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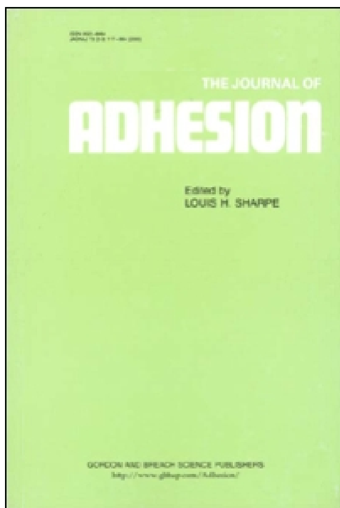

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Effect of Silane Adhesion Promoters on Subcritical Debonding of Epoxy/Glass Interfaces After Hygrothermal Aging

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Subcritical debonding is of particular concern for microelectronic packaging, coating, and adhesive applications. Time-dependent subcritical debonding at polymer/substrate interfaces occurs at lower mechanical loads and strain energy release rates compared with those required for catastrophic interface fracture. In this work, the role of organosilane adhesion promoters, 3-aminopropyltriethoxysilane and glycidoxypropyltrimethoxysilane, in subcritical debonding of epoxy/glass interfaces under hygrothermal condition is investigated. The epoxy systems studied included a thermally cured bisphenol F-based epoxy resin and a bisphenol F-based epoxy resin cured with a UV active curing agent. Subcritical debonding results revealed that there are two regions, the threshold strain energy release rate (G_{TH}) and the power law region, observed in subcritical debonding curves. Hygrothermal aging not only lowers the critical debonding driving energy required for debond extension (G_C) but also lowers G_{TH}, below which interfacial crack growth does not occur. Interestingly, applying silane adhesion promoters on glass surfaces increased G_{TH} values and decreased debonding growth rate. Therefore, the subcritical debonding growth rate mechanism was found to be sensitive to interface chemistry. An attempt to correlate the results of critical and subcritical debonding was undertaken. It was found that as aging time increased, the role of subcritical debonding became less important compared with the critical debonding component. However, the presence of subcritical debonding at applied driving energies significantly below G_C has important implications for the long-term reliability of interfaces.

Keywords: Adhesion promoter; Epoxy; Glass and subcritical debonding; Hygrothermal aging; Organoilane

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1. INTRODUCTION

Adhesive strength of epoxy/glass interfaces is of significant importance for a range of modern technologies, including polymer/glass composites and microelectronic/optoelectronic devices. Such interfaces can fail or debond after prolonged exposure to hot, humid environments. It is well-accepted that hot/wet adhesion can be improved by forming chemical bonds between the adherend and adhesive [1]. Adhesion promoters with dual functionality are widely used to form chemical bonds between polymers and inorganic substrates. Chemical bonding can produce durable interfaces, even under severe humidity and thermal conditions.

Critical strain energy release rate (G_C) is an important factor for quantifying reliability and/or interfacial strength when interfaces are subjected to a critical force. However, time-dependent subcritical debonding at polymer/substrate interfaces can occur at lower mechanical loads compared with those required for catastrophic interface fracture. Therefore, subcritical debonding is of particular concern for packaging, coating, and adhesive applications. Subcritical interfacial debonding may be studied using fracture mechanics, where delamination is modeled as a crack propagating along the interface between two materials [2].

Quantifying subcritical crack growth is important because it is often the precursor to delamination at an interface. Subcritical debond growth may be driven by residual stresses, thermomechanical cycling, and mechanical or vibrational loading. Thermal expansion mismatch and polymer curing strains generate residual stresses at interfaces during processing and in use. The mechanism involves the synergistic interaction of strained atomic bonds and an environmental species [3]. Some studies have suggested hydrolysis as the principal reason for weakening of polymer/substrate interfaces in moist environments [4,5]. Moisture, which lowers the debond driving energy required for debond extension, may be present in the materials themselves, in operating environments, or accumulated during processing steps that involve exposure to aqueous environments. The effect of a number of key parameters including interface chemistry and morphology, plasticity in adjacent ductile polymer layers, and environmental factors such as temperature and moisture have been documented [3,6–9].

1.1. Brief Review of Previous Studies on Subcritical Interfacial Crack Growth

The work on subcritical crack propagation along an interface is relatively sparse when compared with the massive amount of work

on monolithic materials. Mostovoy and Ripling [10] were among the earliest researchers to investigate subcritical crack propagation in adhesively bonded joints. They reported that slow cracking always starts in the regions of the crack tip (where the stresses are the highest) at the air (or water) exposed portions of the adherend-adhesive interface. If water vapor or water is excluded from this location, cracking at less than the critical strain energy release rate for the onset of rapid fractures does not occur. The minimum value of the applied crack-extension force below which slow cracking did not occur was found to decrease as the relative humidity increased. Their work can be considered as very experimental and no model was proposed.

Adopting the Boeing wedge test, Cognard [11,12] conducted a series of subcritical debonding measurements of an adhesive-stainless steel system. It was found that adhesive joints of epoxy resin and stainless steel were easily cleaved by a wedge. The length of the crack characterized the resistance to fracture (R) of the adhesive which was affected by humidity. Water decreased R and induced an apparently interfacial failure on polished surfaces. Both liquid water and high humidity caused debonding of cleaved joints. The results indicated two different processes in the debonding of adhesives: one occurring at high speed, characterizing the initial strength of the joint, and another at low speed, characterizing the durability of adhesive joints. Solvents had a greater adverse effect on the strength of epoxy adhesive joints than humidity. Epoxy adhesives were particularly sensitive to CH_2Cl_2. Failure of epoxy-metal joints was accelerated by atmosphere pollutants, *e.g.*, a vapor mixture of H_2SO_4, HNO_3, HCl, Na_2S, and $NaNO_2$, in the presence of humidity. In 3 days' exposure to air pollutants the joint lost strength equivalent to 300 days tropical exposure. In summary, Cognard found different behavior for different combinations of adhesive and liquids.

Subsequently, Crosley and Ripling [13] proposed a thick double-cantilever beam (DCB) geometry for measurement of adhesively bonded metal joints. Ritter and others [14–17] explored the subcritical debonding behavior of the polymer-glass interface using various testing geometries, *e.g.*, DCB specimen, four-point flexural sandwich specimen, and double cleavage drilled compression (DCDC) specimen. Arnott and Kindermann [18] used a constant load-point displacement rate method to test double cantilever beam specimens of an aluminum alloy bonded with adhesive, and found that in humid air at elevated temperature, G_C depends strongly on load-point displacement rate. Frantizs [19] reported a new test device for measuring sub-critical crack propagation along an adhesive-adherend interface. The test configuration consisted of a double torsion specimen and a graphite gauge for the measurement of crack length. Recently, Gurumurphy and

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Kramer [20] investigated the subcritical debonding behavior along a polymer/polymer interface using an asymmetric DCB (ADCB) specimen, and proposed a theory based on thermal activation energy to predict the experimental results.

