mold release contamination spots at either 100% or 85% RH.

A scalpel was used to remove adhesive from 3 blistered and 3 nonblistered sites on Epoxy 2 specimens. Scanning electron micrographs and energy-dispersive X-ray analyses showed no significant differences in the aluminum oxide morphology or composition at these locations, indicating that corrosion of the aluminum was not involved in the formation and growth of these blisters. Furthermore, there was no evidence of anodic undermining of the epoxy layer, which is a common form of corrosion in coated aluminum and manifests itself as threadlike filaments under the coating [8].

A scanning optical profilometer was used to produce high-resolution three-dimensional images of the adherend surface under 5 blisters on open-face specimens of Epoxy 2 and Epoxy 1. In 2 cases, small pits (approximately 20 μm deep and 200 μm diameter) were found at the center of the blister. For example, Figure 3 shows such a pit in the three-dimensional surface profile of a 1.2 × 0.9 mm area of the aluminum at the center of a blister on a Epoxy 1 open-face specimen. In one case, the center of a blister was marked by a raised lump (approximately 14 μm high and 600 μm diameter) that was



Mag: 5.3 X
Mode: VSI

Surface Statistics:
Ra: 1.97 um
Rq: 3.09 um
Rz: 25.69 um
Rt: 26.94 um

Set-up Parameters:
Size: 368 X 236
Sampling: 3.20 um

Processed Options:
Terms Removed:
Tilt
Filtering:
None

FIGURE 3 Optical profilometer measurement of morphology of adherend beneath a blister on an open-face specimen of Epoxy 1 aged for 3 weeks at 65°C, 100% RH. (See Color Plate III).

TABLE III Average composition of liquid within several blisters found on single open-face specimens of Epoxy 2 and Epoxy 1; results of neutron activation analysis

Species	*Epoxy 2* *Concentration in blister liquid (ppm)*	*Epoxy 1* *Concentration in blister liquid (ppm)*
Ba	20.1	–
Mg	240.3	354
Na	21.1	61
Cl	60.3	2662
Al	4.5	12
Ca	–	–
Mn	–	–

identified as aluminum alloy using energy dispersive X-ray analysis. The central regions of the other blisters were not distinguished by any special topographical features. It seems, therefore, that blisters could initiate at a variety of sites.

The water from within the blisters was collected for chemical analysis by penetrating the adhesive layer using 3 ml syringes. Samples were taken from a Epoxy 2 open-face specimen (65°C, 100% RH, aged 170 days) and from a Epoxy 1 specimen (85°C, 100% RH, aged 119 days). The liquids were analyzed using neutron activation (Slowpoke reactor facility, University of Toronto) with the results shown in Table III. In order to identify the source of these elements, neutron activation analyses were also performed on samples of the two cured adhesives (110 mg of Epoxy 2, 310 mg of Epoxy 1), as reported in Table IV. In neutron activation, samples are first irradiated by neutrons and the subsequent radioactive decay is measured with a gamma-ray spectrometer to identify elements quantitatively. Finally, to measure the tendency for some of the elements of Tables III and IV to leach from the adhesives into water, 1 g of cured Epoxy 2 ($22\,cm^2 \times 0.4$ mm thick, cast wafer) and 2.4 g of cured Epoxy 1 ($27\,cm^2 \times 0.8$ mm thick, cast wafer) were each soaked in 20 ml of distilled water at 65°C for 4 weeks. The water was then analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) for Al and Mg, and ion chromatography (IC) for Cl (Dept. of Chemistry, University of Toronto). Approximately the same amount of pure distilled water (from the same source as the soaking water) served as the blank during the analysis. Table V shows the concentrations of Al, Mg and Cl ions that were found in the water that had held the cast adhesive samples.

Comparing Tables III and IV, it is seen that both the blister liquids and the adhesives contained significant amounts of Mg, Na, Cl, Al,

TABLE IV Results of neutron activation analysis of samples of Epoxy 2 and Epoxy 1

Species	*Concentration in Epoxy 2 (ppm)*	*Concentration in Epoxy 1 (ppm)*
Ba	20040	–
Ti	1280	–
Sr	795	–
Mg	16650	54510
Na	1012	557
Cl	1167	51545
Al	486	689
Mn	53	192
Ca	–	91730

TABLE V Composition of water that had been in contact with cured Epoxy 2 and Epoxy 1 for 4 weeks at 65°C

Leachate species	*Epoxy 2 Concentration in water (ppm)*	*Epoxy 1 Concentration in water (ppm)*
Al	0.10	0.03
Mg	8.34	3.22
Cl	5.82	68.30
Ca	–	1.10

and in the case of Epoxy 2, Ba. Furthermore, Table V confirms that significant amounts of Mg and Cl can leach from both of these adhesives into water, and that Ca can leach from the Epoxy 1. Therefore, it appears as if the adhesive itself can be the source for dissolved species in the blister liquids. Such dissolved salts would lead to the relatively rapid filling of voids by diffusing water through osmosis, and then to the generation of significant osmotic pressures.

