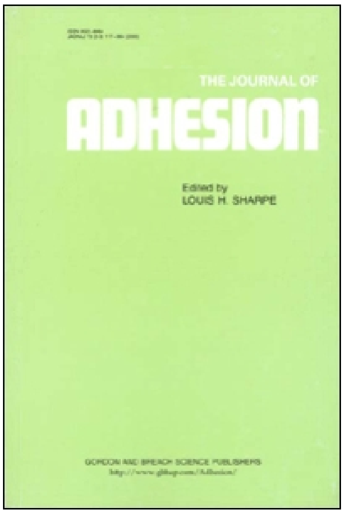

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Adhesive Joint Durability Assessed Using Open-faced Peel Specimens

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This paper presents an investigation of the durability of two aluminum-epoxy adhesive systems by means of open-faced peel specimens. A peel analysis model was used to determine the fracture energy from the peel data. Both *wet* and *dry* peel tests were conducted in order to distinguish between the reversible and the permanent effects of water. The effects of water on the cohesive properties of the adhesives were also assessed by tension tests. It was found that, for the two-part epoxy adhesive, which plasticized to a large extent, the peel testing should be carried out in a dry state to assess the interfacial weakening. It was also observed that the two-part adhesive was much stiffer in the dry, degraded state, and it was important to take account of such permanent changes in the cohesive properties associated with water uptake when determining the fracture energy from the peel data. In contrast, the one-part epoxy system did not suffer from appreciable cohesive changes, either reversible or permanent. In this case, both wet and dry failure loci were interfacial, and some of the interfacial damage was found to be reversible. Finally, surface analyses of the peel failure surfaces were carried out, and the formation of micro-debonds was identified as a possible mechanism of degradation for the two-part system.

Keywords: Adhesive joints; environmental degradation; cohesive failure; interfacial failure; peel test; fracture energy; plastic dissipation; adhesive plasticization

1. INTRODUCTION

It is well documented that adhesive joints undergo a loss in strength with prolonged exposure to a moist environment, and that the

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interfacial region in adhesive joints is particularly susceptible to degradation by moisture [1]. This phenomenon limits the potential applications of adhesive joining technology, despite the fact that such joints offer a number of distinct advantages compared with traditional methods of fastening.

There have been numerous studies, *e.g.* [2–5], directed towards the understanding of environmental degradation, using standard specimens such as the lap shear joint. A major difficulty with traditional geometries is that it takes a relatively long time to condition the joint to a given environment (humidity/temperature) because of the very long diffusion path (Fig. 1(a)). The degradation of the joint proceeds

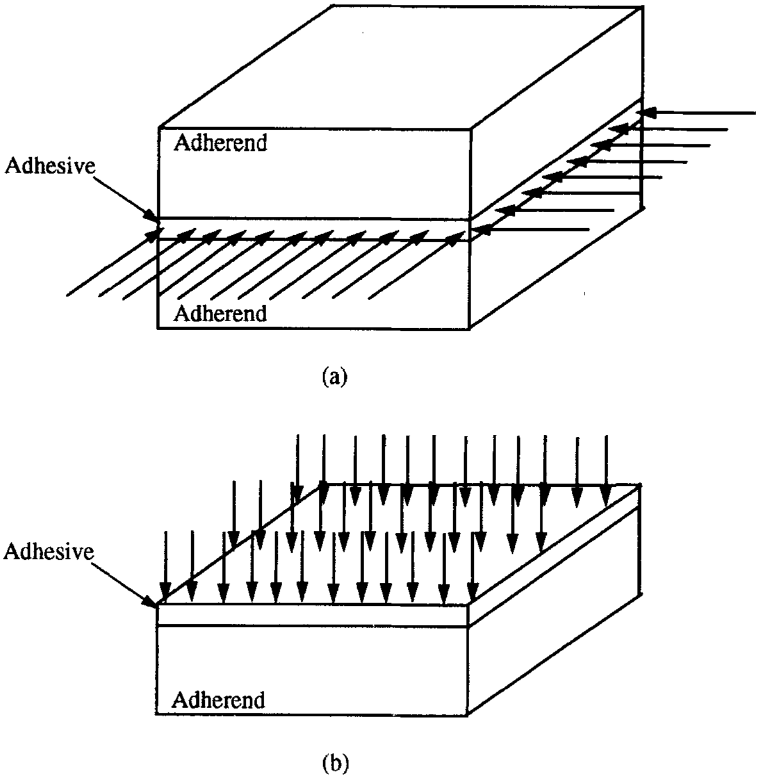


FIGURE 1 Moisture diffusion path in the traditional geometry (a), and in the open-faced geometry (b).

while it continues to absorb water from the environment, such that the concentration of moisture within the joint and the degree of degradation is spatially nonuniform. This makes it difficult to study the time-dependency of joint degradation and to associate a measured decease in strength to a particular exposure condition.

