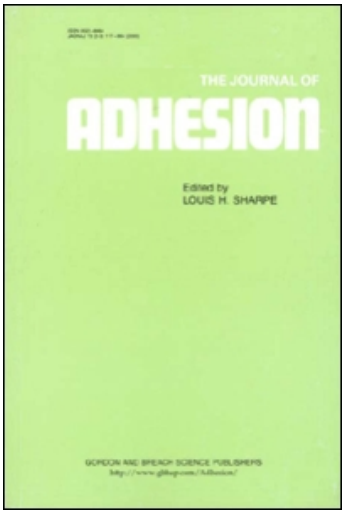

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NOTE

A Test Method for Accelerated Humidity Conditioning and Estimation of Adhesive Bond Durability†

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KEY WORDS: Durability; environmental attack; interfacial attack by moisture; coating; notched coating adhesion test; propagation of debond; strain energy release rate; accelerated characterization; accelerated humidity conditioning.

INTRODUCTION

The ability to determine the durability of adhesive bonds remains an elusive task, especially when the service environment involves exposure to diluents such as water. Moisture continues to be of major concern for many adhesive bond systems for a number of reasons including:

1) many adhesives are hydrophilic, picking up significant amounts of moisture over time;
2) most adhesives and some adherends allow moisture permeation, eventually reaching the adhesive/adherend interface;
3) the high surface energies of metallic and certain other substrates result in moisture migrating to the adherend surfaces and displacing the adhesive from the substrates, and possibly oxidizing the adherend, etc., and
4) absorbed moisture induces swelling stresses which can reduce the bond strength.

Recognition of this susceptibility to moisture has led to extensive studies aimed at evaluating the effects of moisture, developing an understanding of the responsible

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mechanisms, and predicting the performance of adhesive bonds subjected to humid environments. While some studies have focused on the effect of humidity on neat adhesive samples, most studies have recognized the significance of the adhesive/adherend interactions, and have evaluated strength of actual bonded joints. Unfortunately, the time required for typical bonded geometries to reach moisture equilibrium can be quite long. Single lap joints (SLJ) and double cantilever beam (DCB) specimens with a width of 25 mm may take several years to equilibrate, depending on the temperature and adhesive. Such lengthy conditioning times hamper the development of improved adhesives, and may delay the acceptance of these adhesives because of the time required to certify them. Methods to accelerate the conditioning of test specimens would be of significant benefit to adhesive formulators and users.

Currently, one common method for accelerated testing of adhesive strength is by conditioning DCB or SLJ specimens at high temperature and high humidity levels.[1-3] The high temperature can increase the diffusivity, thus decreasing the time required to saturate the specimens. Use of increased temperature to accelerate humidity conditioning, however, raises concerns about whether the elevated temperatures are introducing anomalous damage modes. Placing specimens in boiling water is a routine practice to screen specimens, and yet extrapolating results from this accelerated conditioning process to durability in service is questionable. Furthermore, the conditioning time under these elevated temperature conditions may still be rather long considering that the moisture has to diffuse through the edges. Another popular accelerated testing method is the wedge test. After the wedge is driven into a bonded specimen, the loaded specimen is placed into a water bath or environmental chamber. Over time, the debond may propagate, alleviating the strain energy imposed by the wedge. Although the moisture state is not well understood ahead of a propagating debond, the adhesive does become saturated ahead of a slow growing or equilibrated debond. Results are frequently given as debond length as a function of exposure time, although the critical strain energy release rate can be calculated from this testing method.[4]

This paper proposes an alternate test geometry for accelerating humidity conditioning of adhesive/substrate systems. The approach is based on the observation that, for most structural adhesives, the interfacial regions are most susceptible to environmental attack by water.[1] It is widely reported that failures resulting from long-term exposure to humid conditions tend to be interfacial. A further assumption is made that the presence of moisture at the interface leads to a rather rapid degradation in interfacial strength. Thus, if the time required for the interfacial region to saturate with moisture is reduced, the time required to measure the degraded strength can also be reduced. While there may be some adhesive/substrate systems which are not appropriately modeled by these assumptions, the approach is believed to be appropriate as a preliminary screening tool for many systems of practical interest. The acceleration in conditioning is achieved by testing the adhesive as a coating bonded to a single substrate rather than as an adhesive bonding two substrates together.