1.2. Describing Subcritical Interfacial Crack Growth Behavior

In a subcritical debonding test, debond growth rates, da/dt, are usually measured in terms of the applied strain energy release rate, G_A (J/m^2), which represents the macroscopic energy required to separate the interface in the environment of interest. A schematic illustration of the resulting crack-growth rate versus applied strain energy release rate (da/dt-G_A) curve is shown in Fig. 1 where changes in slope indicate a change in the rate-limiting step for crack advance [21–24]. The threshold strain energy release rate, G_{TH}, is defined as the G below which interfacial crack growth does not occur [9]. The stress-dependent

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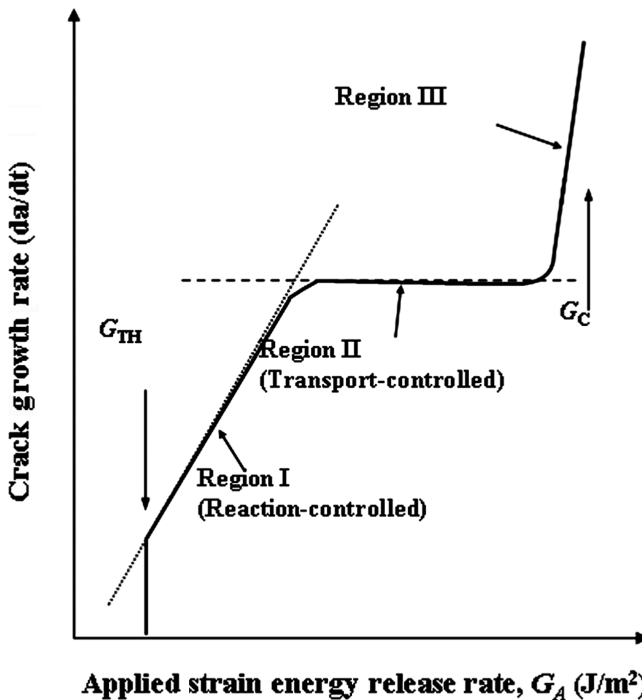

FIGURE 1 Schematic diagram of crack-growth rate *vs*. applied strain energy release rate curve. Reprinted with permission from [24]. Copyright 2002 American Institute of Physics.

chemical reaction dictates growth rates from threshold to intermediate values (Region I). For Region I, transport of moisture to the debond tip is sufficiently rapid so that debond growth is limited only by the rate of reaction between water and debond tip bonds. The debond-growth rate depends sensitively on G_A. In Region II, the debond-growth rate becomes limited by mass transport of H_2O to the debond tip. Region III is related to the onset of critical fracture events and typically occurs at G_A values approaching the macroscopic adhesion limit, G_C. In Region III, growth rates are typically very sensitive to G_A and almost insensitive to environment.

First, the da/dt-G_A curve (Fig. 1) was developed to describe the behavior of environmentally assisted crack growth or stress-corrosion cracking which has been studied in a wide range of bulk glasses where crack tip plasticity does not occur and cracks are assumed to be sharp to atomistic dimensions [5,21,22,25,26]. A three-step dissociative chemical reaction is assumed to occur between a corrosive species (usually H_2O) and strained glass network bonds (typically Si–O) at the crack tip. Weiderhorn *et al.* [22] have explained that in the presence of corrosive environments, structural materials often experience delayed failure when subjected to mechanical loads. These environments react chemically or physically with the stressed material causing subcritical crack growth that results in structural failure when the crack has grown to a critical size. The time to failure is the total time required for the nucleation and growth of a crack to that critical size. Known as stress-corrosion cracking, this process is superficially the same for ceramic, metallic, and polymeric materials since all three kinds of material exhibit similar types of delayed failure curves. Failure occurs most rapidly at high loads. Below a critical value of the load known as the stress-corrosion limit, failure does not occur regardless of the length of time for which the load is supported.

Debond growth in Region I is found to be controlled by the rate of a stress-dependent chemical reaction involving dissociative adsorption of atomic bonds at the debond tip. In amorphous glasses, water molecules found in atmospheric environments react with strained crack tip bonds to cause time-dependent crack growth. Subcritical crack growth behavior can be described by the chemical reaction rate theory [27] and predictions obtained for the crack growth rate, da/dt, as a function of the applied strain energy release rate, G_A. A simple empirical power-law relationship is often used and has been found to represent adequately the observed moisture-assisted debond growth rate behavior:

$$\frac{da}{dt} = A\left(\frac{G_A}{G_C}\right)^n, \qquad (1)$$

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where A and n are fitting parameters which depend on the material and testing conditions [15]. Linear regression of two sets of data in this region can be used to calculate the values of A and n. It has been found that the power exponent, n, is not a strong function of relative humidity within experimental scatter; however, the multiplicative constant, A, depends strongly on the environment [15].

For a thin film coating under residual tensile stress, the applied crack driving force (strain energy release rate) for a crack propagating along an interface between a polymer film and glass substrate can be shown to be [25,28]:

$$G_A = \frac{s^2 h}{2E}, \tag{2}$$

where s is the uniform, residual tensile stress in the film, h is the film thickness, and E is the elastic modulus of the film. Integration of Eq. (1) using Eq. (2) gives an expression for the delamination time, t, for an initial interfacial crack of size a_0 to grow to final size a_f as:

$$t_f = \left[\frac{a_f - a_0}{A}\right]\left[\frac{2EG_C}{s^2 h}\right]^n. \tag{3}$$

The influence of humidity on delamination time for a given adhesive can also be easily determined from Eq. (4) [6] since

$$\frac{t_2}{t_1} = \left(\frac{A_1}{A_2}\right)\left(\frac{G_{C2}}{G_{C1}}\right)^n, \tag{4}$$

where subscripts indicate two different lengths of aging time in hygrothermal conditions. Therefore, the delamination time can be predicted by using the results from both critical and subcritical debonding tests.

1.3. Objective

While much recent attention has been focused on understanding the effect of hygrothermal conditions on subcritical debonding rate, only a few studies have addressed the improvement in subcritical debonding of epoxy/glass interfaces by organosilane adhesion promoters under hygrothermal aging. Since adhesion promoters improved both dry and wet adhesive strength in terms of G_C of the epoxy/glass interface in our previous investigation [29], in this work, the role of organosilane adhesion promoters on subcritical debonding is studied. Furthermore, a relationship between the G_C and G_TH is explored.

