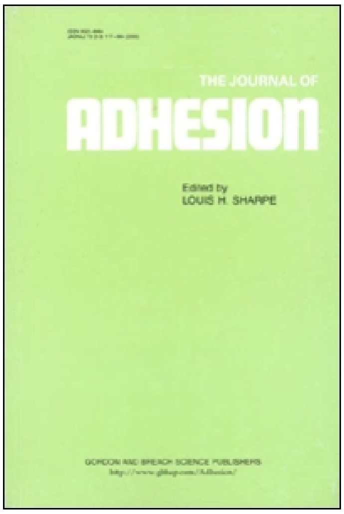

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Subcritical Delamination in Epoxy Bonds to Silicon and Glass Adherends: Effect of Temperature and Preconditioning

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The effects of temperature and preconditioning in deionized (DI) water and a cyan ink vehicle used in inkjet printer cartridges on the durability of glass/epoxy and silicon/epoxy systems have been investigated. A test matrix consisting of test temperatures, preconditioning temperatures, preconditioning times, and nature of adherends and adhesives was developed and a series of experiments was conducted using wedge test specimens (glass or silicon coupons bonded with epoxy) to investigate the subcritical adhesion performance of the glass/epoxy and silicon/epoxy interfaces. The glass/epoxy and silicon/epoxy interfaces were found to be relatively insensitive to temperature over a range of 22–60°, but significant temperature effects, more complex than suggested by time-temperature superposition (TTSP), were observed above 60°C, depending on the environmental chemistry and nature of the adhesive used.

Specimens made of silicon coupons bonded with epoxy were subjected to preconditioning in DI water and the cyan ink vehicle prior to wedge insertion to study the effect of prior environmental exposure. The wedge test data from preconditioned specimens were compared with standard wedge test results and the Si/epoxy interface was found to be insensitive to preconditioning in DI water but was affected significantly by preconditioning in the cyan ink vehicle. Plots of crack velocity versus *applied strain energy release rate for particular sets of environmental conditions are presented and a comparison is made for different environmental conditions to quantify the subcritical debonding behavior of systems studied.*

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INTRODUCTION

Epoxies are used in microelectronic components as encapsulants and underfill materials to increase their durability by acting as both a structural reinforcement and as a sealant, providing a physical barrier to moisture and other fluids. A number of interfaces involving epoxies can be found in a typical ink jet printer, such as the epoxy/passivation layer, epoxy/silicon dioxide, epoxy/metal, epoxy/printed circuit board (PCB), and epoxy/solder interfaces. These adhesive interfaces lie in contact with aggressive inks at elevated temperatures for a long period of time. Over time, environmental factors such as temperature and the presence of liquid can lead to failure at substrate/epoxy interfaces. Since interfacial bond integrity is a major concern for performance and reliability of modern electronic devices, such as inkjet printers, the need to evaluate the fracture resistance and long term durability of various interfaces is very important.

In general, the primary component of printer ink is water but the ink may also contain other agents such as salts, dyes, and surfactants. Water is typically regarded as the primary agent in the degradation process of adhesive bonds [1–3]. Water is absorbed into polymeric adhesives, accumulates at the interface, and displaces the polymer from the adherend surface [4,5]. Water-assisted subcritical crack growth has been measured along glass/epoxy interfaces by Ritter *et al.* [6], Conley *et al.* [7], Lane [8,9], Hohlfelder [10], and Dauskardt *et al.* [11]. Although subcritical debond mechanisms at interfaces are not clearly understood, there seems to be a possible interaction between strained atomic bonds and environmental species [12–15]. Subcritical debonding may be driven by residual stresses, thermomechanical cycling, and the presence of moisture. Residual stresses arise due to thermal expansion mismatch and polymer curing strains. The thermal cycles during device operation may produce significant mechanical stress cycling. Moisture may be present in the materials themselves during manufacturing or processing operations. Moisture ingression into the adhesive or along the interface often lowers the energy required for debond extension and may be dependent upon the level and nature of stress concentrations in the adhesive layer [16].

The kinetics of debond growth depend on the activity of the environmental species at the crack tip, which, in turn, depends on the operating temperature. Time temperature superposition (TTSP) is a useful technique applied to predict the temperature dependence of the rheological behavior of a polymer. This method presumes that a temperature change is related to a shift in log time, so that the data taken at higher temperatures on a rapid time scale can be used to determine data at lower temperatures on a much slower time scale. The underlying bases for time/temperature superpositioning are (1) that the processes involved in molecular relaxation or rearrangements in viscoelastic materials occur at accelerated rates at higher temperatures and (2) that there is a direct equivalency between time and temperature. Hence, the time over which these processes occur can be reduced by conducting the measurement at elevated temperatures and transposing (shifting) the resultant data to lower temperatures. The result of this shifting is a "master curve" where the material property of interest at a specific temperature can be predicted over a broad time scale. Theoretical principles of TTSP have been extensively developed and can be found elsewhere [17]. While this principle has been successfully used for most polymeric materials, a strong deviation has been observed by several researcher [18–20] owing to the presence of more than one relaxation mechanism with distinct by different temperature dependencies. A similar deviation observed for the substrate/epoxy interfaces studied herein will be demonstrated when the effect of temperature on the subcritical debonding behavior is discussed.