A number of specimens have been proposed and utilized for testing coating adhesion, often including the effects of environmental conditioning. These include the scratch indentation test,[5] the pull-off test,[6] and the cross-hatch type test. In the scratch test, coatings may be environmentally conditioned, and then scraped with a scratch probe, recording the load required to scrape the coating from the substrate. Although useful

for testing coatings, the results are difficult to interpret quantitatively. Several pull-off tests have been proposed for bonding a stud to a coating, and then pulling in tension to determine the load required to debond the coating. The cross-hatch tape test, ASTM D 3359,[7] involves using a knife to cross-hatch a coating. A pressure sensitive adhesive tape is then applied to the cross-hatched region and peeled away from the substrate. Coating adhesion is qualitatively determined from the number of coating fragments which remain on the substrate. Use of this method after humidity conditioning is widespread, but inconsistencies result from a failure to account for changing adherence between the pressure sensitive tape and the exposed coating surface.

USE OF COATINGS TO ACCELERATE CONDITIONING

An ASTM D 3433 standard DCB specimen[8] consists of an adhesive sandwiched by two substrates and only the edges of the adhesive are exposed. If a 25.4 mm wide DCB specimen is environmentally conditioned, water can diffuse into the adhesive only through the edges (assuming that the adherends are not permeable). Thus, the diffusion path is half the specimen's width or 12.7 mm. For a SLJ (ASTM D 1002) with bonded dimensions of 12.7 x 25.4 mm, the closest edges are 12.7 mm apart, resulting in a diffusion path of 6.35 mm. Assuming the adhesive is an epoxy which obeys Fickian behavior, the diffusion coefficient is about 2.5×10^{-9} cm^2/sec at 20 °C.[1] For the conditions outlined above, an epoxy bonded DCB or SLJ would require about 7,000 days or 1,800 days, respectively, to reach 90% of the saturation value at the center of the specimen.

To reduce the conditioning time, one can either increase the diffusion coefficient or decrease the diffusion path. A common method to increase diffusion coefficient is by increasing the conditioning temperature. For epoxy, increasing the conditioning temperature from 20 °C to 60 °C can increase the diffusion coefficient by up to 9 times.[1] The center of a 25.4 mm wide DCB at 60 °C would then reach 90% of saturation in about 700 days. If the specimen is conditioned in a 90 °C environment, the diffusion coefficient becomes 60×10^{-9} cm^2/sec and the exposure time for the DCB specimen is reduced to 300 days. Although this is a substantial acceleration, the possibility of introducing spurious degradation modes exists.

One can drastically decrease the conditioning time by decreasing the diffusion path since duration of uptake experiments increases with the square of the diffusion distance. An adhesive coated to a single substrate offers the advantage of a short diffusion path since the diffusion path is the thickness of the adhesive coating. Assuming the coating is 0.1 mm, and using the same epoxy described above, only 11 hours is required to condition the specimen to 90% of saturation at 20 °C. Once the coating specimen is equilibrated, it can be tested using any appropriate coating test method. A particularly appropriate test geometry is proposed below to take advantage of the short diffusion path in order to accelerate humidity conditioning and estimate the bond durability.

NOTCHED COATING ADHESION TEST

The proposed notched coating adhesion (NCA) specimen consists of a thin layer of adhesive bonded to a single substrate as illustrated in Figure 1. A cut is introduced into