2. EXPERIMENTAL

2.1. Materials

Two epoxy systems, a thermally cured and a UV-cured epoxy, were used in this study. The first formula is a thermally cured epoxy system based on a diglycidyl ether of bisphenol F epoxy (Bis F) cured with 2-ethyl-4-methyl-imidazole (2,4-EMI). Bis F resin was provided by Shell (EPON® 862 Resin 2 Hexion Specialty Chemicals, Houston, TX, USA) while 2,4-EMI curing agent was provided by Air Products and Chemicals, Allentown, PA USA (IMICURE® EMI-24.) The second formula consists of Bis F epoxy resin cured with mixed triarylsulfonium hexafluoroantimonate salt (UVI-6974) from Union Carbide Corp. (Danburg, CT, USA). This epoxy formula is a model of a UV-cure epoxy which cures cationically, wherein the photoinitiator generates a proton on exposure to UV light. Chemical structures of all materials used are shown in Fig. 2. The amount of curing agent used in both epoxy systems was 4 parts per hundred parts resin (phr).

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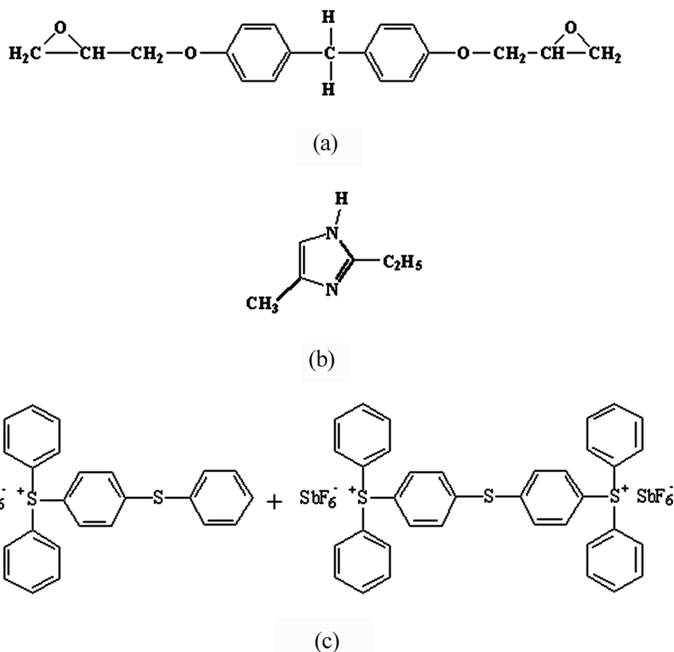


FIGURE 2 (a) Diglycidyl ether of bisphenol F, (b) 2-Ethyl-4-methyl-imidazole, and (c) Mixed triarylsulfonium hexafluoroantimonate salt.

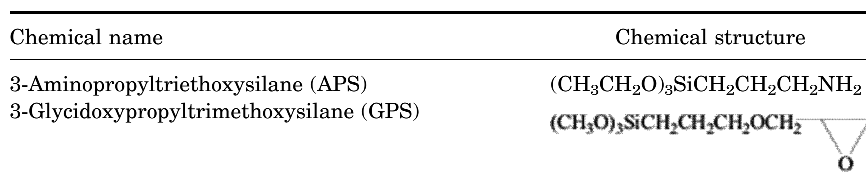
The adhesion promoters used were 3-aminopropyltriethoxysilane (APS) from Sigma-Aldrich Chemical Co., Inc. (St. Louis, MD, USA) and 3-glycidoxypropyltrime-thoxysilane (GPS) from Dow Corning Corporation (Midland, MI, USA). Table 1 shows chemical structures of both organosilane adhesion promoters. A borosilicate glass (BOROFLOAT) from Erie Scientific Co. (Portsmouth, NH, USA) was used in this study as a substrate for the epoxy. The glass was received in the form of $12.7 \times 76.2 \times 3.2$ mm slabs.

2.2. Double Cantilever Beam (DCB) Specimen Preparation

The DCB testing specimens with the (APS-coated glass)/Epoxy/(glass coated with the experimental formulation) structures were prepared. Silane adhesion promoters, APS and GPS, were diluted to a final concentration of 1% by weight in 95% methanol/5% deionized water. The glass surfaces were first degreased using isopropyl alcohol and then treated by UV/O_3 for 20 minutes. Glass substrates were dipped for 2–3 minutes in adhesion promoter solutions. The treated glass was dipped into a methanol bath to rinse off excess coupling agent. The glass plate was then air dried for 10 minutes and placed in a 110°C oven for 8 minutes.

The top adherend (glass plate) was treated with 1% solution of APS solution. The bottom adherend (glass plate) was treated with the experimental adhesion promoter. In order to create a weaker interface for crack initiation, an 11×17 mm area on the glass was sputter coated with Au/Pd. The bottom plate along with 250-μm shims was placed in a silicone mold. The epoxy resin mixture was placed on the bottom plate. The APS-coated glass plate was placed on the top and was allowed to settle under its own weight for a few minutes before it was gently pressed against the shims to squeeze out excess resin and any trapped air. The epoxy was then cured by the cure schedule shown in Table 2. The specimen was cooled to room temperature. Excess epoxy was removed from the edges by a grinding and polishing method. The final DCB specimen is shown in Fig. 3. A starter crack was created on the Au/Pd-coated end of the bottom plate by using a jeweler's saw. Aluminum stubs were glued to the Au/Pd side of the bottom plate using a

TABLE 1 Chemical Structures of Organosilane Adhesion Promoters



Chemical name	Chemical structure
3-Aminopropyltriethoxysilane (APS)	$(CH_3CH_2O)_3SiCH_2CH_2CH_2NH_2$
3-Glycidoxypropyltrimethoxysilane (GPS)	$(CH_3O)_3SiCH_2CH_2CH_2OCH_2$–(epoxide ring, O)

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TABLE 2 Cure Schedules for Epoxy Systems

Model epoxy system	Cure schedule	Glass transition temperature
(1) Bis F/2,4-EMI	60°C for 4 hours 150°C for 2 hours	139°C
(2) Bis F/UVI	UV for 2 minutes	153°C

Note that Tg was measured using a DSC at 10°C/min.

room temperature-cured adhesive (Loctite Superbonder 409, Henkel Corporation, Philadelphia, PA).