The primary objective of this study was to characterize subcritical debonding of silicon/epoxy and glass/epoxy interfaces utilizing a wedge test geometry in conditions mimicking service conditions of microfluidic electronic devices for inkjet printers. The wedge test [21] is a commonly utilized method to evaluate the durability of precracked and stressed adhesive joints that are often exposed to chemical environments. This fracture test is an ASTM Standard (ASTM-D3762) and utilizes a Mode I specimen configuration [22]. By driving a wedge between the ends of two bonded beam adherends, an initial crack is introduced. When such a specimen is placed in an environment, the crack tip is exposed directly to the test environment while subjected to an applied opening stress. A schematic illustration of the resulting crack growth rate *versus* crack driving energy ($da/dt - \mathcal{G}$), such as used by Gurumurthy *et al.* [23], is shown in Figure 1. There is a threshold value of G ($G_{\text{threshold}}$) below which subcritical crack growth does not occur. When $\mathcal{G}$ is above $G_{\text{threshold}}$, the relationship between da/dt and $\mathcal{G}$ typically results in a sigmoidal shape which incorporates the familiar velocity regions: Region I, stress-dependent, chemically-assisted crack propagation; Region II, transport-controlled debonding; and Region III, critical fracture events. For classic fracture of bulk glasses, processes in Region III are independent of the

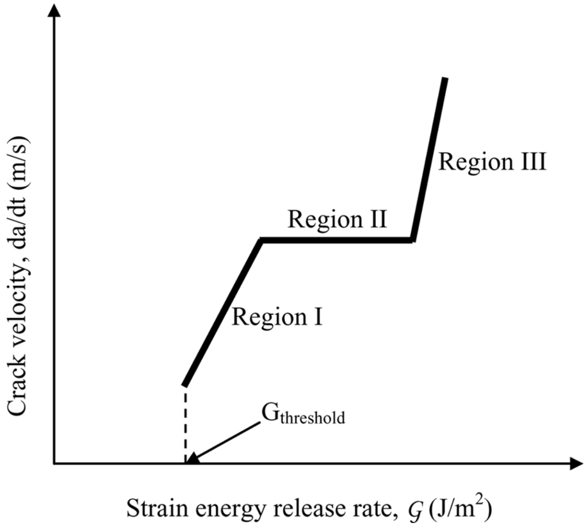

FIGURE 1 Schematic illustration of a typical *da/dt versus* $\mathcal{G}$ curve illustrating three regions of crack growth for subcritical crack growth.

environment since there is limited time for molecular interactions. Changes in slope indicate changes in the rate limiting step for crack advance [10,24–25]. Since the energy release rates provided to the crack tip in the current tests are well below the critical value, Region III was not included in the measurements.

EXPERIMENTAL PROCEDURE

Materials

Borosilicate glass (100 × 10 × 2 mm) and silicon (77 × 6 × 0.98 mm) substrates were bonded using Loctite® L4 (Henkel Corporation, Irvine, CA, USA) and a model epoxy to make wedge test specimens. The borosilicate glass strips and the silicon wafers were provided by Hewlett-Packard Compnay (Corvallis, OR, USA). L4 is a commercial, filled (21% by weight) epoxy adhesive manufactured by Loctite and obtained from Hewlett-Packard Company. The L4 epoxy is cured at 140°C for 30 minutes. The glass transition temperature is 110°C. The Young's modulus is approximately 4 GPa. Details of the material properties can be found elsewhere [26]. The model epoxy adhesive consists of bis-phenol-F diglycidyl ether (EPON™ 862), 10 parts per hundred resin™ 1, 4-butanediol, and 3 phr 4-methyl-2-phenylimidazole as a curing agent. The EPON™ 862 resin (Hexion Specialty Chemicals Inc., Houston, TX, USA) has an epoxide equivalent weight of 171 g/mole. To prepare the model epoxy, a relatively low viscosity clear liquid was obtained by stirring EPON 862 and 1, 4-butanediol together at about 80°C for several minutes. Subsequently, 4-methyl-2-phenylimidazole catalyst was dissolved in this mixture with stirring for about 15 minutes to obtain a homogenous mixture. This homogeneous epoxy mixture was used for casting the epoxy films. The bulk epoxy mixture cast on silicon or glass substrates was cured at 150°C for 30 minutes. A differential scanning calorimetry (DSC) study showed that the fully cured model epoxy had a glass transition temperature of 110°C [27]. More details on the properties of the model epoxy can be found elsewhere [28].

Fluid Environments

Deionized water (DI) water and the cyan ink vehicle were used as the environmental fluids for this study. The ink vehicle, supplied by Hewlett-Packard Company, does not contain dye molecules and is, therefore, optically clear. A clear fluid is especially advantageous for adhesive testing on glass specimens because the crack length measurements can be performed on immersed test specimens with the help of an x-y stage and optical microscope, eliminating the need for removing the specimen from the liquid. In addition to water, the ink vehicle contains, aggressive components such as surfactants, salts, alcohols, and other proprietary chemicals.