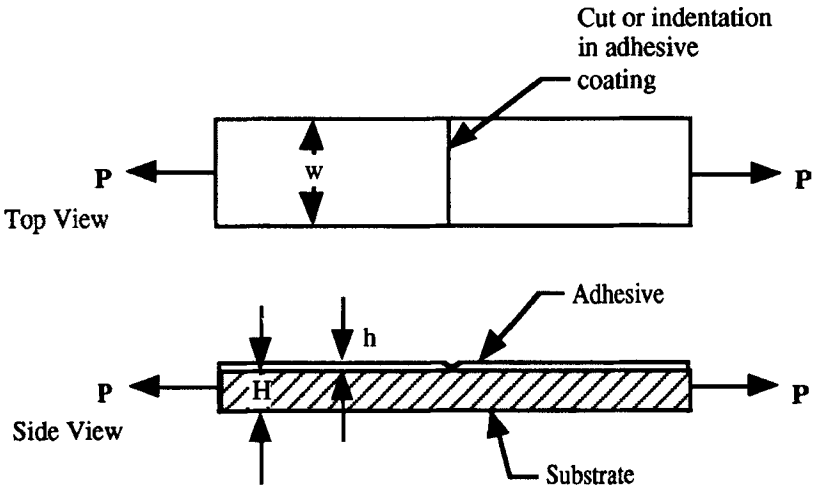

FIGURE 1 Notched coating adhesion specimen.

the adhesive layer near the center of the specimen by using a razor blade as an indenter. Frequently, the stresses imposed by the blade cause the adhesive to debond locally near the cut,[9] thus producing sharp-tipped cracks propagating along the interface. The length of the local debond (a) is typically five times that of the thickness of the coating, and a third of the width. Reference 10 contains more analysis on the importance of local debond and debond length effects. Using an axial loading device, the specimen is loaded in tension perpendicular to the cut. The stress state generated causes the debonds to propagate. Being a constant strain energy release rate specimen, the debond propagation does not alleviate the applied strain energy, and the resulting debonding is quite rapid and easily observed. The strain at which the debond starts to propagate is recorded. A wide latitude in specimen dimensions is possible.

Assuming uniform stresses and modulus through the thickness of the film, the strain energy release rate for the film can be expressed as:

$$G = \frac{h\sigma^2}{2\hat{E}} \tag{1}$$

where σ is applied stress;
h is adhesive thickness, and
$\hat{E}$ is the effective modulus.

$$\hat{E} = \begin{cases} E & \text{for plane stress} \\ \dfrac{E}{(1-\upsilon^2)} & \text{for plane strain} \end{cases}$$

υ is Poisson's ratio, and
E is modulus of the adhesive

The above relationship assumes that the debond is propagating in a self-similar manner with a straight debond front. This requires that the initial debond be several

times longer than the coating thickness in order to have self-similar propagation. If the debond length is long compared with the width, the plane stress modulus should be used. For shorter cracks, the behavior can approach the plane strain condition. Under other conditions, neither solution is expected to be exactly valid, but they would narrowly bracket the actual solution. For NCA test analysis, equation (1) must be modified to account for the residual stress due to curing, the stress caused by the swelling of the adhesive due to moisture ingression, and the modulus of the saturated adhesive. The mixed mode (Mode I and II) strain energy release rate for the NCA may be determined as:

$$G = \frac{h}{E}\left\{[(\sigma_t + \sigma_m)^2 + (\sigma_t + \sigma_m)\varepsilon E](1 - \nu) + \frac{1}{2}(\varepsilon E)^2\right\} \tag{2}$$

Where σ_t is residual biaxial stress due to curing;
σ_m is residual biaxial stress due to moisture swelling, and
ε is applied uniaxial tensile strain.

Equation (2) takes into account the overall strain of the specimen; therefore, as long as the strain is not large enough to cause necking, the plastic deformation of the adherend should not have any significant effect. If, however, the adhesive deforms plastically or viscoelastically, equation (2) is no longer valid.

The strain energy release rate that causes the debond to propagate is referred to as the "critical strain energy release rate". The NCA specimen can be modeled as a layered bi-material where the adhesive is a very thin layer on top of a thick substrate. To determine the contribution from each mode in the strain energy release rate obtained, Hutchinson and Suo's[12] layered bi-material analysis is applied. Since the adhesive is much thinner than the substrate, the substrate can be considered to have infinite thickness. Therefore, mode mixity is a function of the angle ω^2:

$$\frac{G_{II}}{G_I} = \tan(\omega)^2 \tag{3}$$

ω is a function of Dundurs' parameters α and β[12]; that is, the mode mixity is a function of the material mismatch parameters, An inherent advantage to this type of mixed mode fracture test is that for typical film coating/substrate combinations, the preferred failure direction is directed towards the interphase, just the opposite of many tests, including the peel test. This means that there is an incentive for the adhesive to fail near the interface. About 50 specimens have been tested to date, and all adhesive bond failures appeared (visually) to be interfacial.