2.3. Critical Strain Energy Release Rate Measurement by DCB Testing

Of the various test specimens that have been used to measure the critical strain energy release rate, G_C, the DCB specimen has been one of the most popular. In this study, DCB specimens were exposed to moisture in a Despatch Ecosphere Series (Despatch, Minneapolis, MN, USA) controlled humidity chamber at 85°C/85% relative humidity (RH) for different periods of time in order to study the effect of aging time on adhesive strength. The DCB specimens were precracked prior to testing. DCB testing was performed using a computer controlled screw driven Instron materials testing machine (model 5521, Instron, Canton, MA, USA) in displacement control, at a speed of 0.127 mm/min, with 500 N load cell. Tensile force was applied at the end of a specimen in a direction normal to the crack surface; this is called cleavage mode

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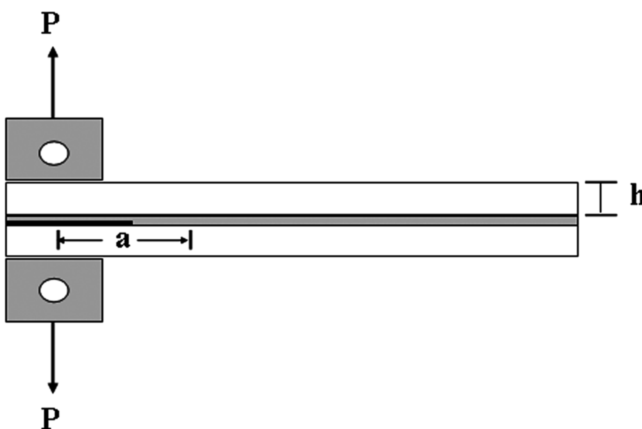

FIGURE 3 Double cantilever beam (DCB) specimen.

or Mode 1 fracture as shown above in Fig. 3. As the load was applied, the crack propagated, leading to a load drop, then unloaded further using the crosshead position and subsequently reloaded using the crosshead position. This cycle was repeated in order to get several strain energy release rate (G_C) values for averaging. G_C values can be determined from the load-displacement plot shown in Fig. 4.

By using the maximum load of each cycle and a crack length, G_C values, which are in units of J/m^2, can be calculated from the following relation from Blackman *et al.* [30]:

$$G_C = \frac{12P_C^2a^2}{w^2h^3E}, \tag{5}$$

where P_C is the critical load, a is the crack length, w is the specimen width (12.7 mm), h is the beam height (3.2 mm), and E is the plane strain modulus of glass (62 GPa).

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2.4. Subcritical Debonding Test

Subcritical debonding tests were conducted using load relaxation techniques by loading a precracked DCB specimen to a predetermined load ($P_O < P_C$) and then fixing the displacement. The load-time curve, as seen in Fig. 5, was recorded. Then the crack growth rate (da/dt) can be calculated by using Eq. (6) [31,32]:

$$\frac{da}{dt} = -\frac{dP}{dt}\frac{P_o a_o}{P^2}, \tag{6}$$

where a is the crack length at any time, t; P is the applied load; P_0 is the initial load; and a_0 is the initial crack length. By applying the

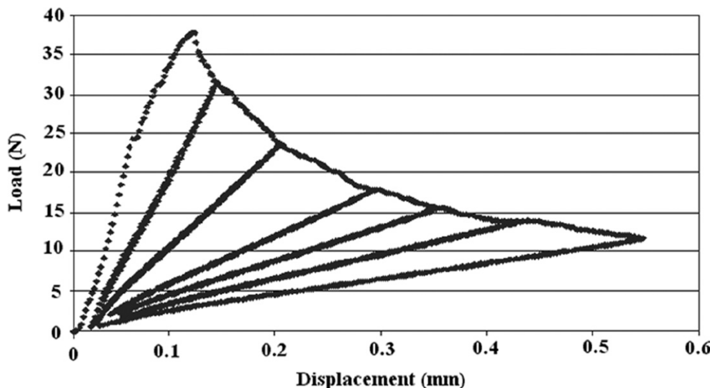

FIGURE 4 Typical double cantilever beam (DCB) analysis.

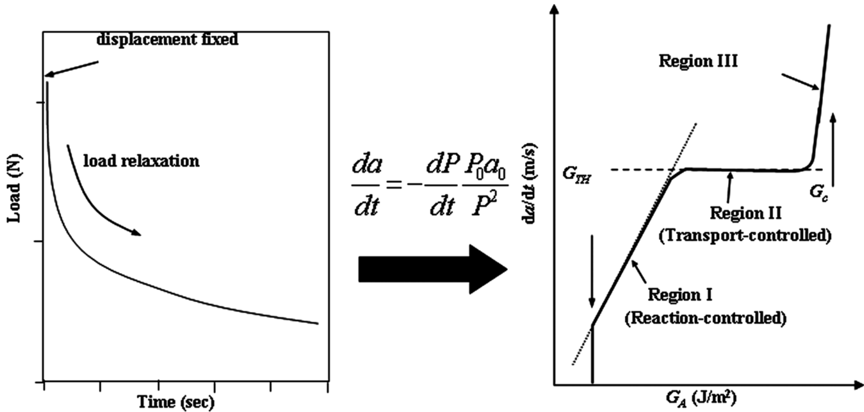

FIGURE 5 Conversion of load-time curve to *da/dt-GA* curve [7].

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equation above, the plot of da/dt *vs*. G_A is obtained. Growth rates for moisture-assisted subcritical debonding were typically measured over a range of da/dt from 10^{-3} to 10^{-8} m/s.

In this study, subcritical crack growth was examined on epoxy/glass interfaces of untreated, APS-, and GPS-, treated DCB specimens which were aged in an environmental chamber at 85°C/85% relative humidity (RH) for 0, 7, 14, 28, and 56 days for Bis F/2,4-EMI epoxy and for 0, 2, 4, and 8 days for the Bis F/UVI epoxy (shorter times since the drop in G_C was more rapid). Tests were performed in ambient conditions after removal from the controlled humidity chamber. The results are displayed in the form of a da/dt-G_A curve which is expected to show a threshold strain energy release rate, G_{TH} value, Region I slope, and Region II growth rate plateau. Moreover, the relationship between these subcritical results and critical G_C results are examined.

3. RESULTS AND DISCUSSION

3.1. Effect of Surface Chemistry on Critical Strain Energy Release Rate

The effect of surface chemistry on G_C values was studied in order to compare with the subcritical results. Figure 6 shows the dry G_C values of untreated, APS-, and GPS-, treated DCB specimens for two epoxy systems, Bis F/2,4-EMI and Bis F/UVI. There were three kinds of surface chemistries studied: untreated, APS-, and GPS-, treated borosilicate glass. As seen from Fig. 6, both APS- and GPS-treated glass surfaces showed improvement in adhesive strength for the Bis F/2,4-EMI system compared with the untreated glass surface. For Bis

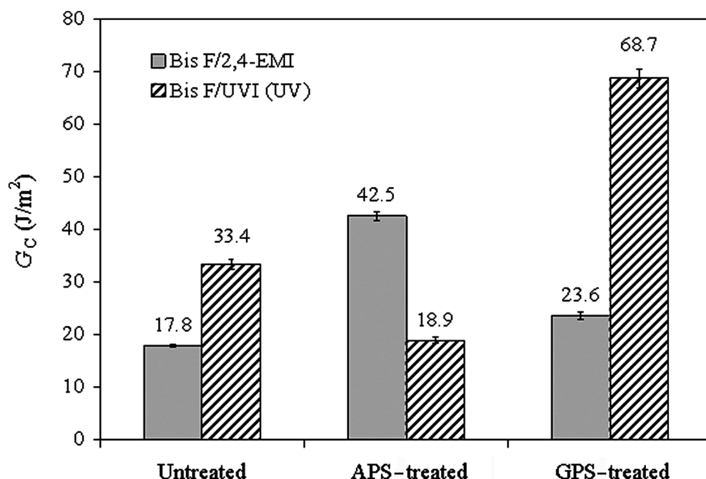

FIGURE 6 The dry G_c values of untreated, APS- and GPS-treated DCB specimens for two epoxy systems, Bis F/2,4-EMI and Bis F/UVI.