In some cases, relatively small blisters (less than 0.3 mm in height) were found to form relatively quickly in the environment chambers at all relative humidities. These blisters appeared to originate from small bubbles within the adhesive layer, and were attributed to the swelling distortion of the unrestrained adhesive layer overlying the bubble. A simplified buckling analysis showed that such a disk of adhesive would distort into a raised spherical cap of the observed size using an estimated value of approximately 2% for the linear expansion of the adhesive due to water absorption at 85°C. It is believed that blistering due to swelling is a relatively short-term phenomenon that would occur well before the gas bubble becomes filled with water as a result of osmosis.

Blistering in Closed Joints

Blisters on Epoxy 1 specimens with 0.1 mm thick adherends were visible on both sides of the joint after 110 days of aging at 100% RH at 85°C. On the specimens with 0.24 mm bondline thickness, the same blister could often be seen on either adherend if the diameter was over 3 mm. Of the 18 Epoxy 1 closed joints aged at 85°C with 100% RH, all had developed blisters, with the number on each specimen ranging from 2–5, with a maximum diameter of approximately 6 mm. None of the Epoxy 1 specimens with 0.1 mm thick adherends aged at 65°C, 100% RH appeared to have blistered after 300 days of aging. Similarly, none of the 6 Epoxy 2 closed-joint specimens aged at 65°C, 100% RH appeared to have blistered after 150 days of aging. Therefore, blistering in the closed joints seemed to be more prevalent at 85°C than at 65°C, and, as may be expected, took longer to become noticeable than in the open-face specimens. This is partly due to the temperature-dependence of the diffusion coefficient and the resulting difference in the rate of water absorption; based on water absorption data for cast wafers, the diffusion coefficient of Epoxy 1 at 65°C and 85°C, is $6.9 \times 10^{-13}\,m^2/s$ and $12.3 \times 10^{-13}\,m^2/s$, respectively.

The 0.1 mm adherends of two of the Epoxy 1 closed joints that had been aged at 100% RH and 85°C were peeled off to examine the blisters. Out of a total of 19 blisters on these 2 specimens, 14 had a considerable amount of adhesive residue in the central two-thirds of the blister, suggesting that the crack propagation was initially cohesive (in the adhesive layer), becoming interfacial nearer the blister edge. Figure 4 shows such a surface of a 0.1 mm thick adherend at the site of a blister.

Due to the stiffness of the 1 mm thick adherends, blisters could not be seen on the outer surfaces of these 8 joints made with Epoxy 1. After 78 days of aging at 100% RH at both 65°C and 85°C (Tab. II), the adherends of these specimens were etched using an NaOH solution until approximately 0.1 mm of aluminum remained, which was then peeled off. Among these 8 joints with 1 mm adherends, the only one that developed blisters had been aged at 85°C with 100% RH. This blister was approximately 4 mm in diameter, and appeared to have originated within the adhesive, since there was a distinct, central 0.3 mm diameter spot of residual adhesive on the peeled aluminum with most of the remaining blister area largely free of residual adhesive. This illustrates that blisters can initiate at sites away from the

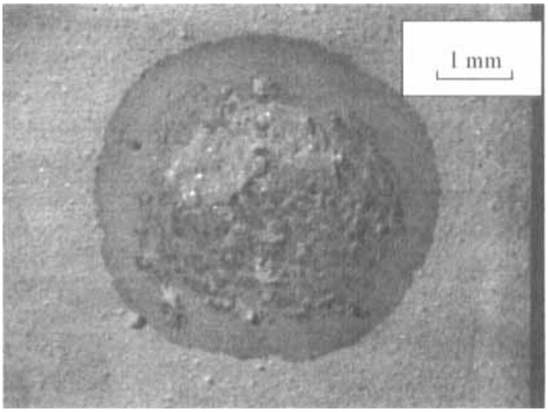


FIGURE 4 Surface of 0.1 mm thick aluminum adherend at the site of a blister in a closed joint of Epoxy 1 aged 110 days at 85°C, 100% RH. (See Color Plate IV).

aluminum, and that initiation is not necessarily associated with surface defects, corrosion or contamination. The crack path at the blister edge can change, however, becoming interfacial as growth continues.