Another approach to the experimental investigation of degradation is to utilize an open-faced specimen (Fig. 1(b)), where the adhesive is bonded to only one adherend and the other face is left exposed [6–8]. In this case, since the adhesive thickness offers a much shorter diffusion path, the time for water uptake is greatly decreased, and equilibrium with a controlled environment can be achieved in a relatively short time. Another advantage of the open-faced specimen is that it allows *wet* (as conditioned) and *dry* (after drying out the absorbed water) testing of joint strength [8].

The strength of degraded open-faced joints may be measured using peel [7] of fracture [8] tests, by bonding the exposed face of the adhesive to a second adherend by means of a secondary adhesive bond. The peel test has the advantage that the failure path is very close to the interfacial region of the joint, especially when the thickness of the flexible adherend is relatively small. This is attractive for characterizing joint degradation because the effect of moisture on the interfacial region is of particular concern. Also, any effect of the secondary bond on the peel force is negligible provided that the secondary bondline is kept very thin. However, a major concern in using the peel test is the uncertainty regarding the fraction of the measured peel energy that is attributable to plastic dissipation due to bending in the flexible adherend (peeling arm). To overcome this difficulty, an analytical model was developed to calculate the plastic dissipation in the flexible adherend, thereby allowing the extraction of the fracture energy from the peel test data [9, 10].

In this work, the durability of two aluminum-epoxy structural adhesive systems has been investigated using the open-faced geometry and the peel test. There are several novel aspects to the present work. Firstly, the peel analysis model [9,10] was used to design a peel test in which the adherend plastic dissipation effects were relatively small. The model was also used to determine the fracture energy as a function of degradation. Secondly, most of the data in the literature correspond to a *wet* condition and there have been no attempts to compare *wet* and *dry* behavior systematically. This work distinguished the reversible and permanent effects of water on the joint, bearing in mind that the permanent degradation of the interfacial region was of particular interest. The peel failure surfaces were examined to gain insights into the mechanism of degradation.

2. ANALYSIS

The interfacial fracture energy of adhesive joints may be calculated from the peel test data by using the following energy balance [9, 10]:

$$G_c = W_{\text{ext}} - W_{et} - W_{pt} - W_{pb} \tag{1}$$

where G_c is the fracture energy, W_{ext} is energy input which can be calculated from the peel force and peel angle, W_{et} is the stored elastic energy in tension of the flexible adhered, W_{pt} is the plastic dissipation due to tensile deformation of the adherend, and W_{pb} is the plastic dissipation due to bending of the adherend. For metal-to-metal adhesive joints, W_{et} and W_{pt} are negligible compared with W_{pb}.

Expressions have been developed [9, 10] to calculate the plastic dissipation in the flexible adherend due to bending (W_{pb}), thereby allowing the determination of the fracture energy from Eq.(1). The approach utilized a large displacement analysis of an elastic-plastic beam on an elastic foundation to predict the deformation of the adherend at the peel front, assuming a bilinear stress-strain behavior of the adherend. The input parameters required for the calculation of the critical fracture energy were the adherend properties (thickness, h, Young's modulus, E_s, Poisson's ratio, ν_s, strain-hardening parameter, α, and yield strength, σ_y), the adhesive properties (thickness, t, Young's modulus, E_a, and Poisson's ratio, ν_a) and the peel force per unit width (P).

The adherend plastic dissipation energy can be many times greater than the fracture energy, depending mainly on the thickness and yield stress of the flexible adherend, the adhesive modulus, the peel angle and the value of fracture energy itself. It has been established previously that, for typical aluminum-epoxy structural adhesive joints, the effects of plastic dissipation can be kept relatively small by employing a thin, flexible adherend with a low yield strength, and a relatively low peel angle [9]. Based on this finding, 0.12 mm thick, AA1100-O aluminum, which has a yield stress of about 50 MPa, was chosen as the material for the flexible adherend in the present durability experiments. The peel angle was chosen to be 45°.

3. EXPERIMENTAL PROCEDURE

Two commercial epoxy adhesives were investigated: Hysol EA 9346 which is a one- part, heat-curing adhesive, and Permabond E04 which is two-part room-temperature curing adhesive. Open-faced joints were prepared using the flexible adherend, 100 mm by 80 mm, that was pretreated using the FPL-etch procedure (ASTM D 2651). The adhesive was applied to the adherend, and the uncured joint was clamped between Teflon-coated steel plates. Teflon shims were used to control the adhesive thickness at 0.60±0.05 mm. The Hysol EA 9346 was cured for 90 minutes in an oven preheated to 120°C ensuring that the bondline was at 120°C for at least one hour. The specimens were then allowed to cool to the room temperature. The Permabond E04 adhesive was cured at room temperature (25°C) for at least 24 hours.