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F/UVI systems, both untreated and GPS treated glass surfaces showed greater G_C values compared with the thermally cured system (Bis F/ 2,4-EMI). The higher G_C values indicate more energy required to propagate the crack. However, APS-treated glass surfaces showed lower G_C values for the UV cured systems than for the thermally cured system.

It is well known that organosilane-based adhesion promoters form Si–O–Si bonds to a glass surface and exist as a multilayer film on the glass [33]. Organofunctional groups on the opposite end of the silane molecules are reasonably assumed to form covalent bonds to the epoxy resin. In this study, APS and GPS form oxide linkages with the glass surface. However, the organofunctional groups at the other end of the silane molecules are different. An APS molecule has an amino functional group forming the bond with the epoxy resin while the GPS molecule has an epoxide functional group instead.

For the thermally cured epoxy system, the amino groups of APS can react with the epoxide ring of the Bis F epoxy resin. On the other hand, the epoxide ring of GPS is likely to react with the 2,4-EMI curing agent in the resin. The possible chemical reactions of APS and GPS adhesion promoters with Bis F/2,4-EMI epoxy system are shown in Fig. 7 (a) and (b), respectively. Since the number of epoxide functional groups of Bis F is much larger than that of the amino groups of 2,4-EMI, the reaction between the amino group of APS and the epoxide group of Bis F is preferable. Note that the 2,4-EMI-cured Bis F epoxy system contains only a catalytic amount of 2,4-EMI (4 phr). This explanation implies that the

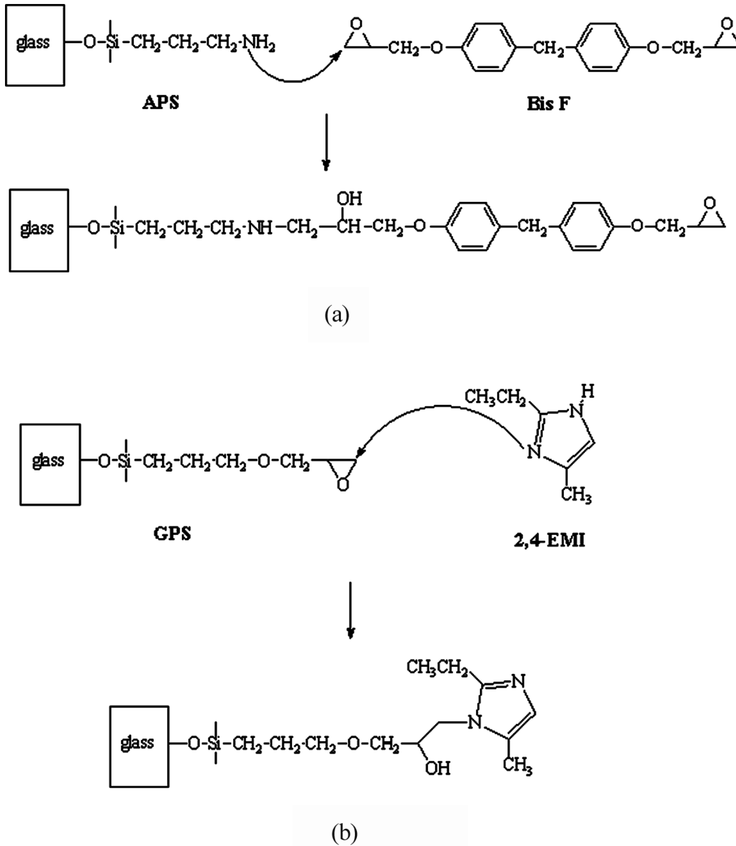

FIGURE 7 Possible chemical reactions of (a) APS and (b) GPS adhesion promoters with Bis F/2,4-EMI epoxy system.

APS-treated interfaces provide higher areal chain density compared with the GPS-treated interfaces. According to Kent *et al.*, there is a relationship between the in-plane distribution of interfacial interactions and engineering fracture quantities such as G_C [34]. Therefore, if applying APS to the glass surface increases the areal chain density then one would expect higher mechanical adhesive strength.

Another explanation for better adhesive strength improvement by APS-treated specimens compared with GPS-treated specimens is that the primary amine of the APS molecule has been claimed as the most reactive towards the epoxy functional group compared with the secondary and tertiary amines of the 2,4-EMI molecule [35,36]. By this explanation, the G_C values of APS-treated specimens were greater

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than those of GPS-treated specimens. The results obtained from this study agree with those reported by Walker [37], who found that for amine and polyamide cured epoxy resins, amino end group silanes, such as APS, have superior improvement compared with epoxide end-group silanes such as GPS [37,38].

For UV-cured systems, the great enhancement in adhesive strength of GPS can be explained in terms of chemical bond formation in the interphase region by GPS adhesion promoter molecules. The chemical reaction between GPS and the Bis F/UVI-6974 mixture is expected to be similar to the reaction of the mixture itself, since GPS has an epoxide functional group like that of Bis F molecules. GPS molecules can react with a superacid generated from UVI-6974 or a living cationic polymer chain of Bis F/UVI by a phenomenon typically referred to as dark cure [39]. The possible chemical reactions between GPS and the Bis F/UVI-6974 mixture are shown in Fig. 8. Organosilane-glass bonds are known to be resistant to hygrothermal conditions, which leads to higher wet adhesive strength in GPS treated specimens compared with untreated specimens. Moreover, improvement in the dry G_C value of GPS-treated specimens indicates that the effective areal bond density is significant increased. For this definition, the effective areal bond density refers to the number of covalent links per unit area that can transfer stress between the epoxy and the glass substrate. It is not defined by the number of covalent bonds that pass through a particular plane (*i.e.*, the substrate surface), but rather includes the number of mechanically distinct bonding paths that cross the interface.

The lower G_C values for APS-treated surfaces can be explained in terms of negative effects of the amino group in APS molecules. The amino group, which is a nucleophilic agent, tends to neutralize the cationic catalyst (UV curing agent) and results in poor cure response in the epoxy layer, especially in the interphase region. As a result, the presence of amino groups from APS molecules caused poor adhesion in Bis F/UVI systems [40].

