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Fatigue resistance of silane-bonded epoxy/glass interfaces using neat and rubber-toughened epoxies

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The influence that the energy absorbing ability of an epoxy has on the cyclic fatigue resistance of a silane-bonded epoxy/glass interface in moist air was studied using the double cleavage drilled compression (DCDC) test. The material properties of two epoxies with similar chemical structures were controlled through the manipulation of the molecular weight between cross-links, M_c, of the epoxy network. Two rubber-toughened epoxies with different nominal particle sizes (10–40 μm and 1–2 μm) were fabricated by adding a liquid butadiene/acrylonitrile copolymer to the epoxy resins. Mixtures of the silane-coupling agents 3-aminopropyltriethoxysilane (3-APES) and propyltriethoxysilane (PES) were used to treat the glass substrate in order to control the number of covalent bonds between epoxy and the glass. 3-APES has the ability to form primary bonds with both the epoxy and the glass, while PES forms primary bonds with only the glass. Experimental results showed that the manipulation of M_c had little effect on the cyclic fatigue resistance of the epoxy/glass interface. However, incorporation of rubber particles gave a significant improvement in the fatigue resistance. The rubber particles allowed the microscopic, non-linear deformation mechanisms of cavitation and shear yielding to dissipate energy during fatigue crack growth. Smaller particles gave the greatest improvement to fatigue resistance; about a 75% improvement compared to the neat (non-modified) epoxy. Adjustment of the number of silane bonds between the neat epoxies and the glass had little effect within experimental scatter on the fatigue resistance of the interfaces, suggesting that the energy dissipated through the breaking of bonds at the interface was insignificant compared to the energy dissipated through plastic and other inelastic deformation mechanisms in the epoxy. © *2002 Kluwer Academic Publishers*

1. Introduction

For catastrophic crack propagation along a ductile/brittle interface, the fracture toughness of the interface is determined principally by two energy absorbing mechanisms in the crack tip region [1]. 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 other inelastic deformations of the ductile layer. Kramer and coworkers [2] noted that when one of these materials is a polymer, mechanisms such as crazing and shear yielding can absorb large amounts of energy prior to crack propagation. This energy absorption increases the total amount of energy that must be applied to the interface to extend a crack. It is the basic assumption of this research that cracks propagating sub-critically, such as in cyclic fatigue, are governed by the same toughening mechanisms.

Kramer and coworkers [2, 3] were able to increase the fracture toughness, G_c, of a polystyrene/glass interface from 1 J/m^2 to 40 J/m^2 by modifying the interface with a deuterated PS − poly(2 vinylpyridine) (dPS-PVP) diblock copolymer. The unmodified PS/glass interface had a low fracture toughenss (1 J/m^2) because the bonding between the PS and glass was due to weak secondary forces that were insufficient to generate high enough stresses at the crack tip to cause inelastic deformation in the polystyrene. For the modified interfaces, the PVP side of the copolymer adheres itself well to the glass while the dPS block is sufficiently long to entangle in the PS homopolymer. This permits high enough stresses across the interface to allow energy dissipation through the formation of a craze in the PS adjacent to the interface and subsequent breakdown of the craze by pull-off of the PVP anchor from the glass. Kramer *et al.* [2] noted that for cross-linked polymers, such as epoxy, shear yielding could be the inelastic deformation mechanism for increasing fracture toughness of the interface.

Pearson and coworkers [4–8] were able to induce shear yielding in a bulk epoxy through the incorporation

of rubber particles. The rubber was incorporated into the matrix by adding a liquid carboxyl-terminated butadiene nitrile (CBTN) rubber to the resin. The rubber particles precipitate out during curing with their size dependent upon the solubility of the copolymer. During crack propagation, rubber particles smaller than the plastic zone ahead of the crack tip first cavitate, dissipating bulk strain energy, then the voids left behind by the cavitated particles act as stress concentrators, allowing shear-strain to build up to the point where shear yielding can take place. Rubber particles larger than the plastic zone did not cavitate, providing a slight improvement in toughness through a crack bridging mechanism. For the epoxy modified with small particles ranging from 1–2 μm, fracture toughness was increased by a factor of eight compared to that of the corresponding neat epoxy (180 J/m^2). A "stress-whitened zone" caused by scattering of light from the voids was birefringent under crossed polarized light, which suggested the presence of shear bands [5–7]. Resistance to fatigue crack propagation (FCP) showed similar toughening mechanisms [8].

