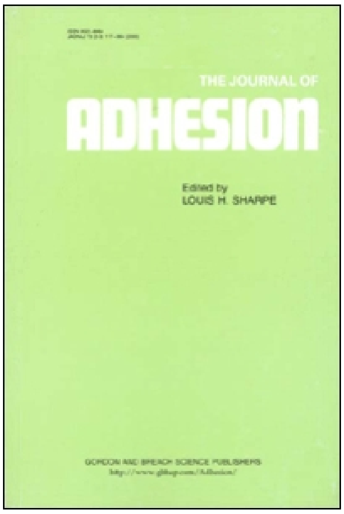

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Fatigue and Durability of Silane-Bonded Epoxy/Glass Interfaces

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Fatigue (slow) crack growth in epoxy/glass interfaces bonded with the silane coupling agent 3-aminopropyltriethoxysilane was studied under static and cyclic loading at 23°C, 95% RH using the double cleavage drilled compression test. Crack growth rates under cyclic loading were significantly greater than under static loading, in contrast to crack growth rate results in monolithic glass. After aging up to 34 h at 94°C in distilled water, the silane-bonded epoxy/glass specimens exhibited somewhat greater resistance to fatigue crack growth than the unaged samples; however, after aging at 98°C in distilled water and at 70°C in an aqueous KOH solution at pH 10, crack growth became cohesive and exhibited fractal behavior. Mechanisms for fatigue crack growth at silane-bonded epoxy/glass interfaces are proposed.

Keywords: Polymer adhesion; Epoxy/glass interfaces; Silane bonding; Fatigue crack growth; Durability

1. INTRODUCTION

Silane coupling agents are widely used to promote adhesion of polymers to glass [1, 2]. For these adhesive systems to perform satisfactorily, the interface must be resistant to crack growth under cyclic,

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as well as static, loading and must be durable when exposed to aggressive, aqueous environments.

Ritter *et al.* [3] measured moisture-assisted crack growth in epoxy/soda-lime and fused silica glass interfaces bonded with and without a silane coupling agent, 3-aminopropyltriethoxysilane (3-APES), using the double cleavage drilled compression (DCDC) test. They found that the resistance to moisture-assisted crack growth of untreated epoxy/glass interfaces under static loading at 95% RH and 23°C was significantly less than that of monolithic glass specimens. However, the resistance to moisture-assisted crack growth at silane-bonded epoxy/glass interfaces could be comparable with or greater than that of monolithic glass. Silane bonding of epoxy to glass was found to be more effective with fused silica than with soda-lime glass, with the fatigue limit of silane-bonded epoxy/fused silica interfaces being about 2.5 times greater than that for silane-bonded epoxy/soda-lime glass.

In this research, cyclic and static fatigue crack growth in epoxy/glass interfaces bonded with the silane coupling agent 3-APES was measured using the DCDC test before and after the samples were exposed to a range of accelerated aging conditions. Aging up to 36 h was carried out in distilled water at temperatures ranging from 70 to 98°C and 70°C in an aqueous KOH solution at pH 10. X-ray photoelectron spectroscopy (XPS) was used to characterize the nature of the silanized surface and to determine the influence of accelerated aging on the bonding between the silane 3-APES and the glass surface.

2. EXPERIMENTAL PROCEDURE

The DCDC specimen geometry is a rectangular beam (about 6.0 × 6.0 × 60 mm) with a hole (0.79 mm radius) drilled into the center, see Figure 1. The DCDC test was chosen because it has been shown that cracks tend to propagate at the interface even when the interfacial fracture toughness greatly exceeds the toughness of the adjoining materials [3, 4] due to the stabilizing role of the compressive load. Both monolithic soda-lime glass specimens and epoxy/glass sandwich specimens were tested. For the monolithic glass specimens, the rectangular beams (6.0 × 6.0 × 60 mm) were cut from a soda-lime glass plate and the cut edges were polished with 120 through 600 grit silicon carbide paper. For the epoxy/glass sandwich specimens, two

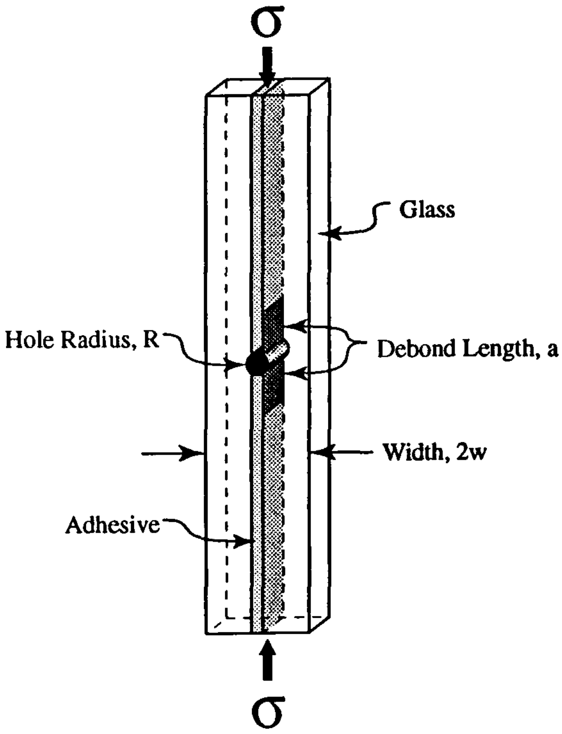


FIGURE 1 Schematic of the fracture mechanics double cleavage drilled compression (DCDC) specimen.