The NCA test geometry is a modification of the cracked lap shear specimen. Papers on similar tests have been published in the past. Several researchers[13–16] used analogous geometries to study residual stress and critical thickness for spontaneous debond of coatings. Hu and Evans[17] conducted four-point flexure tests on a similar geometry to study cracking and decohesion of thin films. Compared with these tests, the NCA testing methodology differs in that a small debond is introduced into the specimen before loading, and that the adhesive thickness is kept well under the critical thickness. By inducing an interfacial debond during the coating indentation process, a defect with a well-known and repeatable singularity is produced. Furthermore, the

NCA test is designed to determine the critical strain energy release rate of the adhesive system.

PRELIMINARY EXPERIMENTS

Several preliminary experiments conditioned in different environments were conducted on steel/epoxy specimens. The substrate was a 1.5 mm thick cold rolled 1018 steel. A model rubber-toughened epoxy adhesive was cast on the steel panel to a thickness of 0.1 mm. After the panel was cured at 155 °C for 90 minutes, 100 × 12.5 mm specimens were cut from the panel. These specimens were conditioned at different relative humidity levels at 60 °C until moisture saturation. According to water uptake data on the bulk adhesive, 90% moisture saturation at the interface of the NCA was achieved in three hours, although the specimens were typically conditioned for 24 hours prior to testing.

In order to estimate thermal residual stress of the NCA specimen, both the curing temperature and the coefficient of thermal expansion (CTE), α, of the substrate and the adhesive must be known. The CTE of the epoxy was determined to be $78 \times 10^{-6}/°C$ by thermal mechanical analysis, and the CTE of steel was taken from standard tables. To determine the modulus and the swelling of the adhesive due to moisture ingression, 0.5 mm thick bulk adhesive dogbone specimens were conditioned by hanging in conditioned air in an environmental chamber. Before conditioning the dogbone specimens, a razor blade was used to mark two points on the specimens. Using an optical microscope, the distance between these two points was measured to approximately 20 mm. Because of the moisture-induced swelling of the specimen, this distance was measured to be larger after the moisture uptake reached equilibrium. The swelling data for the model epoxy can be expressed by the linear equation:

$$(\%\ \text{Linear swelling}) = 0.0009 \times (\%\ \text{Relative humidity}) \tag{4}$$

The dogbone specimens were then tested under tension to determine modulus as a function of moisture content. The modulus data are shown in Figure 2.

A cut and a local debond were introduced into equilibrated coating specimens by tapping a sharp razor blade into the adhesive coating. The specimen was then loaded in tension at a cross head speed of 1 mm/min until the debond started to propagate. Since the debond of the adhesive did not alleviate the applied strain energy, once initiated, debonding was catastrophic. An extensometer attached to the specimens measured the critical strain at which the debonds started to propagate. Note that for a single cut, there are two debonds which can propagate. Additional cuts could be made on the coating of each specimen, although watching multiple debond sites may pose problems.

Figure 3 shows a comparison of the mode I portion of the critical strain energy release rate for the NCA and DCB specimens as a function of the relative humidity of the conditioning environment. Since it is difficult to compare critical energy release rates with different mode mixes, we have chosen to compare only the mode I portions of the energy release rate at debonding. The NCA specimens were conditioned for 3 days, and the DCB specimens for approximately one year. The favorable comparison of results with a significant acceleration is encouraging.