3.2. Effect of Surface Chemistry on Subcritical Debonding Behavior

In this study, subcritical debonding of two epoxy systems, Bis F/2,4-EMI and Bis F/UVI, was investigated. The effect of interface chemistry on subcritical debonding was evaluated using two silane adhesion promoters, APS and GPS. The effect of silane adhesion promoters on subcritical debonding growth rates is shown in Figs. 9 and 10. Subcritical debonding growth rates, $\mathrm{d}a/\mathrm{d}t$, as a function of the applied strain energy release rate, G_A, for Bis F/2,4-EMI epoxy/glass interfaces

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(a)

(b)

FIGURE 8 Possible chemical reaction between GPS and Bis F/UVI-6974 mixture (a) GPS with photoinitiator (b) GPS with cationic living polymer chain.

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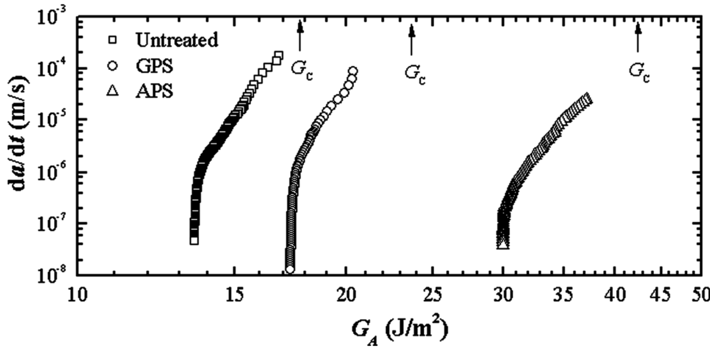

FIGURE 9 Plot of da/dt as a function of G_A for untreated, GPS-, and APS-treated DCB specimens of Bis F/2,4-EMI epoxy system before moisture exposure.

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of untreated, GPS-, and APS-treated DCB specimens before hygrothermal aging are shown in Fig. 9. Interestingly, subcritical debonding growth rates were sensitive to the presence of the silane adhesion promoters. The adhesion promoters had little effect on the shape of the curves but shifted the positions of the curves to higher values of G_A due to stronger interfaces provided by chemical bonding from the silane adhesion promoters. This trend has been observed by a number of researchers including Dauskardt and others[24,41] and Conley *et al.* [15]. For the Bis F/2,4-EMI epoxy system, at the same crack growth rate, the G_A values are reported in the following order: APS > GPS > Untreated which is consistent with the critical debonding results shown in Fig. 6. Figure 10 contains plots of da/dt as a function of G_A for untreated, GPS-, and APS-treated DCB specimens of the Bis F/UVI UVI epoxy system before moisture exposure. As expected, a similar behavior is shown for the Bis F/UVI epoxy/glass interfaces. The subcritical debonding curve of GPS-treated samples shifted to a much higher G_A value while the curve of APS-treated samples shifted to a lower G_A value.

The results shown in Fig. 9 and 10 clearly exhibit G_{TH} and Region I as shown schematically in Fig. 1. Note that Region II cannot be seen in Figs. 9 and 10 since the experiments were conducted at room conditions immediately after the DCB specimens were removed from the environmental chamber at a certain aging time. Therefore, the moisture content in the interphase region near the crack-tip was essentially constant and a moisture transport controlled region cannot be observed. Therefore, the subcritical debonding curve that is expected to be obtained in this experiment is shown in Fig. 11 which

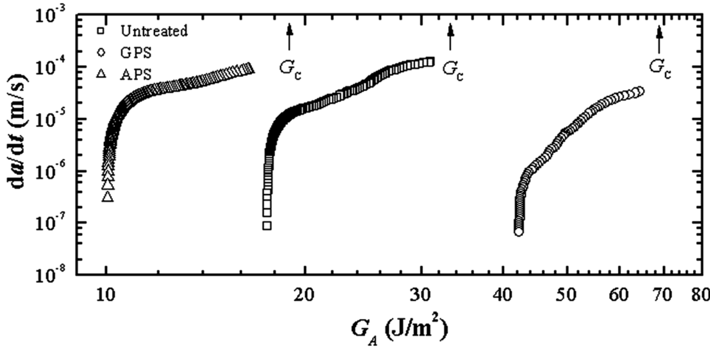

FIGURE 10 Plot of da/dt as a function of G_A for untreated, GPS-, and APS-treated DCB specimens of Bis F/UVI epoxy system before moisture exposure.

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is quite different from the subcritical debonding behavior in bulk glass reported by Weiderhorn *et al.* [22].

In Region I, the crack will be initiated if G_A exceeds G_{TH}. The higher G_{TH} value indicated the higher energy that can be absorbed at the crack tip before debonding occurs. In Region II or the subcritical

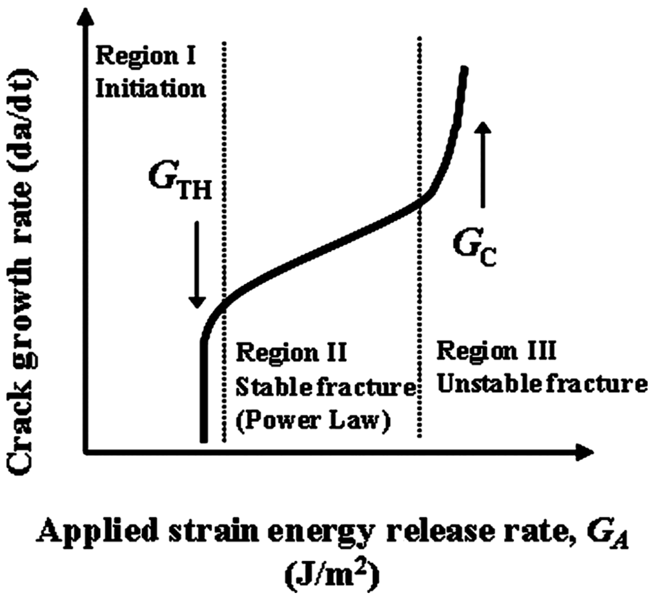

FIGURE 11 Schematic curve of subcritical debonding.

region, stable growth of debonding is expected. The curve in Region II can typically be described by a power law as seen in Eq. (1). If the G_A value approaches the G_C value, crack growth rate significantly increases with increasing G_A and unstable fracture occurs.

By applying Eq. (1), the A and n constants in the power-law region obtained by fitting subcritical debonding curves of both Bis F/2,4-EMI and Bis F/UVI systems (Fig. 9 and 10) are reported in Table 3. Obviously, n is a strong function of the interface chemistry. In other words, the subcritical debonding growth rate mechanism appears to be sensitive to interface chemistry, as might be anticipated from the physics of the chemistry reaction process [24].