The cured specimens were immersed in de-ionized water at 67±3°C, and periodically removed in order to investigate various levels of degradation. The open adhesive faces of the specimens that were selected for *wet* testing were secondary-bonded immediately after removal from the water bath to a 1.6 mm thick sheet of AA 1100-H14 aluminum alloy using Permabond E04 adhesive. The thickness of the secondary bondline was less than 0.1 mm. The specimens for *dry* testing were kept under vacuum at 70°C for 3 days after removal from the water, in order to dry out the absorbed water. They were then secondary-bonded to a 1.6 mm thick, rigid adherend as were the wet specimens. The final step was to cut these wet and dry specimens into strips, at least 15 mm wide, for peel testing.

The peel testing was conducted at a rate of 5 mm per minute using an Instron-1000 with computerized data collection. The flexible adherend was peeled from the adhesive for a length of at least 50 mm, and two to six peel specimens were tested for each degradation condition. Analysis of the failure surfaces was carried out using a scanning electron microscope (SEM) with an energy dispersive spectroscopy (EDX) facility.

The elastic properties of the adhesive were measured using tensile tests of bulk adhesive specimens in a fresh state, as well as in wet and dry states after exposure to water at 67±3°C. The cast adhesive specimens, which had a thickness of 0.55 mm, were prepared by curing the adhesive between two Teflon-coated steel plates. Teflon shims were used to control the thickness of the case specimens. Water diffusion studies were also conducted by measuring the mass uptake of water by 0.55 mm thick, cast adhesive specimens as a function of duration of exposure to 67±3°C.

4. RESULTS AND DISCUSSION

4.1. Two-Part Adhesive

The water uptake by the cast adhesive specimens of the two-part system (Permabond E04) did not show a Fickian behavior. A secondary stage of water uptake was observed after an apparent initial equilibrium. After a final maximum was reached, the weight of the specimens was observed to decrease, presumably due to leaching of the adhesive. The final equilibrium water content of cast adhesive specimens was about 5.9%, and the equilibrium was reached in about 250 hours.

Figures 2 and 3, respectively, show the measured wet and dry peel force *vs.* time of exposure for the two-part system (AA 1100-O bonded with Permabond E04). Figure 4 gives the tensile test results for cast Permabond E04 adhesive in fresh (as cured), and in both the wet and dry states after 100 days immersion.

The wet and dry peel results show markedly different behavior, mainly due to the plasticization of the adhesive in the wet samples. This is evident from Figure 4 where the Young's modulus, (defined at 0.5% strain), of a wet adhesive is observed to decrease to 0.22 GPa from an initial value of 0.48 GPa. As a result of plasticization, the fracture mechanism for the wet specimens was primarily cohesive, with large chunks of adhesive present on the flexible strip. For severely

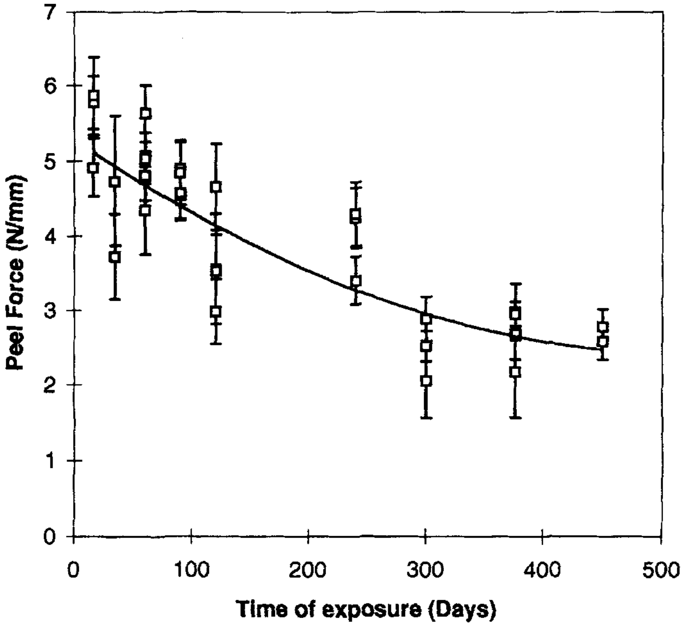


FIGURE 2 Peel force *vs.* exposure time for two-part (Permabond E04) *wet* case. Each point represents the average peel force for a single specimen, and the bars represent one standard deviation within the peel trace. Multiple dots represent different samples tested, and the curve is a quadratic fit ($R^2 = 0.8131$).

degraded wet samples (> 300 days), the amount of residual adhesive on the peel strip was observed to decrease, presumably as the interface became weaker. The peel forces were much higher for the wet case (Fig. 2), compared with the dry case case (Fig. 3), because of the increased crack-tip dissipation effects due to the cohesive nature of the fracture and the relatively high compliance of the adhesive.