More experiments were conducted with another adhesive system to verify the proposed testing method. Titanium substrates having dimensions of 100 × 25.4 ×

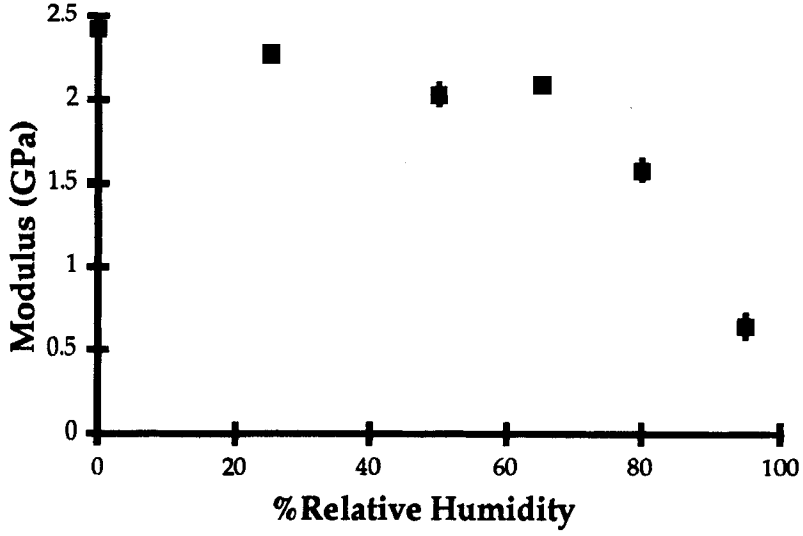

FIGURE 2 Modulus of the model epoxy adhesive as a function of percent relative humidity.

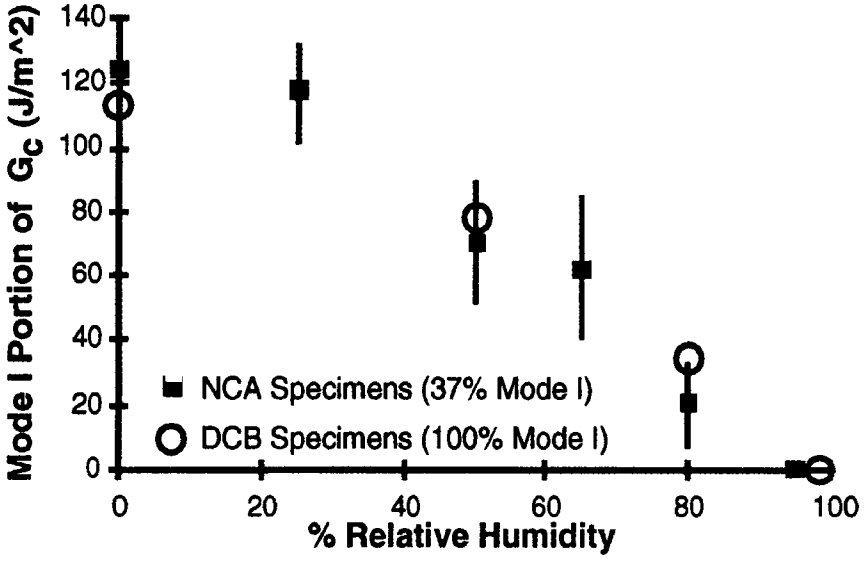

FIGURE 3 A comparison of the mode I portion of the critical strain energy release rates for the NCA and DCB as a function of relative humidity used for conditioning.

1.78 mm were coated with a 0.16 mm film of glass scrim cloth supported LaRC PETI-5 adhesive. To fabricate the NCA specimen, an adhesive film with same dimensions as the titanium was placed between the substrate and a sheet of Teflon. The system was cured in a hot press at a constant pressure of 516 KPa. After the temperature was ramped at

5.5 °C/min to 350 °C, it was held constant for 1 hour, and then lowered back to room temperature at 15 °C/min. After cure was completed, the Teflon sheet was removed. Without taking into account the effect of residual stress, the average critical strain energy release rate obtained from NCA tests was 1,150 J/m^2. DCB tests were conducted for comparison purposes. The average critical strain energy release rate values obtained from DCB tests was 1,950 J/m^2. The adhesive peeled off at the interphase in the NCA tests, and the crack propagated cohesively in the DCB tests. This failure mode difference and the difference in mode mixity might explain the difference in the critical strain energy release rate values.