beams of glass (3.0 × 6.0 × 60 mm) were cut from the plates. To establish an interfacial precrack (about 3 mm) in the epoxy/glass specimens, a thin layer of Au (about 30 nm) was vapor deposited along a length near the center of one of the glass beams prior to the silanizing treatment. The glass beams were then cleaned in a 1 : 9 by volume solution of H_2O_2/H_2SO_4, rinsed in acetone, distilled water, and dried in a nitrogen chamber. To promote epoxy/glass adhesion, the glass beams were soaked for 5 min. in a 0.1 M aqueous solution of the silane coupling agent 3-APES (Fluka Chemical Corp.). It should be noted that in our previous study [3] the preparation of the glass surface for silanization was not as stringent, which contributed to relatively poor adhesion compared with the current results. Also, in our previous research the silanization time was 3 h. XPS results indicated that the silanized surface was saturated after about 3 min. Therefore, in this research the silanization time was reduced to 5 min. The beams were bonded together with an epoxy adhesive (2-Ton, Devcon Corp.) by pressing the bonded beam between stops that controlled the adhesive thickness at 40 μm (± 10 μm). After curing the epoxy for 24 hours in ambient air, the edges of the specimens were polished to eliminate any excessive adhesive that had squeezed out between the glass beams. A diamond core drill (radius 0.79 mm) was used to drill a hole through the center of each specimen.

To test the effects of aging in aggressive, aqueous environments, some specimens were aged in distilled water at temperatures from 70 to 98°C and in an aqueous KOH solution at pH 10. After aging, the samples were placed in a desiccator. All specimens were preconditioned in a high humidity environment (> 95% RH) for 1 hour prior to testing to equilibrate the specimens to the test condition.

With the DCDC test, compressive loading causes tensile stresses to develop at the poles of the drilled hole. Cracks then nucleate, extend from the poles, and propagate axially along the interface in the sandwich specimens. Finite element analysis [5] shows that the energy release rate, G, for a monolithic glass specimen is given by:

$$\sigma\left(\frac{\pi R}{GE'}\right)^{1/2}=\frac{w}{R}+\left(0.235\frac{w}{R}-0.259\right)\frac{a}{R} \qquad (1)$$

where σ is the compressive stress, R is the hole radius, a is the crack length, 2w is the specimen width, and E′ is equal to $E/(1-\nu^2)$ where E is the elastic modulus and ν is Poisson's ratio. The phase angle, ψ, for the monolithic glass specimen is 0° [5], which corresponds to pure normal, *i.e.*, mode I, loading at the crack tip. Because the adhesive layer is thin, G for the epoxy/glass sandwich is approximately equal to that of the monolithic glass specimen [6] and the phase angle for the epoxy/glass interface, given by the asymptotic solution of Suo and Hutchinson [6], is $-11°$.

The compressive load was applied in a servo-hydraulic Instron testing machine (Model 1321) that applied a constant or a sinusoidal load with a frequency of 3 Hz. Graphite foil was placed on the ends of the specimens to compensate for any surface roughness. The minimum load for all tests was set at 130 N, corresponding to a G of about 0.008 J/m^2. All tests were carried out at high humidity (> 95% RH) by enclosing the test fixture with a plastic envelope and then piping in moist air. After establishing a precrack to a length of about 3 mm, the load was cycled and crack growth was measured as a function of time using a Questar telescopic microscope, coupled to a television monitor (see Fig. 2). An analysis of this data using the finite difference between data points then gave the crack growth rate as a function of the applied G.