DISCUSSION

The following model of the blistering process seems to fit the present observations: Water molecules, diffusing within the adhesive, form clusters or microdroplets in voids, either in the adhesive or at flaws such as pits on the aluminum surface. Evidence of water clusters has been reported previously with Epoxy 1 [9]. This process is facilitated by the presence of hydrophilic sites or salts that serve to decrease the vapor pressure required for water condensation [1, 2, 4]. The process of water clustering requires a sufficiently high relative humidity (greater than 85% RH in the present experiments), a fact that may correspond to the critical relative humidity reported in earlier studies of adhesive joint degradation [2]. The water clusters then absorb ionic species from the surrounding adhesive or from the adherend. This causes an acceleration in the rate of water entering the microdroplet due to osmosis, with the adhesive exhibiting some of the characteristics of a semipermeable membrane [1, 2, 4]. Water absorption by the droplet will now be much faster than the Fickian diffusion rate. In addition, osmotically-driven water absorption will lead to the filling of the void with liquid water, whereas Fickian diffusion would cease when the void space became saturated with water vapor. After the void is filled, the osmotic pressure will cause the adhesive layer to crack either cohesively or interfacially. The osmotic pressure may continue to increase as more water-soluble ions are leached from the surrounding adhesive or interface. The growth of the blister provides additional space for water, causing a drop in the internal pressure, and a resumption of the osmotic filling.

The expansion of the blisters is facilitated by the fact that the critical pressure for the growth of a blister is inversely proportional to its diameter (see Eq. (1) below). Growth may also be promoted by a decrease in the critical energy release rate of fracture caused by degradation due to the presence of the blister liquid. In closed joints (as opposed to open-face specimens), blister growth would be slower because of the decreased rate of water uptake and the constraint imposed by the adherends. Nevertheless, as observed in the present experiments, blister growth may still occur in joints with relatively thick aluminum adherends due to the very high pressures that can result from osmosis; for example, pressures up to 50 MPa can be generated for common inorganic aqueous salt solutions [3]. An interesting observation, that remains unexplained, is the lack of residual adhesive under blisters on open-face specimens, implying interfacial crack initiation and propagation, whereas blisters in closed-joints frequently have residual adhesive in the center. This may be due to the mechanics of crack path selection [10].

The osmotic pressure within a blister will, in general, depend on the dissolved molecular species and their concentrations which, in turn, will vary with time as species are leached from the surrounding adhesive. Concentration will only be constant if blister growth occurs at a slow, steady rate that is comparable with the rates of water diffusion and species leaching into the blister liquid. An estimate of the average osmotic pressure in the present experiments can be made using the total solute concentrations in the blister liquids reported in Table III (the liquids were collected from several blisters). Using the Van t'Hoff equation for an ideal dilute solution, for Epoxy 2 and Epoxy 1, respectively, the estimated osmotic pressures are 36 kPa and 280 kPa. An order-of-magnitude comparison can be made between these osmotic pressures and the estimates of the blister pressure to cause fracture using the membrane model [11]

$$G_C = \left(\frac{P_{\mathrm{cr}}^4 r^4}{576(1-\nu)^2 EH}\right)^{1/3} \tag{1}$$

where G_C, ν, E and H are, respectively, the critical fracture energy, Poisson's ratio, tensile modulus, and thickness of the adhesive layer, r is the blister radius, and P_{cr} is the critical pressure. The following approximate adhesive and blister properties were used in Eq. (1): the radius of a typical blister on Epoxy 1 open-face specimens was 3 mm; the adhesive was leathery at 85°C, 100% RH, suggesting a tensile modulus of 7 MPa (in comparison, the elastomeric adhesive used in Ref. [11] had $E = 4.1$ MPa); the blister was assumed to extend under mode I fracture, and previous studies [7] indicate that a reasonable estimate of the critical energy release rate $G_{IC} = 220\,\mathrm{J/m^2}$ Poisson's ratio was taken to be 0.4 and the thickness of the adhesive was 0.4 mm. Under these conditions, P_{cr} would be approximately 530 kPa. Although this is only a rough estimate, the fact that it is reasonably close to the estimated average osmotic pressure of 280 kPa for this adhesive is consistent with the model of blister growth due to osmotic pressure.

CONCLUSIONS

The osmotic blistering mechanism is a form of degradation for open-face and closed adhesive joints at elevated temperatures and high relative humidity. It was noticed that there seemed to have existed a critical relative humidity (higher than 85% at both 65°C and 85°C for Epoxy 2 and Epoxy 1 specimens) for joints to blister in the present research. This is consistent with earlier reports of accelerated durability testing of adhesive joints. The existence of a blistering threshold has important implications for the selection of appropriate accelerated aging conditions; *i.e.*, blistering may never be encountered under actual service conditions at less than 100% RH, and would be a misleading failure mechanism in accelerated testing at such high relative humidities.

Although osmotic blistering is promoted by contaminant salts on the adherends, such residual species are not a prerequisite for blistering. Soluble species can also be leached from the adhesive itself and lead to the osmotic filling of voids that have served as sites of water clustering.

The use of open-face adhesive specimens serves as a rapid means of detecting blistering degradation. Relatively small blisters that form quickly on such specimens are due to the swelling of the adhesive that covers small gas bubbles.

Acknowledgements

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