It was therefore apparent that, in the presence of a large amount of adhesive plasticization, the peel tests must be carried out in a dry state in order to characterize permanent, interfacial strength degradation. In contrast to the wet case, the failure loci for the fresh and dry cases were close to the interfacial region with a very thin residual adhesive layer on the peel strip. The dry peel force data (Fig. 3) indicate considerable degradation only after a long exposure time (> 300 days). However, it is noted from Figure 4 that the adhesive in a dried,

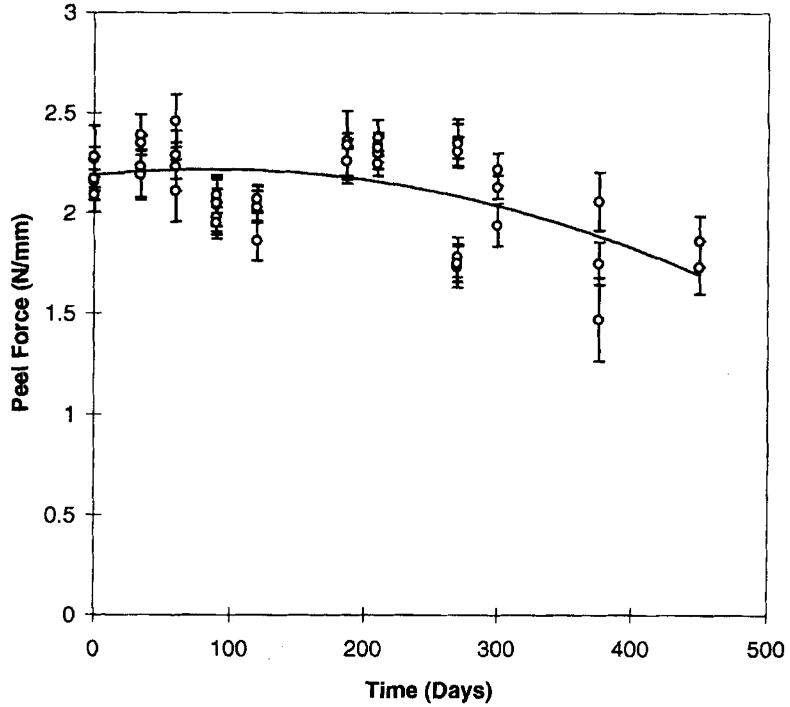


FIGURE 3 Peel force *vs*. exposure time for two-part (Permabond E04) *dry* case. Each point represents the average peel force for a single specimen, and the bars represent one standard deviation within the peel trace. Multiple dots represent different samples tested, and the curve is a quadratic fit ($R^2 = 0.6298$).

degraded condition had become relatively rigid and brittle. Tensile tests were conducted on bulk adhesive at 30, 100 and 210 days exposure, and all showed that the Young's modulus (defined at 0.5% strain) increased to a value of 2.52±0.22 GPa, compared with 0.48 GPa for fresh adhesive. This increase in stiffness with degradation may be due to permanent chemical and physical changes in the adhesive associated with exposure to warm water, such as hydrolysis and the leaching of low molecular weight components. Indeed, the data from the moisture diffusion studies indicated that the weight of cast specimens decreased with time after an apparent maximum.

Noting that the plastic dissipation in the flexible adherend increases with an increase in adhesive stiffness [9], the calculation of the fracture

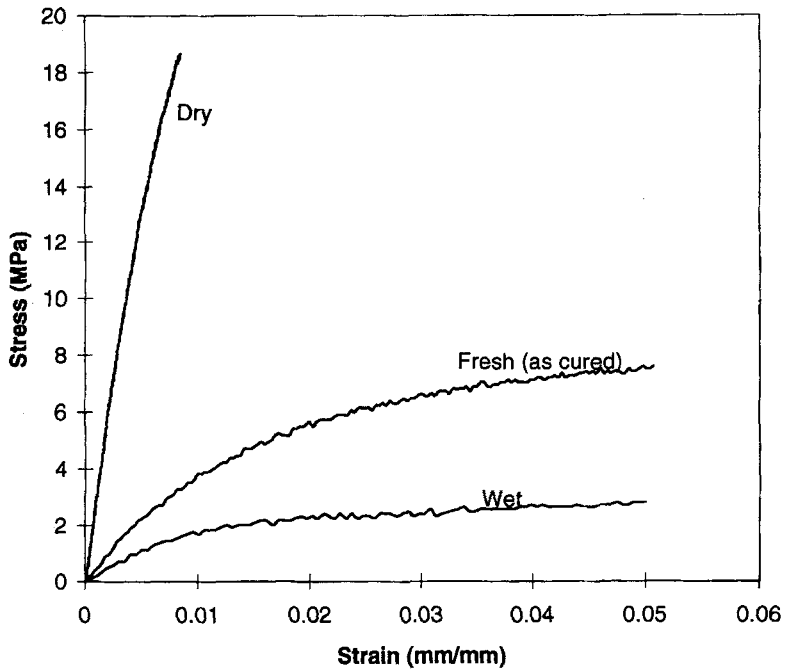


FIGURE 4 Tensile test results for cast E04 adhesive tested in three conditions: i) freshly cured, ii) immersed for 100 days and then tested wet, iii) immersed for 100 days and then tested dry.

energy must account for the changing adhesive modulus. Table I gives the material properties used in the calculation of the fracture energy. Figure 5 shows the fracture energy corresponding to the dry peel force data of Figure 3, calculated with the adhesive modulus equal to 0.48 GPa for fresh specimens and 2.52 GPa for all degraded specimens. In contrast to the trend of Figure 3, the fracture energy is seen to decrease continuously with exposure time.