The adsorbed silane films before and after aging were studied using XPS with a Perkin-Elmer Physical Electronics 5100 operating at a pressure of 10^{-9} Torr with MgKα radiation (400 W). Each specimen was analyzed by a combination of a 89.45 eV survey and a 35.75 eV

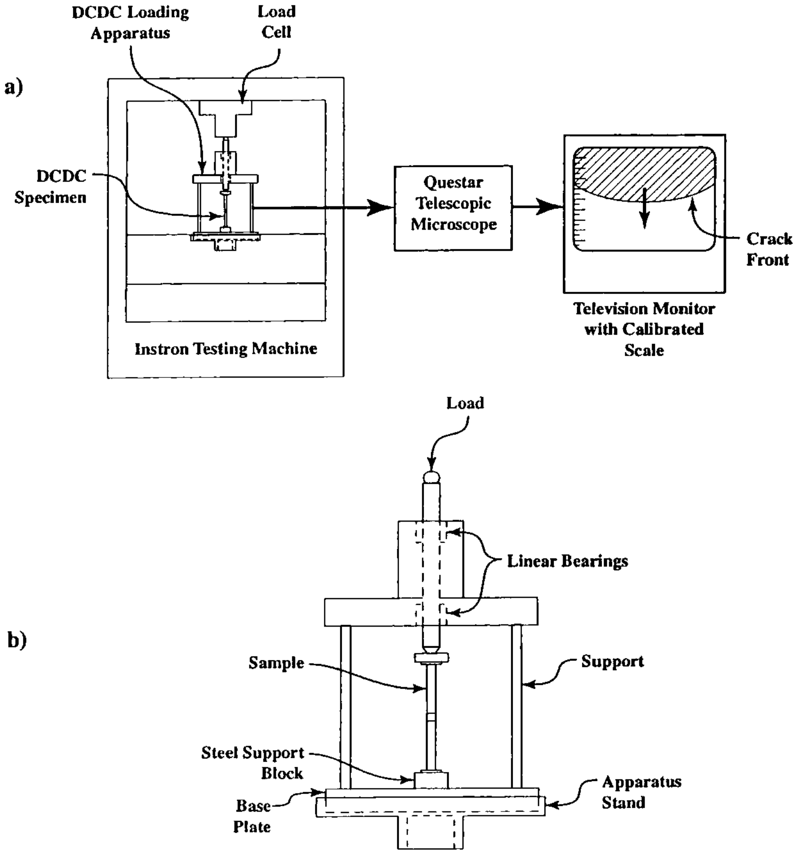


FIGURE 2 (a) Schematic of the DCDC test; (b) Schematic of the DCDC loading fixture.

multiplex scan for all the relevant elements that could be present: carbon, silicon, oxygen, nitrogen, sodium, calcium, and tin. Both the survey and high resolution scans were conducted at take-off angles of 15° and 75° to vary the analysis depth from approximately 1 nm to 4 nm. The fracture surface of failed specimens also were analyzed with XPS to identify the exact location of the interfacial crack path.

3. RESULTS AND DISCUSSION

3.1. XPS Analysis

Table I summarizes the XPS results for silanized soda-lime glass before and after aging. The presence of the silane 3-APES on the surface of the glass is readily detected by XPS by measuring the nitrogen concentration. Since clean glass contains no nitrogen, the nitrogen surface concentration is directly proportional to the number of aminosilane molecules deposited on the glass surface. The sharp nitrogen gradient observed in the as-silanized surfaces, where the N/Si ratio is 0.17 for the 15° take-off angle and 0.07 for 75°, indicates that the thickness of the silane layer is about 6–7 nm. For comparison, this represents about 10 monolayers since the stretched out length of a 3-APES molecule is about 0.67 nm [7].

These XPS results agree quite well with those of Wang and Jones [7] who found that a similar aminopropyltriethoxysilane formed a graded poly(aminosiloxane) network about 6 nm thick on an E-glass surface

TABLE I XPS results of silanized (3-APES) soda-lime glass before and after aging as compared with the clean glass surface

Take-off	*Clean glass*		*As-silanized*		*Silanized, aged* H_2O, *24 h, 98°C*		*Silanized, aged* *KOH, 4 h, 70°C*	
angle element	15°	75°	15°	75°	15°	75°	15°	75°
Atomic surface composition (%)								
C	30.8	10.4	54.0	17.6	47.4	20.4	43.2	14.5
Si	17.1	24.6	12.6	20.7	11.5	18.1	14.3	22.8
O	51.5	62.3	30.4	57.5	37.3	57.3	38.0	57.7
Na	0.1	0.3	0.2	0.7	0.8	1.2	1.4	2.2
Ca	0.1	0.9	0.2	0.8	0.5	1.1	0.5	1.1
Sn	0.5	1.5	0.5	1.4	0.5	0.5	0.6	0.5
N	0	0	2.2	1.5	1.8	1.2	2.0	1.2
N/S_i Ratio	0	0	0.17	0.07	0.16	0.07	0.14	0.05

with the cross-link density being greatest near the surface and with the silane molecules in the outermost layers probably being oriented perpendicular to the glass surface. The fact that the N/Si ratio is not affected by aging in water at 98°C and in an aqueous KOH solution at 70°C indicates that this poly(aminosioxane) network is well adhered to the glass surface.