Sample Preparation

Silicon and glass substrates were first cleaned in a gaseous argon plasma for 10 minutes and were then treated for 30 minutes in a 0.1 M 3-aminopropyltriethoxysilane (3-APS) solution (containing 5% v/v 0.1 M HCl aqueous solution). Nonsilicone polytetrafluoroethylene (PTFE) release agent (McMaster-Carr Supply Company, Los Angeles, CA, USA) was then carefully sprayed on the silicon and glass substrates 25 mm from the end of the silicon or glass beam where the wedge was to be inserted. During spraying the rest of the silicon or glass beam was covered by a plastic sheet. Where the mold release was sprayed on a specific surface, the epoxy adhered loosely to the substrate and provided a site for initial debonds to initiate. Two surface treated silicon or glass strips were then bonded together with the epoxy polymer. The bonded specimens had a bond area of approximately 76 × 5 mm and 53 × 3 mm for the glass and silicon specimens, respectively, and a bond line thickness of 0.25 mm. The bond area was outlined on the substrates by using a 0.25 mm thick window-shaped Teflon® gasket placed between the two shim holders on the bottom part of the aluminum fixture (supplied by Hewlett Packard), as shown in Figure 2. The surface prepared glass or silicon adherend was then placed in a aluminum fixture, and epoxy was then dispensed on the bottom strip using an Automove 402 ASYM402–90036 Asymtek

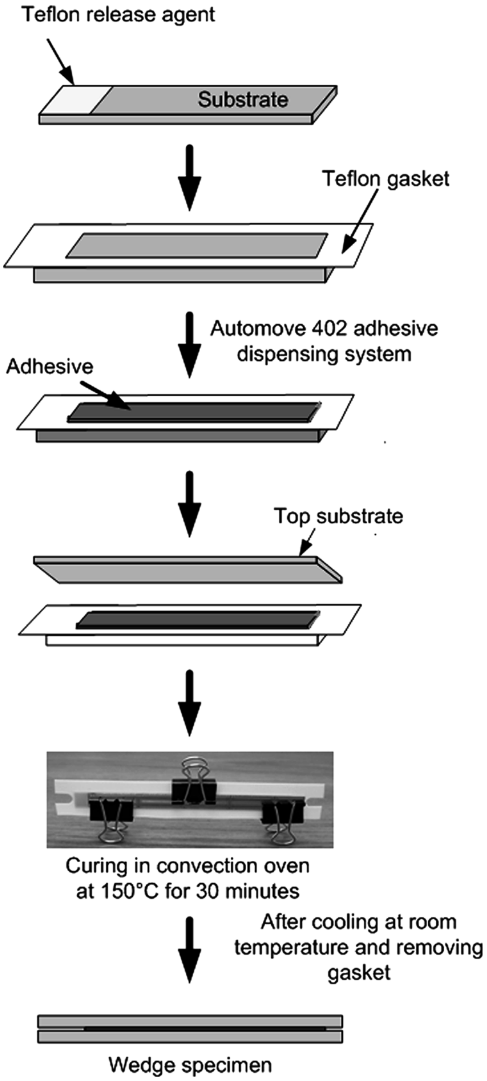

FIGURE 2 Schematic illustration of the sample preparation procedure.

dispensing system, (Asymtek Incorporated, Carlsbad, CA, USA). The microprocessor controlled adhesive dispensing system can be programmed to dispense a controlled amount of epoxy on the substrate. The fixture, when closed, ensured the proper alignment of strips on top of each other with the Teflon shim and adhesive mixture in the middle. Small binder clips were used to hold the beams, sandwiched geometry together. The Teflon shim along with restraining force provided by the binder clips (which held the entire bond assembly together) restricts the movement and dimension of the adhesive within the bonded area during curing. The substrate/epoxy sandwiches were cured in a convection oven at 150°C for 30 minutes. The Teflon gasket in each specimen was removed after the specimens cooled to room temperature.

Specimen Preconditioning

Preconditioning refers to soaking the wedge specimens in a specified environment at a desired temperature for a fixed amount of time before inserting the wedge. The goal of preconditioning was to study the effect of exposure time in DI water and the cyan ink vehicle on the durability of the silicon/L4 adhesive joint. The specimens were preconditioned for 20, 45, and 70 days at 80°C in DI water or for 30 days at 60°C in the cyan ink vehicle. After the desired preconditioning time was reached, the specimens were removed from the liquids and dried with a paper towel. A comparison between preconditioned and non-preconditioned samples provided insights into the subcritical debonding behavior of the substrate/epoxy interface.

Subcritical Debond Measurement

A crack was initiated in each specimen (while being held in air at room temperature) by first inserting a 0.5 mm thick plastic shim between the two adherends at the Teflon release spray end of the specimen. Following this, a 0.78-mm thick stainless steel wedge was inserted. The plastic shim creates an opening between two adherends at one end sufficient to insert the metallic wedge, reducing the likelihood of adherend damage. The plastic shim was then slowly removed as soon as the stainless steel wedge was placed in position between the beams. Wedge specimens were then placed in a custom fixture capable of holding five specimens. For transparent glass specimens, an optical stereomicroscope with a magnification range from 9× to 40× was used to measure the debond length. For silicon specimens, an ultrasonic HS1000 HiSPEED scanning acoustic microscope (SAM) (Sonix Incorporated, Springfield, VA, USA) equipped with a 75 MHz transducer was used to image the debond tip through the opaque silicon. Prior to crack length measurement for both glass and silicon specimens, samples were taken out of the conditioning liquid and cooled to the room temperature.