Analysis of the failure surfaces of the fresh and degraded (dry) specimens was carried out using the SEM. An interesting observation is the formation of micro-defects on the flexible adherend surfaces of the degraded specimens. Figures 6(a) and 6(b) show the SEM micrographs of the adherend surface of a fresh specimen, and Figures 7(a) and 7(b) show the corresponding micrographs of a dry specimen after

TABLE I Material properties used to calculate the fracture energy; degraded adhesive modulus measured after 100 days of water immersion at 67°C

Material	*Thickness (mm)*	*Young's modulus (GPa)*	*Poisson's ratio*	*Yield strength (MPa)*	*Strain hardening parameter*
AA1100-O alloy	0.12	68	0.3	48	0.0065
Permabond E04 adhesive	0.6	0.48 (Fresh) 2.52 (degraded, dry)	0.37	–	–
Hysol EA 9346 adhesive	0.6	2.3 (fresh) 2.0 (degraded)	0.37	–	–

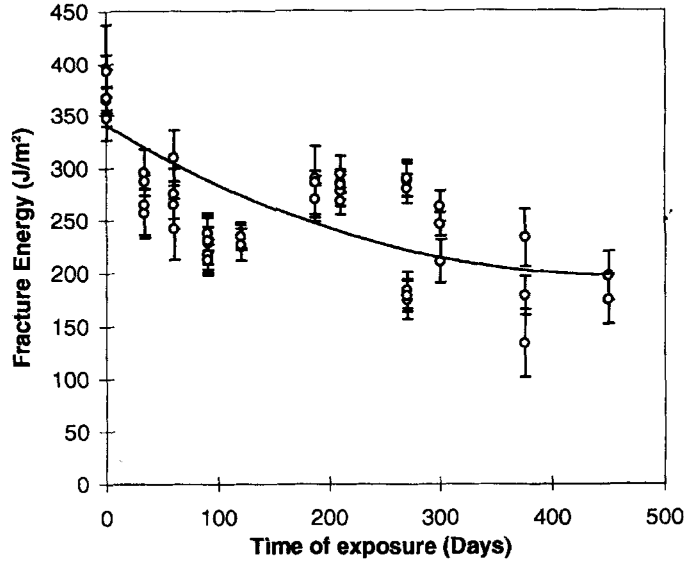


FIGURE 5 Fracture energy *vs.* exposure time for E04 dry case (peel data of Fig. (3)). Each point represents the average peel force for a single specimen, and the bars represent one standard deviation within the peel trace. Multiple dots represent different samples tested, and the curve is a quadratic fit ($R^2 = 0.5087$).

376 days exposure. The micro-defect formation is visible on the degraded sample. The micro-debonds were found to be between 30–150 μm in size, and were consistently evident on specimens after about 300 days exposure. They were also evident on specimens degraded for

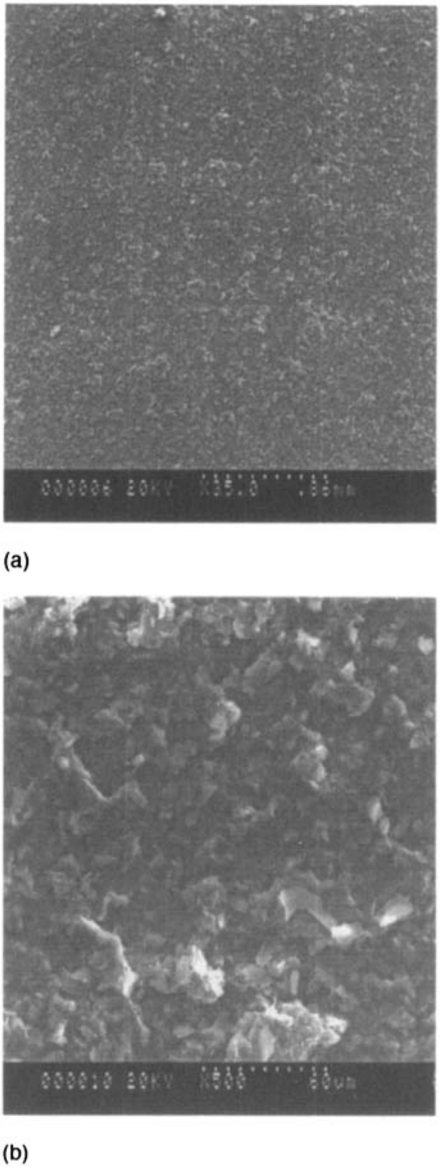
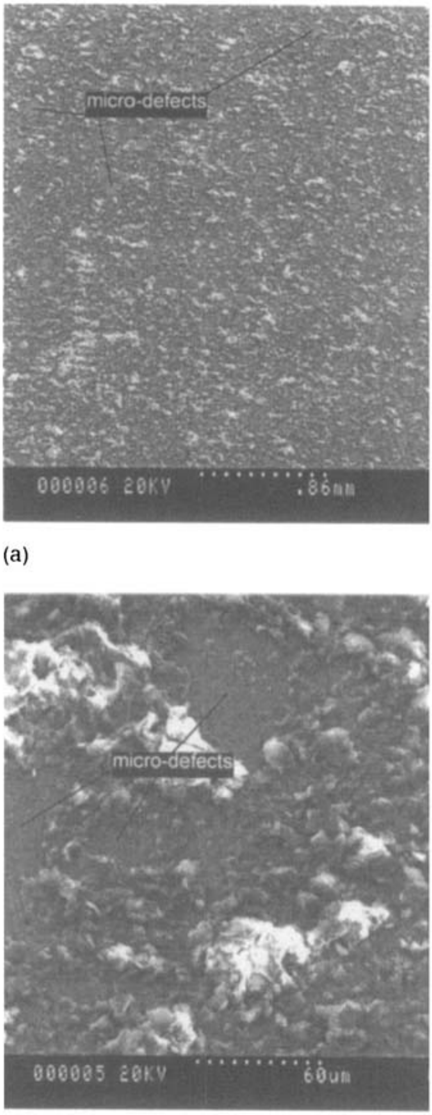