From the results in Table I it can be seen that the cleaning procedure tends to leach the sodium and calcium ions from the glass surface but, on aging in either hot water or KOH solutions, these ions diffuse back to the glass surface and into the poly(aminosiloxane) network. Pawson and Jones [8] also found that for a similar silane deposited on AR-glass, the poly(aminosiloxane) network could not be removed by aging in boiling water and that sodium ions in the glass can readily diffuse into this poly(aminosiloxane) layer. Finally, it should be noted that the presence of tin in the surface of the glass is the result of the glass being manufactured by the float-glass process. From the XPS results it is evident that this tin diffuses into the poly(aminosiloxane) network on the surface of the glass.

3.2. Monolithic Glass

Moisture-assisted crack growth in monolithic soda-lime glass provides a useful baseline for evaluating crack growth at silane bonded epoxy/glass interfaces under static and cyclic loading. Crack growth under static loading, known as stress corrosion, is relatively well understood in silicate glasses [9] where crack growth results from a chemical reaction between the water molecules and the stressed Si—O—Si bonds near the crack tip. The crack growth rate, V_s, under static loading, is generally characterized by a simple power law function of the applied energy release rate, G:

$$V_s = AG^n \tag{2}$$

where A and n are constants dependent on the glass and environmental conditions. Because of the lack of plasticity in silicate glasses, crack growth under cyclic loading is generally found to be a manifestation of moisture-assisted crack growth. Evans and Fuller [10] showed that the crack growth rate under cyclic loading, V_c, could be predicted by replacing G in Eq. (1) with the time-dependent applied

G(t) and integrating Eq. (1) over the applied loading cycle to obtain:

$$V_c = gA\,(G_{\max})^n \qquad (3)$$

where g is a constant (less than one) that is a function of the loading wave form, frequency, the crack growth parameters A and n, and $G_{\max}$ is the maximum G of the loading cycle.

Crack growth rate data in monolithic soda-lime glass obtained under static and cyclic loading at 95% RH are shown in Figure 3. To expedite such comparisons, the data in Figure 3 used $G_{\max}$ in the cyclic loading as equivalent to G for static loading and the number of loading cycles was converted to time, as the frequency of loading was constant at 3 Hz. It is seen that the crack growth rates under both static and cyclic loads can be best-fit with Eqs. (2) and (3), respectively, with $n = 10.15$ and that the cyclic crack growth rates are considerably less than those measured under static loads at $G_{\max} = G$. This decrease in crack growth rates is given by Eq. (3) where the predicted g equals about 0.05, in agreement with the experimental data. This indicates an

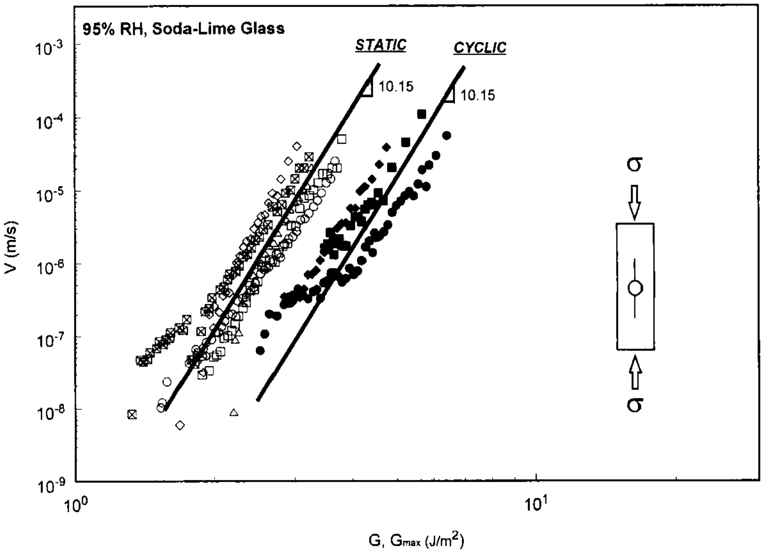


FIGURE 3 Comparison of fatigue crack growth rates in soda-lime glass under static and cyclic loading as measured by the DCDC test at 95% RH. Note that the different data symbols indicate the individual experimental runs.

absence of a mechanical cyclic fatigue effect involving plasticity at the crack tip. Finally, it should be noted that these fatigue results for soda-lime glass agree well with those in Ref. [10].