ALTERNATIVE TESTING METHODS FOR COATINGS

The proposed NCA specimen is one method to obtain quantitative adhesion measurements for coatings. Other methods are possible, including loading NCA specimens in bending rather than tension. At a critical radius of curvature, the stress becomes high enough to cause the adhesive to debond; the resulting strain energy release rate is

$$G = \frac{h}{E}\left\{\left[(\sigma_t + \sigma_m)^2 + (\sigma_t + \sigma_m)\frac{y}{\rho}E\right](1 - \nu) + \frac{1}{2}\left(\frac{y}{\rho}E\right)^2\right\} \tag{5}$$

where y is the distance of the interface from the neutral axis, and
ρ is the critical radius of curvature.

Another quantitative method attempted for testing conditioned coatings was "modified" DCB test. A thin Kapton® or a Teflon® sheet was placed at one end of a substrate to facilitate introducing a pre-crack, and then the adhesive was applied as a coating. After cure was completed, the specimens were environmentally conditioned until saturation levels were achieved, and a second substrate was then bonded to the conditioned coating. By using a room temperature curing adhesive, and testing as soon as bonding occurred, the moisture content at the saturated coating/substrate interface was believed to be unchanged. There are, however, some limitations to this technique. For this test to be successful, the adhesion at the conditioned interphase must be weaker than other bonds in the sandwich. Another possible limitation in this test method is that there is no guarantee that the crack will propagate along the interphase.

DISCUSSION

Additional analytical work is needed to assess the feasibility and limitations of the NCA testing methodology. Preliminary analysis and experiments suggest that the technique should work for ductile substrates of any modulus, coated with adhesives which are relatively stiff. Soft adhesives could be reinforced with a (water permeable) scrim cloth to generate sufficient interfacial stresses for debonding. Increasing the coating thickness can also increase the interfacial stresses. Future work will also aim at finding methods to determine the appropriate or optimal moduli and thickness relationships for the test. Several researchers have reported a critical thickness above

which the coating debonds spontaneously.[11,18,19] This critical thickness will be a consideration in the future to determine the adhesive thickness for NCA tests.

Experimentally, the manual cutting process to start the debond is subject to various factors such as the applied indentation pressure. Reliable methods that generate virtually identical cuts and debonds every time need to be developed. To understand the specimen better, the rate of loading and plastic and viscoelastic effects will be studied. Specimens with different surface treatment will be tested to evaluate the feasibility of using the NCA test as a method to determine surface treatment effects.

The NCA works well with stiff adhesives and coatings. NCA may be a simple method to determine critical strain energy release rate along the interface of the adhesive system. Some possible applications for NCA include studying moisture ingression, redrying and surface treatment effects. Currently, NCA may be used as screening test to obtain, quickly and inexpensively, comparative results on the durability of adhesive systems.

SUMMARY AND CONCLUSIONS

A methodology is presented for estimating adhesive performance and durability through the use of special specimens which greatly accelerate humidity conditioning. Conventional specimens consisting of two substrates bonded with an adhesive require lengthy exposure times in order to allow humidity to penetrate throughout the bond. Coating specimens are proposed in which the adhesive is applied as a coating to a substrate of interest. The shortened diffusion path greatly reduces the time required to saturate the bond and interface region. Assuming that bond degradation is diffusion limited, this accelerated conditioning may provide meaningful estimates of bond strength.

In order to measure directly the critical strain energy release rate, a special test method, the notched coating adhesion geometry is proposed. The coating is notched, severing the coating and initiating debonds near the interface. The specimen is then loaded in tension, recording the strain at which debonding occurs. The test geometry results in interfacial debonds, and the critical strain energy release rate can be calculated by knowing the residual stress state. Initial results have been very encouraging, and compare favorably with critical strain energy release rates measured from DCB specimens.

Further studies are needed to establish the viability of the proposed accelerated conditioning process and test method.[10] Although not intended to replace conventional adhesion tests, the method is believed to have significant potential as a screening test for durability tests on adhesives.

Acknowledgements

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