FIGURE 6 SEM micrographs at two magnifications of the flexible adherend after peeling of fresh E04 specimen.



(a)

(b)

FIGURE 7 SEM micrographs at two magnifications of the flexible adherend of degraded (dry) E04 specimen, after 376 days exposure.

less than 300 days, although not as consistently. The distribution of micro-debonds was nonuniform in all cases.

The mechanism responsible for the micro-debonding is not clear from this work. There are a number of possible mechanisms of interfacial failure discussed in the literature [1]. A number of studies, *e.g.* [11,12], have reported the hydration of the oxide layer to be the major cause of interfacial failure, although others [13] contend that the hydration is a post-failure phenomenon. Energy Dispersion Spectroscopy (EDX) was performed on the present failure surfaces and showed only a strong aluminum peak with very small oxygen and carbon peaks at the defect sites, while the defect-free sites showed mainly the presence of carbon, oxygen, magnesium and silicon. It is difficult to conclude from these data whether the oxide has undergone hydration.

It is noted that there is appreciable scatter in the peel data for degraded specimens as shown by the standard deviation bars for the peel trace of a single specimen, and the sample-to-sample variation at a single exposure time. The wet data (Fig. 2) showed considerably more scatter within the peel trace than did the dry data (Fig. 3), a phenomenon which can be attributed to the cohesive fracture mechanism. The dry data showed relatively greater variability for samples degraded for a long time. The micro-defect distribution also showed appreciable variability. These observations indicate that there is considerable inhomogenity in the degradation process, especially for severely degraded samples.

4.2. One-part Adhesive

The water absorption by the case adhesive specimens of the one-part system (Hysol EA 9346) showed the classical Fickian behavior; a diffusion coefficient of $2.2\times10^{-13}\,\mathrm{m}^2/\mathrm{second}$ was estimated by fitting the Fickian model to the absorption curve. The cast adhesive samples reached equilibrium in about 200 hours, and the equilibrium water content was about 5.3%.

Figure 8 shows the peel force data for the Hysol EA 9346 one-part adhesive for wet and dry cases, while Figure 9 shows the tensile test results for a freshly-cured cast adhesive specimen, and 100-day old wet and dry cast specimens.