3.3. Silane-bonded Epoxy/Glass Interface

Figure 4 compares the fatigue crack growth rates under static and cyclic loading at 95% RH of soda-lime glass with that of the silane-bonded epoxy/glass interfaces. It is evident that the silane-bonded epoxy/glass interface exhibits significantly greater resistance to fatigue crack growth, *i.e.*, it takes a greater G to drive the crack at a similar velocity, under both static and cyclic loading, than the monolithic glass. Also, it is important to note the larger experimental scatter exhibited by the epoxy/glass interface data. This is undoubtedly related to the microstructural variability of the epoxy adhesive from sample to sample. Further, in contrast to monolithic glass, crack growth rates for the silane-bonded epoxy/glass interface are increased by cyclic loading. To demonstrate a cyclic fatigue effect unequivocally, crack growth along a silane-bonded epoxy/glass interface was

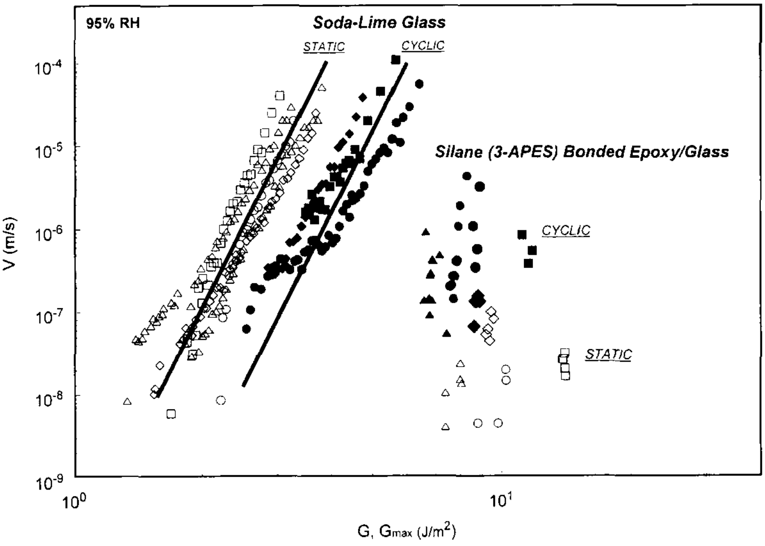


FIGURE 4 Crack growth rates along 3-APES silane-bonded epoxy/glass interfaces under static and cyclic loading compared with those for monolithic soda-lime glass.

measured under static and cyclic loading on the same specimen. Figure 5 gives crack length as a function of time at 95% RH under alternating static and cyclic loading conditions where the static G is approximately equal to the cyclic G_{max}. It is apparent from the figure that upon or with application of cyclic loading crack growth rates are increased, thus, confirming the existence of a mechanical cyclic fatigue effect.

Microscopic observation of the interfacial crack path and the fatigue crack surfaces indicated that the fatigue crack propagated in the epoxy/glass interface, resulting in one of the crack surfaces being essentially glass and the other epoxy. Angular-dependent XPS analysis of the glass fatigue crack surface was done to determine more accurately the exact location of the crack path. Table II summarizes these results. The similarity of these results to those for the as-silanized glass surface (Tab. I) indicates that the fatigue crack propagated in the interphase region formed by the epoxy and poly(aminosiloxane) network. Note that the somewhat greater nitrogen concentration at the 15° take-off angle and the higher carbon content at the 75° take-off

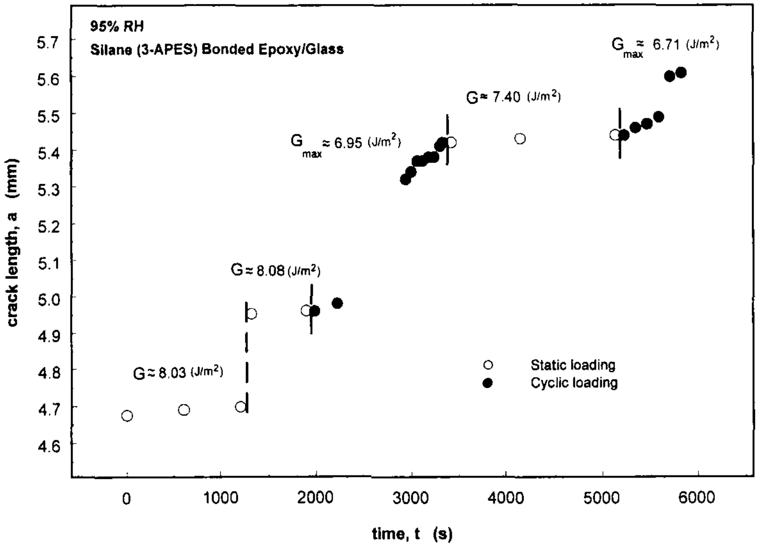


FIGURE 5 Comparison of fatigue crack growth along a 3-APES silane-bonded epoxy/glass interface under alternating static and cyclic loading.

TABLE II XPS analysis of the fatigued crack surface (glass side) from a silane (3-APES) bonded epoxy/glass clean glass surface

Take-off angle element	15°	75°
Atomic surface composition (%)		
C	48.1	49.3
Si	9.7	16.6
O	38.6	32.0
Na	0.6	0.2
Ca	0.4	0.3
Sn	0.1	0.2
N	2.6	1.2
N/S_i Ratio	0.27	0.07

angle is consistent with the fact that the epoxy phase penetrated into the poly(aminosiloxane) network.