3.3. Effect of Hygrothermal Aging on Subcritical Debonding Behavior

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The effect of hygrothermal aging on subcritical debonding was also studied. Obviously, hygrothermal conditions enhance subcritical debonding growth rates. Figures 12 and 13 show the effect of exposure time under 85°C/85% RH conditions on subcritical debonding curves of Bis F/2,4-EMI epoxy/glass and Bis F/UVI epoxy/glass, respectively. As seen from both figures, an increase in moisture content has a significant effect on Region I debond-growth rates by shifting the entire debond-growth rate curve to lower G_A values. Moreover, the shapes of the subcritical debonding curves were also changed after hygrothermal aging. The slopes in the power-law region become steeper as exposure time increases. It is generally accepted that subcritical debonding in this region is a chemical reaction controlled region and is often associated with environmental species that follow first-order reaction kinetics. Reaction kinetics models predict that the crack growth rate is proportional to the concentration of water [H_2O] in the environment at

TABLE 3 Constant in the Power-Law Region of Subcritical Debonding Curves for Bis F/2,4-EMI and Bis F/UVI Systems

		Constant	
Epoxy system	Adhesion promoter	A	n
Bis F/2,4-EMI	Untreated	1.0×10^{-3}	26.4
	GPS treated	3.3×10^{-3}	25.8
	APS treated	5.0×10^{-4}	20.5
Bis F/UVI (UV)	Untreated	2.0×10^{-4}	5.2
	GPS treated	2.0×10^{-4}	11.9
	APS treated	1.0×10^{-4}	2.9

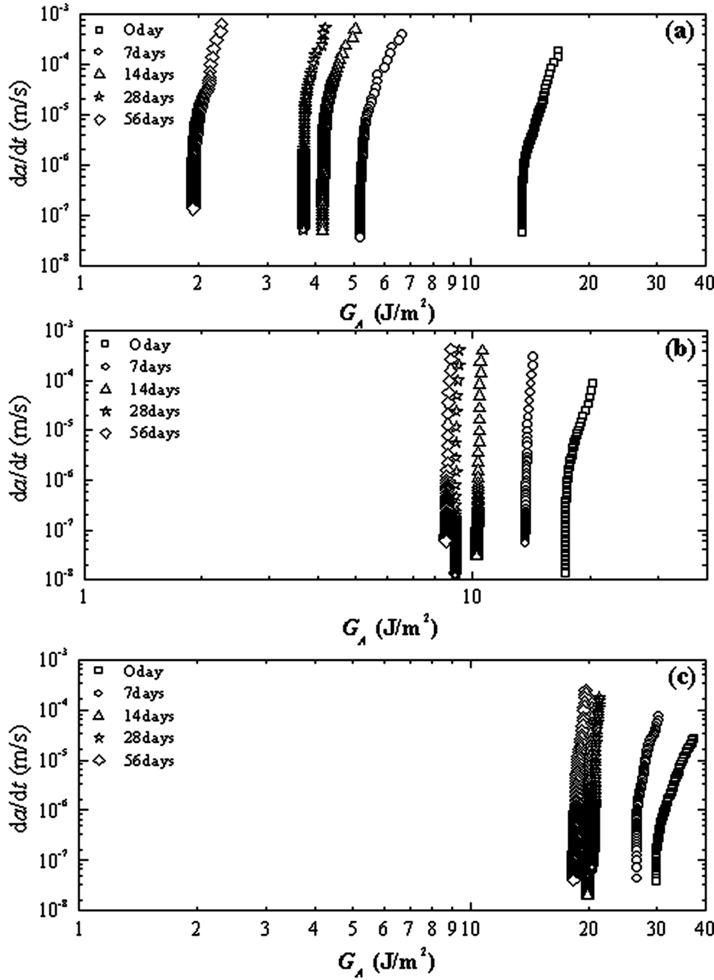

FIGURE 12 Subcritical debonding growfli rates, da/dt, as a function of the applied strain energy release rate, G_A, for debonding of Bis F/2,4-EMI epoxy/glass interfaces from (a) untreated, (b) GPS-, and (c) APS-treated DCB specimens at different aging time under the 85°C/85% RH condition.

the crack tip, as described in Eq. (7):

$$\frac{da}{dt} = v_0[H_2O]k_r, \quad (7)$$

where v_0 is a proportionality constant that incorporates the concentration of the active sites at the crack tip and k_r is the rate coefficient [22].

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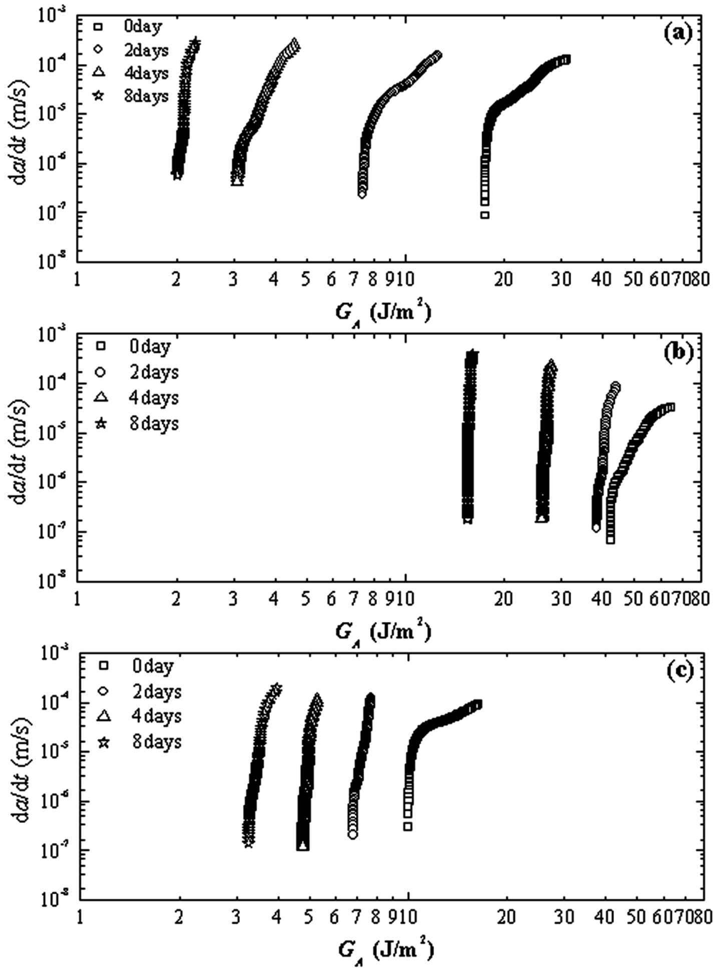

FIGURE 13 Subcritical debonding growth rates, da/dt, as a function of the applied strain energy release rate, G_A, for debonding of BisF/UVT epoxy/glass interfaces from (a) untreated, (b) GPS-, and (c) APS-treated DCB specimens at different aging time under the 85°C/85% RH condition.