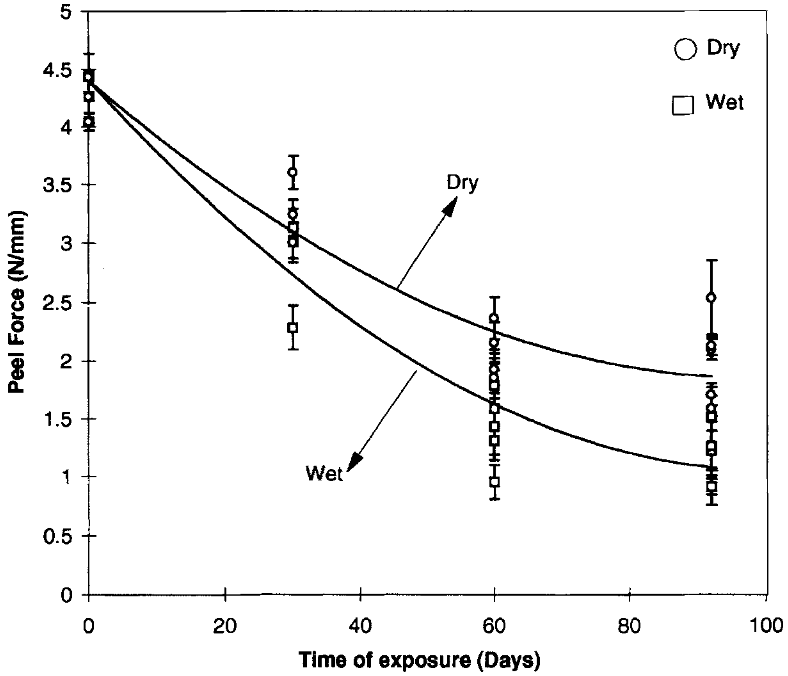


FIGURE 8 Peel force *vs.* exposure time for one-part (Hysol EA 9346) wet and dry cases. Each point represents the average peel force for a single specimen, and the bars represent one standard deviation within the peel trace. Multiple dots represent different samples tested. The curves are quadratic fits ($R^2 = 0.9509$ for dry and $R^2 = 0.9895$ for wet).

The wet and dry tests show similar behavior because the adhesive undergoes very little plasticization. This can be seen from Figure 9, where the Young's modulus of a fresh sample is about 2.3 GPa, and that for degraded samples, both wet and dry, is about 2 GPa. The crack path for both wet and dry specimens were essentially interfacial, again showing the absence of significant adhesive plasticization for the wet samples. Therefore, in this case, both wet and dry results are affected primarily by interfacial weakening. It is noteworthy that some of the interfacial strength is regained upon drying (dry strength was greater than wet strength), indicating that for this system there is some reversible degradation superimposed on a large permanent degradation.

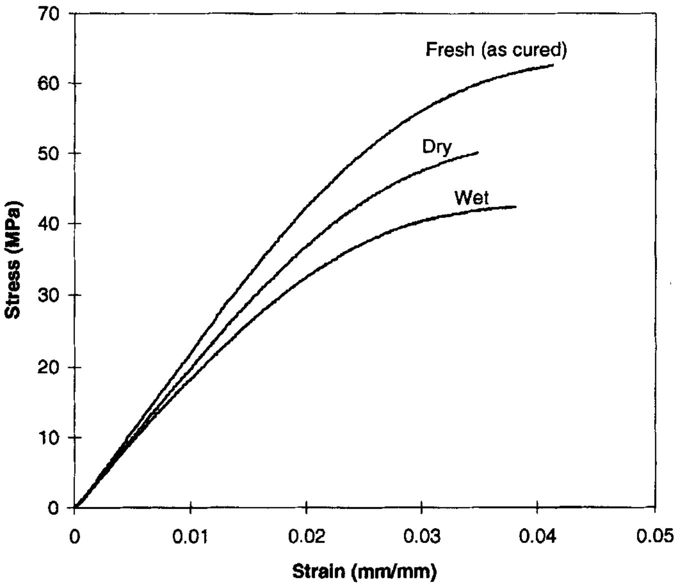


FIGURE 9 Tensile test results for cast EA 9346 adhesive tested in three conditions: i) freshly cured, ii) immersed for 100 days and then tested wet, iii) immersed for 100 days and then tested dry.

Figure 10 shows the fracture energy corresponding to the peel force data in Figure 8, calculated using the material properties given in Table I. In this case, since the cohesive properties do not vary greatly with degradation (Fig. 9), the change in the adherend plastic dissipation due to change in adhesive modulus was negligible.

Visually, the failure loci for fresh, wet and dry specimens were very close to the interfacial region with no residual adhesive visible on the flexible aluminum strip. However, the aluminum surfaces of the degraded samples appeared shiny compared with that of fresh samples, suggesting an extremely thin layer of adhesive on the fresh failure surfaces. In previous work [9] with the same adhesive and a much thicker aluminum adherend (1.25 mm), the residual adhesive layer was thicker. Therefore, it appears that the fresh specimens failed cohesively but that, due to the very thin peel adherend, the residual adhesive layer was extremely thin.

There were no significant differences visible between the surfaces of fresh and degraded (wet or dry) specimens in the SEM micrographs