It is also important to note that a power law fit through either the cyclic or static fatigue data of the silane-bonded epoxy/glass specimens (Fig. 4) would give an n value considerably greater (> 50) than that of the monolithic glass. This implies that the mechanism of fatigue crack growth in silane bonded epoxy/glass interfaces is distinctly different from the stress corrosion mechanism of monolithic soda-lime glass.

For cracks growing on a epoxy/glass interface, the fracture resistance of the interface is determined principally by two energy-absorbing mechanisms in the crack tip region [11, 12]. The first involves the energy to rupture the bonds to create the fracture surfaces and the second is the work dissipated in any plastic and viscoelastic deformation of the ductile layer. With relatively strong interfacial bonding, high stresses are needed around the interfacial crack to rupture the bonds. These stresses then induce plastic and viscoelastic deformation. For unmodified epoxy/glass interfaces Liechti and Chai [11] found that for phase angles close to 0° (as with the DCDC specimen), the contribution of plasticity and viscoelasticity to the fracture toughness (about $5\,J/m^2$) was less than 10%. Since the XPS results of the current research indicate that fatigue crack growth occurred in the silane layer at the epoxy/glass interface, it is believed that fatigue crack growth at the epoxy/glass interface involves the rupturing of Si—O—Si bonds in the poly(aminosiloxane) network by the water molecules, as well as the breaking of C—C, C—N, and C—O bonds of the penetrating epoxy phase. It is believed that this primary bond rupturing is the major contribution to the fatigue resistance of the silane-bonded epoxy/glass interfaces. However, there now exists a complex interaction between the bond-rupturing and plasticity effects occurring at the crack tip. It is the plasticity effect that gives rise to the mechanical cyclic fatigue effect.

Figure 6 compares cyclic crack growth rate data before (unaged) and after the silane-bonded epoxy/glass samples were aged in distilled water at 70°C for 1 or 3 h, 90°C for 3, 12, or 36 h, and 94°C for 3, 10, or 34 h. Note that unaged data in addition to that shown in Figure 4 are given in Figure 6. Since the aged data for the different aging conditions were not significantly different from each other, all the aged data were pooled together as shown in Figure 6. It is evident that accelerated aging did not decrease the resistance of the silane-bonded epoxy/glass interface to crack growth and, in fact, may have caused a modest increase in the resistance of the interface to fatigue crack growth.

To determine if this aging in distilled water affected the plasticity of the epoxy, the Vickers hardnesses [13] of silane-bonded epoxy coatings on glass were determined after aging. After aging for 4 h at 94°C in