Initial crack lengths for the wedge specimen were recorded and subsequent crack length measurements were taken as a function of time. The crack length data were then used to determine the rate of crack propagation (da/dt) and the average value of strain energy release rate (G_{av}). Calculations of $\mathcal{G}$ values were obtained using the method of Cognard [29]:

$$\mathcal{G} = \frac{3\Delta^2 E h^3}{16a^4}, \tag{1}$$

where Δ is the wedge thickness, E is the Young's modulus of the adherends, h is the thickness of the adherends, and a is the crack length, as shown in Figure 3. The wedges were inserted in the specimens and crack lengths were then measured in the acoustic or optical microscope. Debond growth rates, da/dt, and strain energy release rate, G_{av} (both averaged over the increment in time between readings), were determined numerically using:

$$\frac{da}{dt} = \frac{a_{i+\Delta t} - a_i}{\Delta t} \tag{2}$$

$$G_{va} = \frac{G_{a_i} + G_{a_{i+\Delta}}}{2}, \tag{3}$$

where a_i is the crack length at time t and Δt is the time duration between crack length measurements. The effects of test temperature and preconditioning are presented in terms of growth rate, da/dt, as a function of strain energy release rate, G_{av}. In the following figures, thick arrows pointing left indicate the samples that debonded completely during testing and thin arrows pointing downwards indicate

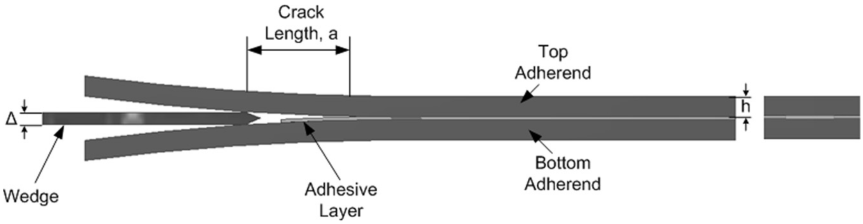

FIGURE 3 Schematic illustration of a wedge specimen.

that the crack ceased to propagate within the measurement resolution capabilities of the microscopes used for measuring crack growth.

RESULTS AND DISCUSSION

Effect of Test Temperature

Plots of *da/dt versus* G_{av} are shown in Figures 4–7 for wedge samples tested at room temperature (RT), 40, 60, and 70°C in the cyan ink vehicle. Since no crack growth was observed at RT and 40°C, either because the crack stopped or grew very slowly, sufficient data could not be collected at these temperatures and, hence, these results are not shown in the figures. Wedge test data obtained from glass/L4 and silicon/L4 in the cyan ink vehicle (Figures 4 and 5, respectively) showed crack growth at 60°C and higher temperatures, with a crack growth rate significantly higher at 70°C than at 60°C. Samples tested at 70°C debonded completely (marked by thick arrow pointing left), whereas the crack had apparently arrested ($da/dt < 10^{-11}$ m/s) for the 60°C exposure. No apparent value of $G_{\text{threshold}}$ was observed at 70°C, whereas data at 60°C suggest an apparent $G_{\text{threshold}}$ in the range of 20–40 J/m^2. Similar effects of test temperature were also observed for glass/model epoxy and silicon/model epoxy interfaces in the cyan ink vehicle, as shown in Figures 6 and 7.

Since an increase in temperature from 60 to 70°C in both the L4 and model epoxy bouded substrates increased the crack propagation rate, additional tests were also conducted on the silicon/L4 system in DI

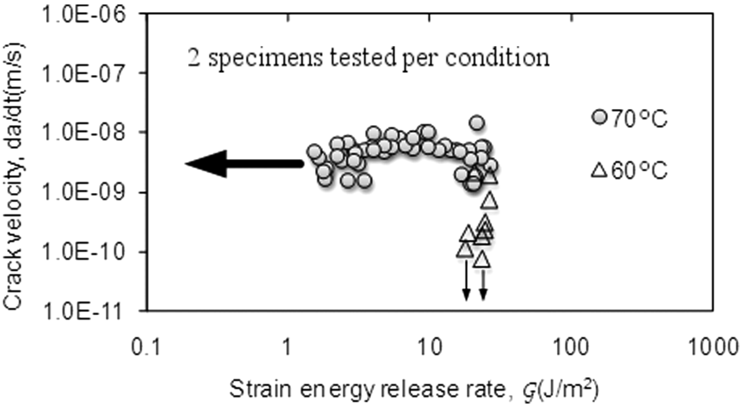

FIGURE 4 Effect of test temperature on debond kinetics for the glass/L4 interface in the cyan ink vehicle.