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Equation (7) was proposed by Wiederhorn, whose work focuses on a bulk glass system. However, there is a difference between the water interaction in bulk glass and the present epoxy/glass interfaces which is the reactivity of the bonds being broken in each case. In the case of glass fracture, a single water molecule is consumed in the cleavage of each Si–O bond. Conversely, for the case of epoxy/glass interfaces,

water molecules may react with the bond being broken, or reactive functional groups in the intermediate vicinity, before it is strained enough to cause a dissociative reaction to occur. These considerations suggest that, at the debond tip, bond breaking may be governed by more than a water molecule. Therefore, Eq. (7) is modified by the degree of water molecules as shown in Eq. (8):

$$\frac{\mathrm{d}a}{\mathrm{d}t} = v_0[\mathrm{H_2O}]^{\mathrm{m}} k_{\mathrm{r}}, \tag{8}$$

where n is the number of molecules of water that are required to break a single bond. That means in the case of bulk glass, n is equal to 1, while in the case of polymer/substrate interfaces, $\mathrm{m} \geq 1$. Kook and Dauskardt reported $\mathrm{m} = 1.19$ for the system of silica-filled epoxy/copper interfaces [24].

According to Eq. (8), the water concentration at the crack tip is related to the debonding growth rate by increasing the chemical reactivity of the water with debond tip bonds. Therefore, increasing water concentration as exposure time increased resulted in shifting the entire subcritical debonding curve to lower G_{A} values and also a steeper slope in the power-law region. Note that the above comparison must be conducted at constant temperature since temperature also affects the kinetics of the reaction. From our previous work, at an early stage, increasing moisture absorption was significantly fast [29]; therefore, a dramatic change in slope and significant shifting of the debonding curve to lower G_{A} were obviously seen from subcritical debonding curves under dry conditions compared with those of short exposure time. The shift of the subcritical debonding curve by increasing the moisture concentration in the environment has been reported by many researchers such as Wiederhorn *et al.* [22] who studied crack growth rate in ceramic and bulk glass; Kook and Dauskardt [24], Hohlfelder *et al.* [3], and Conley *et al.* [15] who investigated moisture-assisted subcritical debonding of epoxy/glass interfaces.

3.4. Correlation Between Critical and Subcritical Debonding

Figures 14 and 15 show the values of G_{C} and G_{TH} as a function of aging time of Bis F/2,4-EMI and Bis F/UVI epoxy systems, respectively. Generally, G_{C} is more sensitive to hygrothermal conditions than G_{TH} for all types of surface chemistries. A significant increase in moisture absorption in the early stages resulted in a dramatic drop of both the G_{C} and G_{TH} values. For the system of Bis F/2,4-EMI, very little subcritical debonding can be associated with the crack growth process in untreated

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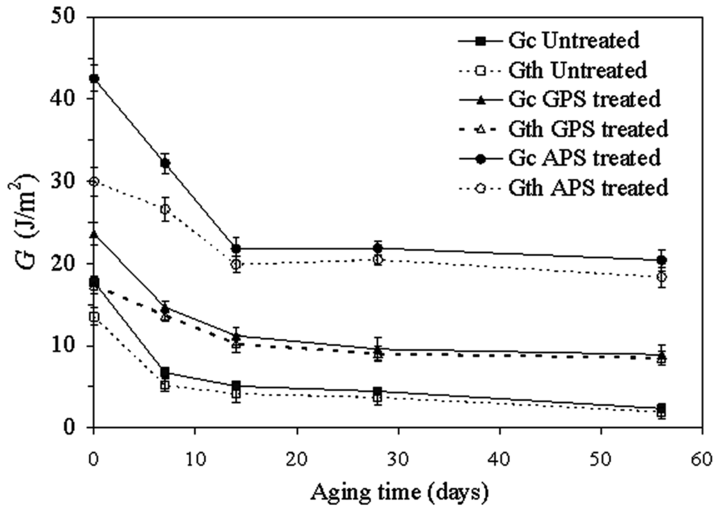

FIGURE 14 G_C and G_{TH} as a function of aging time under the 85°C/85%RH condition for untreated, GPS-, and APS-treated DCB specimens of the Bis F/2,4-EMI epoxy system.

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samples compared with GPS- and APS-treated samples, which could be seen from the difference between the G_C and G_{TH} curves. As the aging time increased, the subcritical component decreased.

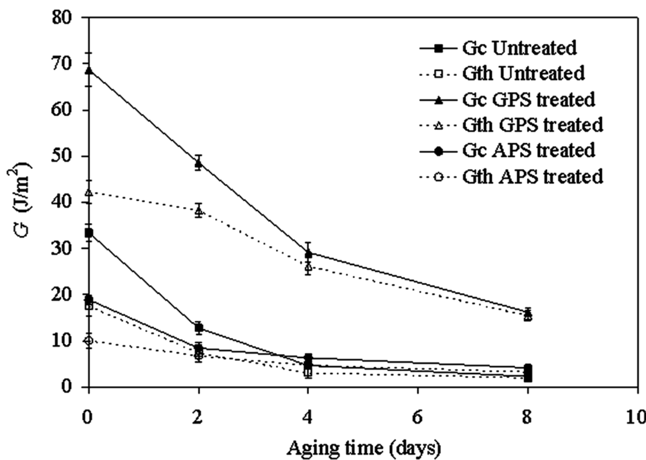

FIGURE 15 G_C and G_{TH} as a function of aging time under the 85°C/85% RH condition for untreated, GPS-, and APS-treated DCB specimens of the Bis F/UVI epoxy system.

For the Bis F/UVI system, a similar trend in G_C and G_{TH} has been observed. However, the difference between G_C and G_{TH} values, which relates to the subcritical component in the debonding process, dropped faster for the Bis F/UVI system compared with the Bis F/2,4-EMI system. In summary, as aging time increases, the role of subcritical debonding becomes less important compared with the critical debonding component. However, the presence of subcritical debonding at applied driving energies significantly below G_C has important implications for the long-term reliability of interfaces prone to time-dependent debonding.

4. CONCLUSIONS

The effect of surface chemistry and hygrothermal aging at 85°C/85% RH on subcritical debonding of epoxy/glass interfaces was studied. Two organosilane adhesion promoters with different active functional groups, APS and GPS, were used to treat borosilicate glass surfaces. Subcritical debonding results revealed that there are two regions, the threshold strain energy release rate (G_{TH}) and power law region, observed in subcritical debonding curves. Hygrothermal aging not only lowers the critical debonding driving energy required for debond extension but also lowers G_{TH}, below which interfacial crack growth does not occur. Interestingly, applying silane adhesion promoters on glass surfaces increased G_{TH} values and decreased debonding growth rate. Therefore, it can be concluded that the subcritical debonding growth rate mechanism is sensitive to interface chemistry. An attempt to correlate the results of critical and subcritical debonding was undertaken due to insufficient understanding of the relationship between critical and subcritical debonding. It was found that as aging time increased, the role of subcritical debonding became less important compared with the critical debonding component. However, the presence of subcritical debonding at applied driving energies significantly below G_C has important implications for the long-term reliability of interfaces prone to time-dependent debonding.

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