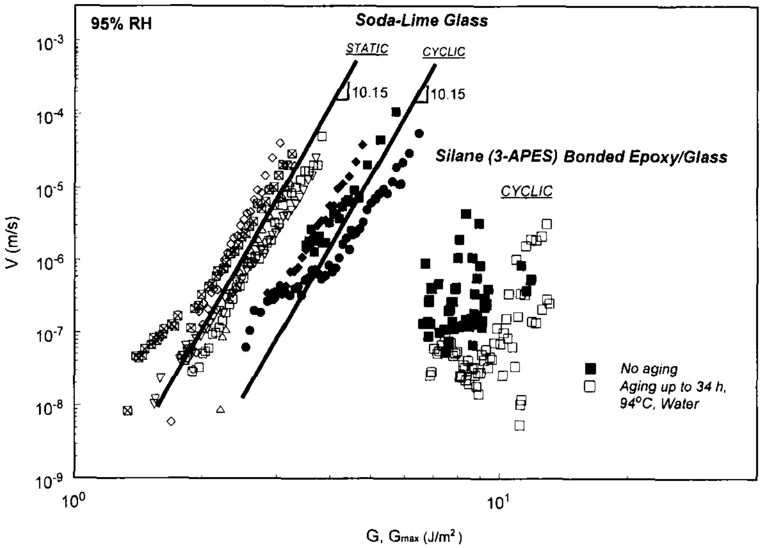
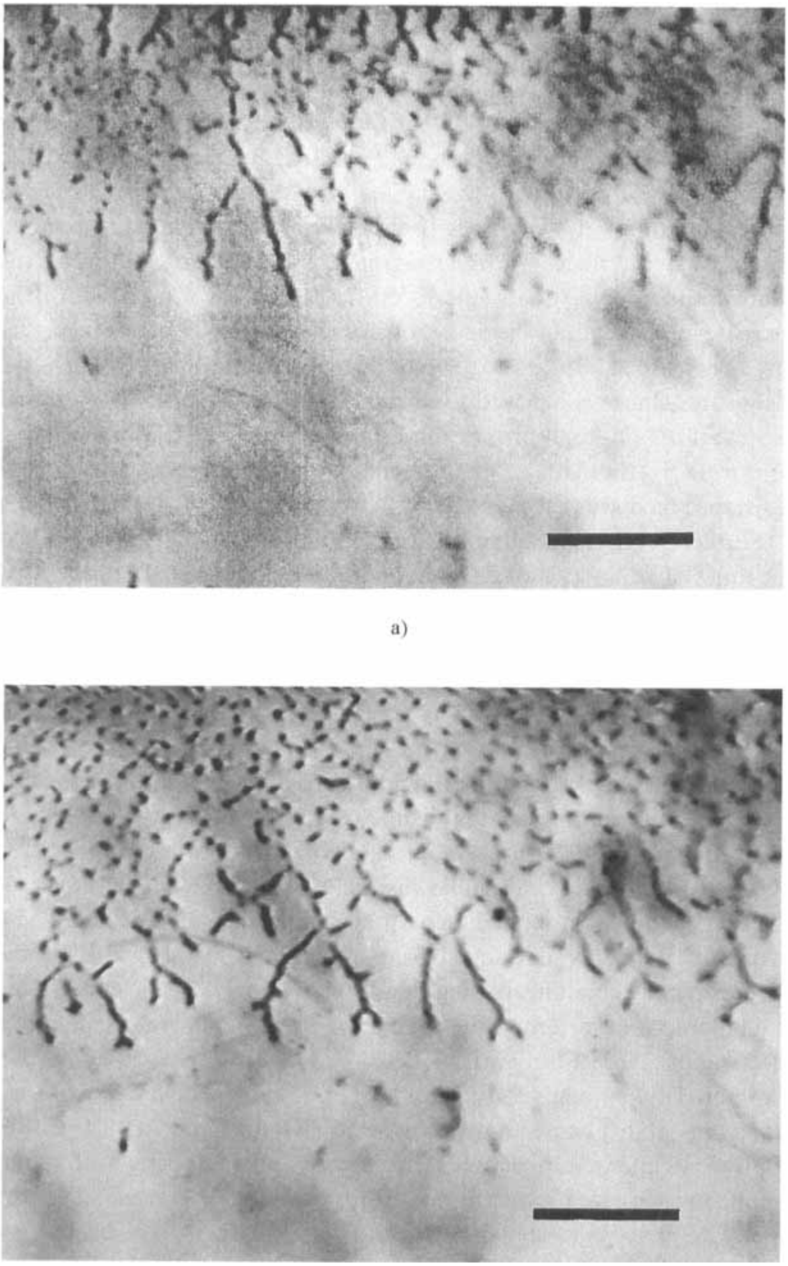


FIGURE 6 Comparison of fatigue crack growth rates in soda-lime glass with that at 3-APES silane-bonded epoxy/glass interfaces before and after accelerated aging in water up to 94°C, 34 h.

water, hardness decreased about 40% and after 24 h at 94°C, hardness further decreased to about 50% of the initial value. For 70%C aging in water, hardness decreased about 15% after 3 h and 25% after 24 h. This decrease in hardness with aging would be expected to lead to greater plasticity associated with crack growth at the silane-bonded epoxy/glass interface. The increase in the fracture resistance of the silane-bonded epoxy/glass interface after aging is consistent with the increase in plasticity of the epoxy on aging. The reason that a relatively large decrease in hardness corresponds to only a modest increase in the fatigue resistance is believed to be due to the fact that plasticity effects represent only a small proportion of the total fatigue resistance. Bond rupturing is thought to be the main contribution to the fatigue resistance as discussed above.