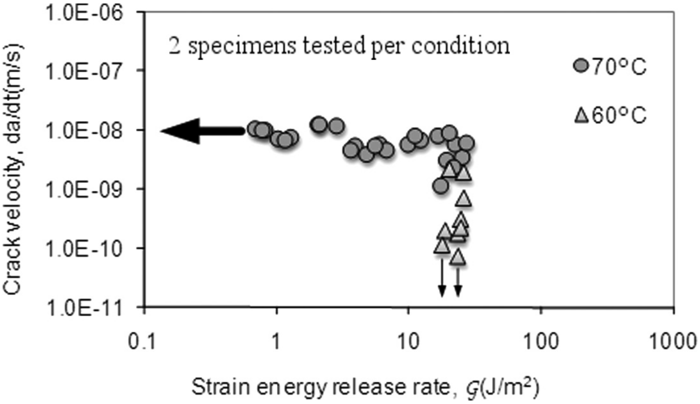

FIGURE 5 Effect of test temperature on debond kinetics for the silicon/L4 interface in the cyan ink vehicle.

water at 60, 70, 80, and 90°C. The purpose of conducting additional tests at higher temperatures was to collect data at higher temperatures that can be used to generate isotherms so that a model can be created according to the time temperature superposition principle (TTSP). The results are shown in Figure 8. Although there is an increase in the crack propagation rate and a decrease in the threshold value of strain energy release rate (from 10 J/m^2 at 60°C to 1 J/m^2 at 90°C), there is no significant difference from 60 to 70°C or from 80 to 90°C. This indicates that the temperature and crack propagation rate do not follow a simple relationship. An increase in crack propagation

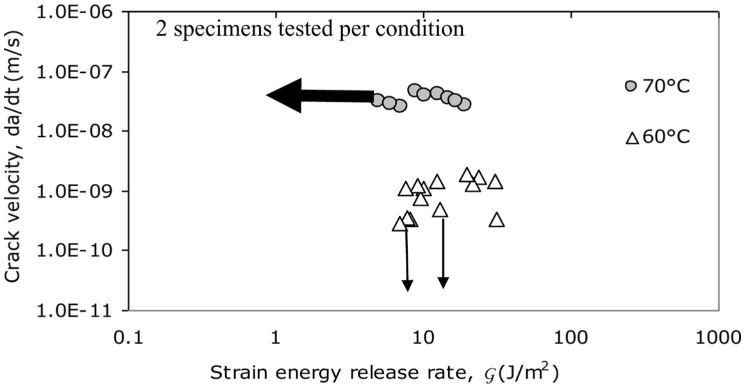

FIGURE 6 Effect of test temperature on debond kinetics for the glass/model epoxy interface in the cyan ink vehicle.

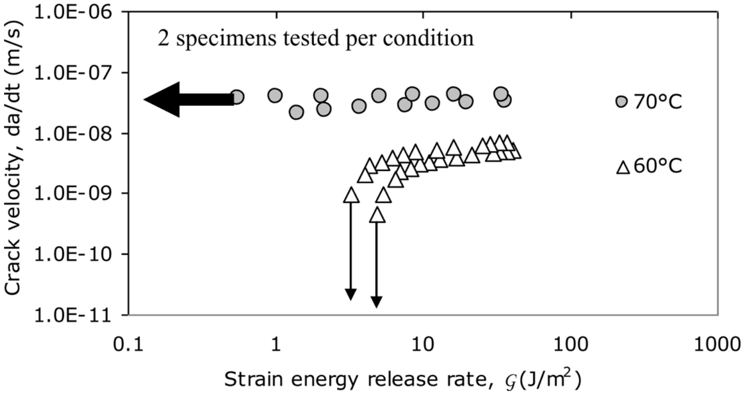

FIGURE 7 Effect of test temperature on debond kinetics for the silicon/model epoxy interface in the cyan ink vehicle.

rate with increasing temperature may only be studied in a temperature window outside which no temperature dependence is exhibited. As an example, for the silicon/L4 interface, the temperature window lies between 70 and 80°C. Two other important observations from the above plots are as follows:

1. A comparison of Figures 5 and 8 (shown in Figure 9) indicates that the cyan ink vehicle is more aggressive or detrimental to the silicon/L4 interface than DI water, inducing a higher crack propagation rate at any given temperature.

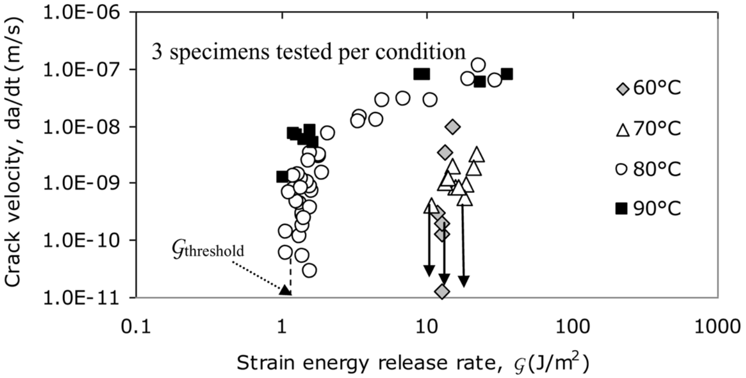

FIGURE 8 Effect of test temperature on debond kinetics for the silicon/L4 interface in DI water.