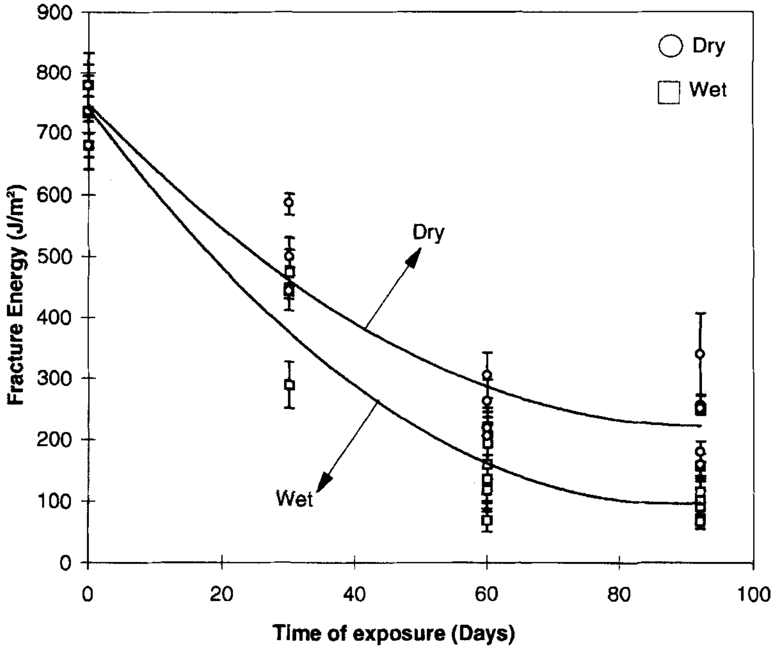
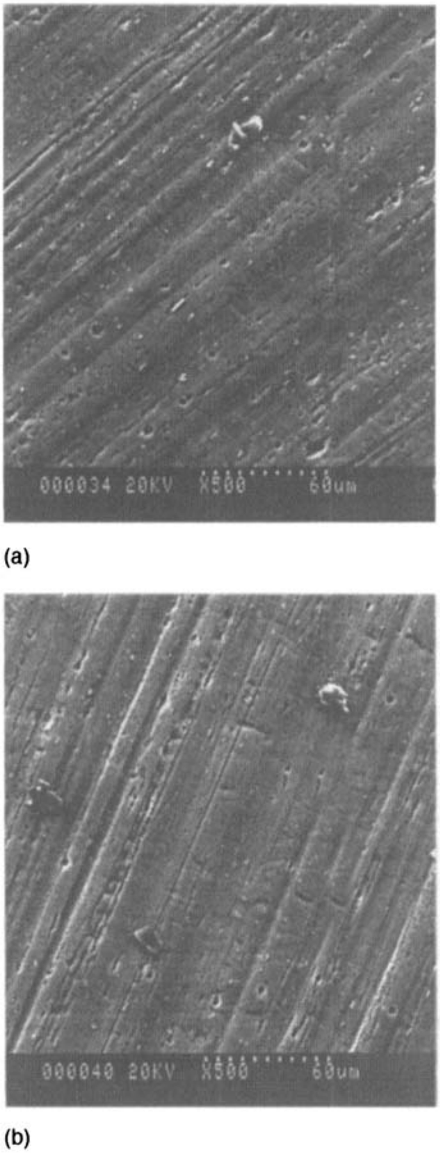


FIGURE 10 Fracture energy vs. exposure time for one-part (Hysol EA 9346) wet and dry cases. Each point represents the average peel force for a single specimen, and the bars represent one standard deviation within the peel trace. Multiple dots represents different samples tested. The curves are quadratic fit ($R^2 = 0.9705$ for dry and $R^2 = 0.9937$ for wet).

(Fig. 11). The X-ray analysis of the aluminum surface also did not show any appreciable differences between fresh and degraded fracture surfaces. The adhesive side of the failure surface was also examined using the SEM, and again no micro-structural differences were found between fresh and degraded samples. However, the X-ray analysis of the adhesive side of degraded specimens did show some traces of aluminum, although this was inconclusive due to lack of consistency. More surface-sensitive analytical techniques such as X-ray Photoelectron Spectroscopy (XPS) may be required for studying the failure surface of this system.

As with the two-part system, there was considerable scatter in the peel force data, with the degraded samples (wet and dry) showing more scatter as the exposure time increased, both within a single specimen, and from specimen to specimen.



(a)

(b)

FIGURE 11 SEM micrographs of the flexible adherend after peeling of (a) fresh and, (b) degraded (wet), EA 9346 specimens, after 2 months exposure.

5. SUMMARY AND CONCLUSIONS

The open-faced peel geometry, in conjunction with a recent model of the peel test, was used to study the degradation of two typical adhesive systems.

It has been shown that for adhesives which plasticize to a great extent, such as the two-part system (Permabond E04), peel testing should be carried out in the dry state to assess interfacial weakening since the failure is mostly cohesive in the wet condition. For moisture-resistant adhesives such as the one-part Hysol EA 9346 adhesive, both wet and dry tests revealed interfacial weakening, although some of the degradation for the wet specimens was found to be reversible upon drying.

The two-part adhesive in the dry state after degradation was found to become relatively stiff and brittle compared with the fresh state. Since the plastic dissipation in the flexible adherend is dependent on the adhesive stiffness, it is crucial to account for this change in the adhesive stiffness when calculating the fracture energy.

For the two-part adhesive system, the formation of micro-debonds was found to be a possible mechanism of interfacial degradation. For the one-part system, more work needs to be done to assess the exact failure mechanism, although visual evidence suggested total interfacial failure. More surface-sensitive analytical techniques such as X-ray Photoelectron Spectroscopy (XPS) may be required for studying the failure surface of this system, since the SEM did not reveal appreciable differences between fresh and degraded surfaces.

Large scatter in the fracture energy was observed for degraded specimens, both within a single specimen and from sample to sample. Although some of the scatter may be attributed to batch variations, it is more likely to be an indication of the inhomogeneous nature of the degradation.

Acknowledgements

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