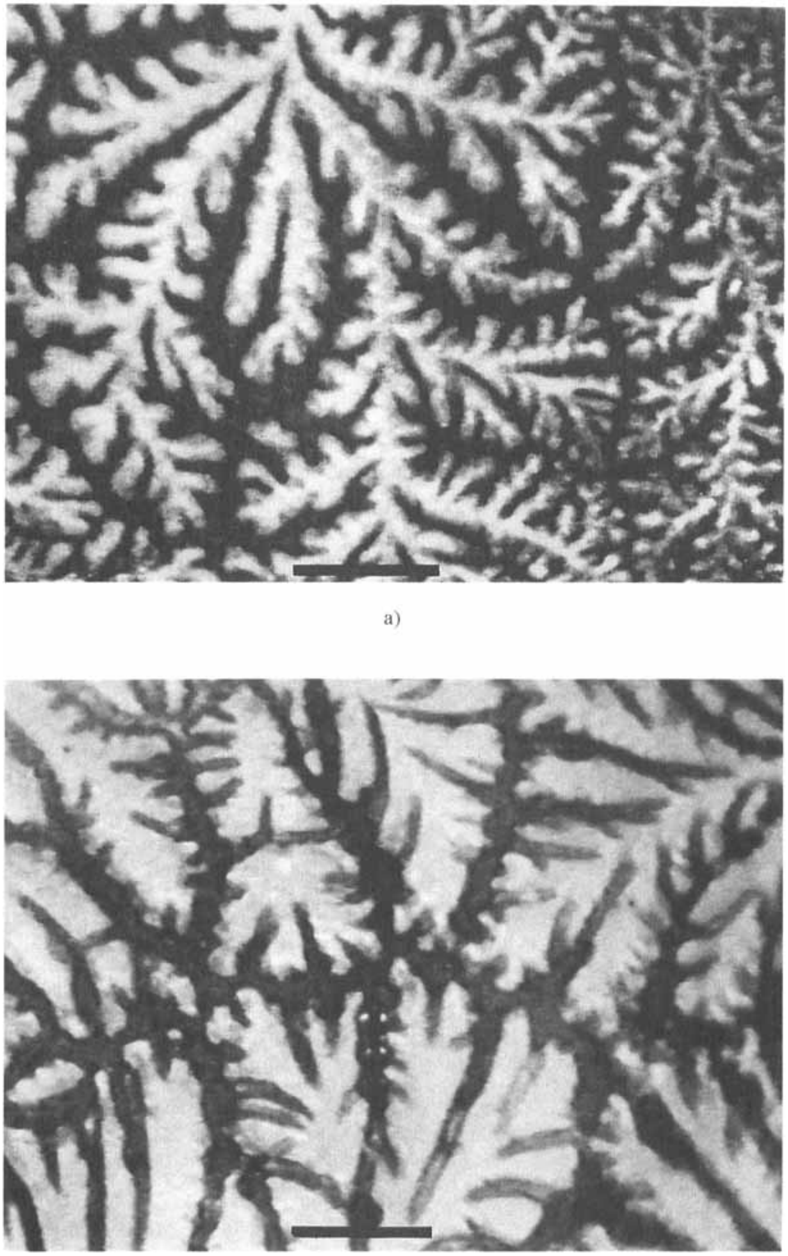
Further accelerated aging was carried out in distilled water at 98°C for times of either 1, 3, or 24 h and in a KOH solution (pH 10) at 70°C for 4 h. For these aging conditions, cyclic fatigue crack growth at the silane-bonded epoxy/glass interface was largely cohesive and became dendritic in character, where instabilities at the interface between the glass and epoxy produced many small fingers that grew with further dendritic branches forming off the main branch. Figure 7 shows this dendritic-like crack growth originating from the hole of the DCDC specimen for a sample aged in distilled water at 98°C for 3 h. Aging in distilled water at 98°C for 24 h or in aqueous KOH solution (pH 10) at 70°C for 4 h caused finger-like instabilities to form at the edges of the specimen almost immediately upon application of the load. These instabilities quickly developed into fingers across the width of the specimen and these fingers then thickened with time, see Figure 8. The fractal fracture patterns that developed in the epoxy/glass interface after aging at 98°C in water or 70°C in KOH are analogous to a Saffman-Taylor meniscus instability [14, 15]. It is believed that this fractal instability came about because accelerated aging at 98°C causes a physical interaction between the epoxy and ingressing water that results in excessive plasticization of the epoxy [1]. This then causes the epoxy to behave as a "viscous fluid" as the two glass beams are separated during the DCDC test. In fact, it was noted that after these aggressive aging treatments the epoxy was tacky and the two glass beams of the epoxy/glass sandwich specimens could slide off one another with finger pressure.



a)

b)

FIGURE 7 Dendritic-like crack growth in a 3-APES silane-bonded epoxy/glass specimen aged in distilled water at 98°C for 3 h. (a) after about 3 min. under load (b) after about 10 min. under load. Bar in photograph represents 0.4 mm.



a)

b)

FIGURE 8 Cohesive, fractal crack growth in a 3-APES silane-bonded epoxy/glass specimen aged in distilled water at 98°C for 24 h. (a) after about 7 min. under load (b) after about 10 min. under load. Bar in photograph represents 0.4 mm.

4. CONCLUSIONS

Similar to monolithic glass, moisture-assisted crack growth under cyclic or static loading at a silane (3-APES) bonded epoxy/glass interface is thought to involve water molecules rupturing the strained Si—O—Si bonds in the poly(aminosiloxane) network. The stresses needed for this bond rupture at the interfacial crack tip also induced plastic deformation in the epoxy layer. It is this complex coupling of bond-rupturing and plasticity effects that leads to a greater sensitivity of the fatigue crack growth rate to the applied energy release rate. The plasticity effects at the crack tip also results in both an increase in the fatigue resistance of the silane-bonded epoxy/glass interfaces, as compared with monolithic glass, and the mechanical cyclic fatigue effect. Aging in aggressive, aqueous environments causes excessive plasticization of the epoxy before a breakdown of the poly(aminosiloxane) network at the epoxy/glass interface. This causes the epoxy to act as a "viscous fluid", resulting in crack growth becoming cohesive and fractal in nature.

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