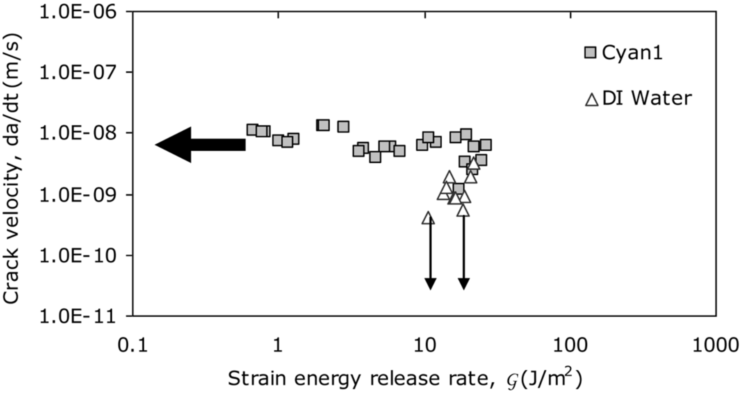

FIGURE 9 Effect of solution chemistry on debond kinetics for the silicon/L4 interface at 70°C.

2. A comparison of Figures 10 and 11 indicates that the model epoxy makes a weaker bond with glass or silicon than the fully formulated commercial adhesive, as suggested by the higher crack propagation rate (evident at 70°C) and lower value of $G_{\text{threshold}}$ (evident at 60°C).

Effect of Preconditioning

The effects of environmental exposure at different temperatures were measured on the silicon/L4 interface by comparing the results obtained from preconditioned and non-preconditioned samples. Wedge specimens made of surface treated silicon substrates bonded with the

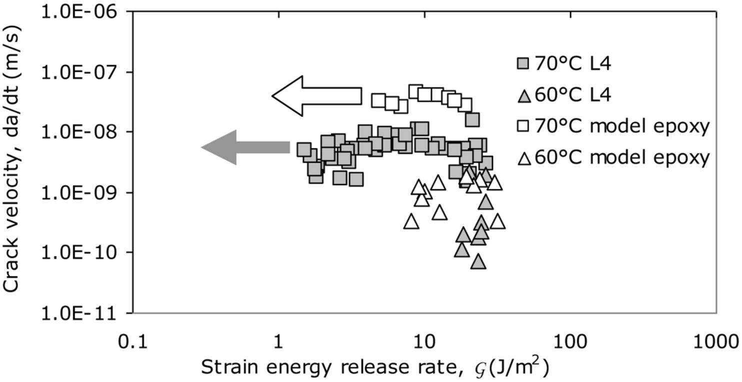

FIGURE 10 Model epoxy and L4 interface with glass in the cyan ink vehicle.

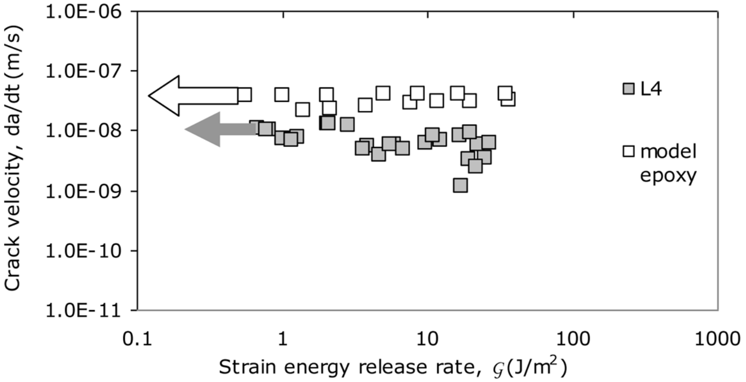

FIGURE 11 Model epoxy and L4 interface with silicon in the cyan ink vehicle at 70°C.

L4 adhesive were preconditioned in DI water at 80°C for 20, 45, and 70 days. Specimens were taken out of the conditioning liquids after the desired preconditioning times and wedges were inserted to introduce sharp initial cracks. The wedge-opened samples were then returned to the same liquid environment at a test temperature of either 70 or 80°C, and the crack length was measured periodically using the SAM. The data obtained were compared against the standard wedge test results (data from non-preconditioned samples). Several interesting results were obtained, as shown in Figures 12–14.

Figure 12 shows the data collected in DI water at a 70°C test temperature, where the first term in the legend is the preconditioning

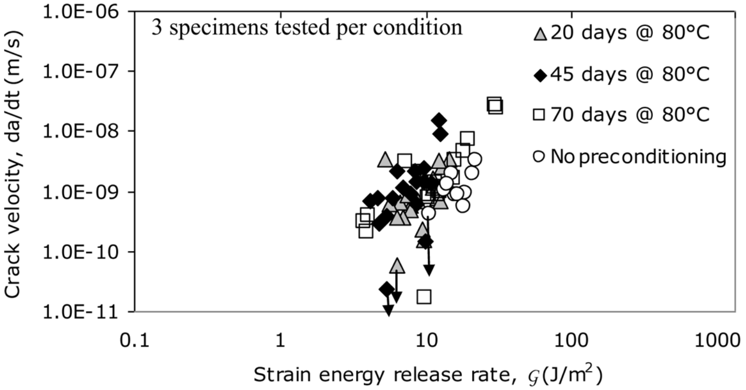

FIGURE 12 Effect of preconditioning on debond kinetics for the silicon/L4 interface at 70°C test temperature in DI water.

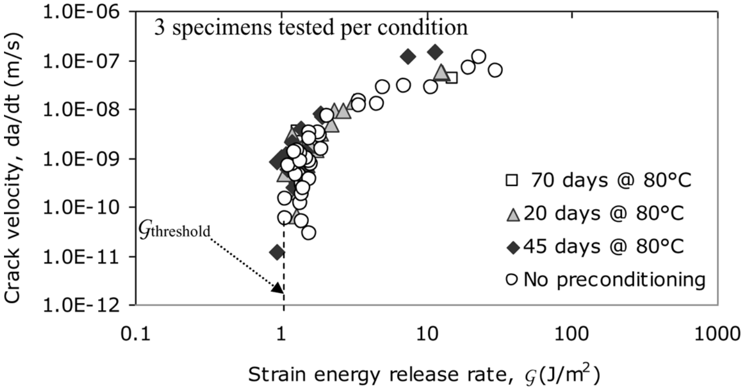

FIGURE 13 Effect of preconditioning on debond kinetics for the silicon/L4 interface at 80°C test temperature in DI water.

time in number of days and the last term indicates the preconditioning temperature. As observed in Figure 12, the data from different preconditioned samples showed no distinguishable trend and, therefore, the effect of preconditioning was negligible. Since an increase in test temperature may result in a higher crack propagation rate, additional samples were preconditioned in DI water at 80°C for 20, 45, and 70 days, and then were tested at 80°C. Again, as shown in Figure 13, no significant effect of preconditioning was observed. This means that preconditioning in DI water does not appear to affect the subcritical bonding behavior of the silicon/L4 interface significantly. The

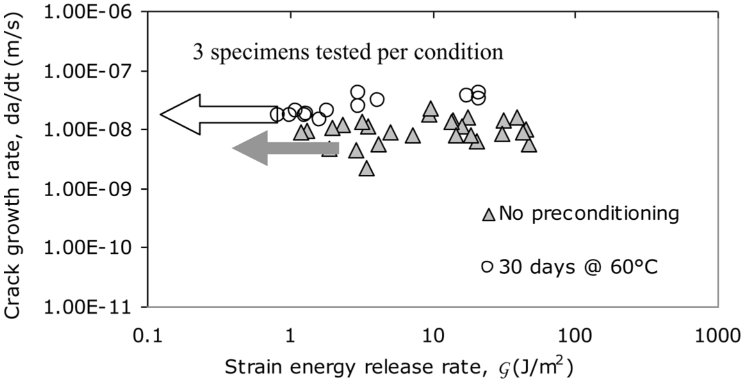

FIGURE 14 Effect of preconditioning on debond kinetics for the silicon/L4 interface at 70°C test temperature in the cyan ink vehicle.

resulting $G_{\mathrm{threshold}}$ values obtained from preconditioned samples were essentially the same as for non-preconditioned samples.

Since the cyan ink vehicle was more aggressive on the silicon/L4 system than DI water (as observed in Figure 9), wedge specimens were also preconditioned in the cyan ink vehicle at 60°C for 30 days. Wedges were then inserted in the preconditioned specimens and samples were tested at 70°C. The data obtained were compared with the standard wedge test results, as shown in Figure 14. In this case, where more aggressive solutions were used for preconditioning, the debonding behavior changed significantly after preconditioning, as indicated by higher debond propagation rates (and possibly lower values of $G_{\mathrm{threshold}}$).

A number of effects result from the ingress of liquid into an adhesive joint, including plasticization of the polymeric adhesive and disruption of the interfacial region between the substrate and the organic phase [30]. X-ray photoelectron spectroscopy (XPS) surface analyses of wedge test specimens that were preconditioned in cyan ink vehicle and DI water were carried out to determine the mode of failure. To carry out such analysis, samples were retrieved from solutions after crack propagation had arrested and silicon DCB strips were separated by mechanical force. The elemental composition and XPS spectral features of the fractured surfaces near the arrested crack front on the failed epoxy side and failed substrate side of the specimens were examined, and compared with the spectral features for the as-prepared epoxy and silicon surfaces prior to bonding, as illustrated in Figure 15 [31].

The atomic % results in Table 1 summarize the compositions of various sample surfaces. For the as-prepared epoxy surface, silicon and nitrogen were not detected. For the as-prepared silicon surface, the Si 2p spectrum showed the SiO_x ($SiO_2 +$ silane) at $\sim$103.1 eV and Si° (elemental silicon) at $\sim$98.8 eV. The C 1s spectra for the as-prepared epoxy surface showed a significant C–O photopeak at $\sim$285.6 eV, which is attributed to the epoxy functionality. The failed epoxy and silicon surfaces showed surface compositions that were different to some extent compared with the respective as-prepared surfaces. On the failed silicon surface, the carbon content was slightly higher and the silicon and nitrogen contents were lower than that for the corresponding compositions on the as-prepared silicon/3-APS surface, which suggests that minor failure occurred at the surface of the epoxy film. A small amount of silicon was detected by XPS on the failed epoxy surface. This is likely due to a few silane chains that are detached from the silicon surface *via* hydrolysis of the Si-O-Si bond in the liquid environment. This observation is consistent with the assumptions of a diffusion driven debond, in which interfacial degradation (*i.e.*, disruption of chemical bonds)

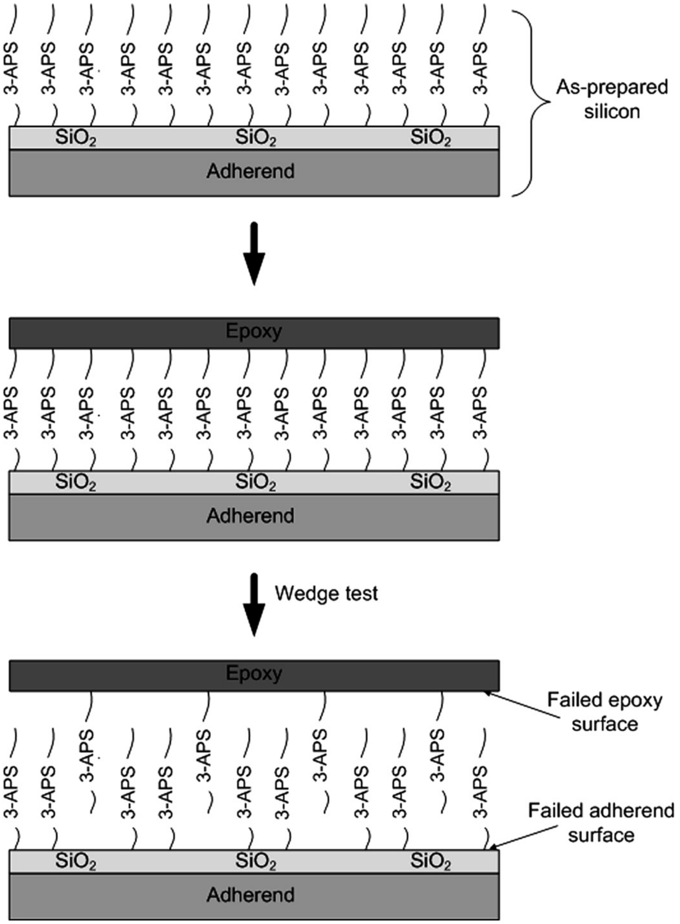

FIGURE 15 Illustration of the wedge test specimen investigated for bond failure using XPS.

TABLE 1 Elemental Surface Compositions (Atomic %) for As-Prepared and Failed Wedge Specimen Surfaces [31]

Type of surfaces	Sample	C	O	Si	N
As-prepared surfaces (prior to bonding)	Epoxy, as prepared	81.6	18.4	<0.1	<0.1
	Silicon + argon plasma + 3-APS	33.2	31.2	32.1	3.5
Failed surfaces (after debonding)	Failed epoxy side	77.9	21.2	0.5	0.4
	Failed silicon side	45.3	34.6	18.3	1.9

occurs in the presence of aggressive environments. It can be argued that the loss of interfacial adhesion from environmental exposure is driven by the rate at which environmental components are delivered to the interface and the subsequent rate of interfacial degradation. From the preconditioning results, it appears that interfacial degradation strongly depends on solution chemistry.

SUMMARY AND CONCLUSIONS

Subcritical debonding behavior, of wedge specimens made from glass or silicon substrates bonded with either Loctite L4 or a model epoxy adhesive and subjected to different environments, has been studied using a wedge test geometry. The crack growth rate, da/dt, has been measured as a function of the average value of strain energy release rate, G_{av}, within a given time interval. The data suggested a possible threshold value, $G_{\text{threshold}}$, (within the resolution limit of the crack length measurement microscopes) for some interfaces and test conditions. No apparent value of $G_{\text{threshold}}$ was observed for the model epoxy interfaces at 70°C but a threshold value in the range of 8 to 12 J/m^2 did exist at 60°C. The values of $G_{\text{threshold}}$ for the L4 interface in DI water were found to be in the range of 1 to 12 J/m^2, depending on the temperature. Also, adhesion degradation at the interface was transport controlled at higher temperatures and for aggressive solutions. Higher temperatures may result in a more severe interaction between strained atomic bonds and liquid molecules, causing a decrease in the $G_{\text{threshold}}$ value and higher crack propagation rates. Moreover, fully formulated L4 adhesive makes a stronger and more durable bond than the model epoxy.

The detrimental effect of preconditioning was evident in aggressive solution environments. The diffusing species diffuse through the polymer or wick along the interface and degrade adhesion. The rate of diffusion is dependent on the nature of the diffusant, the preconditioning temperature, and the nature of the polymer. The extent of damage to the interface and observed adhesion degradation may depend on the interaction of liquid with the polymer.

An understanding of the interface adhesion can provide guidance for developing new processes and materials to enhance surface integrity. Several conclusions drawn from the wedge test data are listed here:

1. The debond growth rate, da/dt, and threshold value of strain energy release rate, $G_{\text{threshold}}$, depend on the adhesive system being tested and environmental conditions.

2. The adhesion degradation of the interface is diffusion controlled at higher temperatures and for aggressive solutions.
3. Weak interfaces, aggressive environments, and high test temperatures result in a higher crack propagation rate.
4. Preconditioning in DI water does not have a significant effect on subcritical behavior in the systems studied, whereas more aggressive environments affect subcritical behavior significantly.

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