In our previous research [9–12], a well-bonded epoxy/glass interface was achieved by modifying the interface with the silane-coupling agent 3-aminopropyltriethoxysilane (3-APES). The improved adhesion over unmodified interfaces occurs because of the ability of 3-APES to form primary covalent bonds with both the epoxy and the glass. The cyclic fatigue resistance of the interfaces tested in moist air, as measured by the maximum energy release rate of the loading cycle necessary to drive a crack at 10^{-6} m/s, increased from 2–4 J/m^2 for an unmodified interface to about 8–10 J/m^2 for the silane-modified interfaces [9, 11]. Control of the density of bonds at the epoxy/glass interfaces was also achieved by modifying the interface with mixtures of the silane-coupling agents 3-APES and propyltriethoxysilane (PES) [12]. Both the 3-APES and the PES chemically bond to the glass through primary Si—O—Si bonds but only 3-APES can bond directly to the epoxy through the terminal amine group. By using 3-APES, PES, or mixtures of the two to silanize the glass surface, the total density of primary bonds between the silane and epoxy was systematically varied. As the amount of 3-APES was increased from 0 to 100%, the cyclic fatigue resistance of the interfaces increased approximately linearly from about 2 J/m^2 to 8–10 J/m^2. The epoxy used in these experiments was the Devcon 2-ton commercial epoxy.

The purpose of this research is to study the influence that the energy dissipating ability that an epoxy has on the cyclic fatigue resistance of various silane-bonded epoxy/glass interfaces. To test the effects that the material properties of a neat (non-rubber-toughened) epoxy have on the fatigue resistance of the interface, a high and a low strength epoxy were fabricated by manipulating the molecular weight between cross-links, M_c, of the epoxy network. Crawford and Lesser [13] found that material properties of a bulk neat epoxy could be controlled through the adjustment of M_c. In their work, the resin Epon 825, a diglycidyl ether of bisphenol A (DGEBA), was cured with differing ratios of ethylenediamine (ED) and 3-methoxypropylamine (3-MPA). The ED reacts with four epoxide molecules, cross-linking the network, while the 3-MPA reacts with only two, extending the length of each chain. By varying the ratio of the two amines, M_c was systematically controlled and the yield strength of the epoxy was varied from 85 to 55 MPa for $M_c = 0.38$ and 2.14 kg/mol, respectively. When fracture toughness tests were carried out on the epoxies the critical energy release rates increased from 190 to 6000 J/m^2 over the same range of M_c, with the lowest M_c epoxies failing in a brittle manner and the highest failing in a ductile manner. For our research the Epon 825 resin was cured with ED and n,n'-dimethylethylenediamine. The latter serves the purpose as the 3-MPA, however, it more closely resembles the structure of the ED. To determine if cavitation and shear yielding could improve the fatigue resistance of the interface, two rubber-toughened epoxies with different nominal particle sizes (10–40 μm and 1–2 μm) were fabricated by adding a liquid copolymer (CTBN) to the epoxy resin. The glass substrates were silanized with mixtures of 3-aminoproplytriethoxysilane (3-APES) and propyltriethoxysilane (PES) to determine the influence of interfacial bonding. The resistance of these interfaces to crack growth under cyclic loading was measured in moist air (>95% R.H.) at room temperature (24°C) with the fracture mechanics double cleavage drilled compression (DCDC) test. Some tests were conducted at 60°C to determine the influence of temperature. Data from our previous research [9–12] of silane-bonded interfaces using a commercial epoxy were used for comparison.

2. Experimental procedure

The neat High Strength Epoxy (HSE) and the Low Strength Epoxy (LSE) were fabricated by curing the Epon 825 resin obtained from Shell Chemical Co. with different ratios of the hardeners ethylenediamine and n,n'-dimethylethylenediamine (Fluka Chemical Corp.). Table I shows the mole fractions of the hardeners used and the corresponding M_c. Φ_4 and Φ_2 refer to the mole fractions of ethylenediamine and n,n'-dimethylethylenediamine, respectively. M_c was calculated from reaction stoichiometry [14].

The tensile yield strength of the HSE and LSE are 91 and 50 MPa, respectively, and the glass transition temperature are 145°C and 60°C [13, 14]. Cure schedules for the epoxies are discussed below. The two rubber-toughened epoxies were created by adding one of the two liquid reactive rubbers, 10% by weight of the resin, to the resin before curing. The two rubbers were Hycar's CTBN 1300X31 and CTBN 1300X13. Each rubber is first adducted with the resin before curing to ensure that

TABLE I Mole fractions of neat epoxies and respective M_c

	Φ_4	Φ_2	M_c
HSE	1.0	0.0	390
LSE	0.3	0.7	1,350

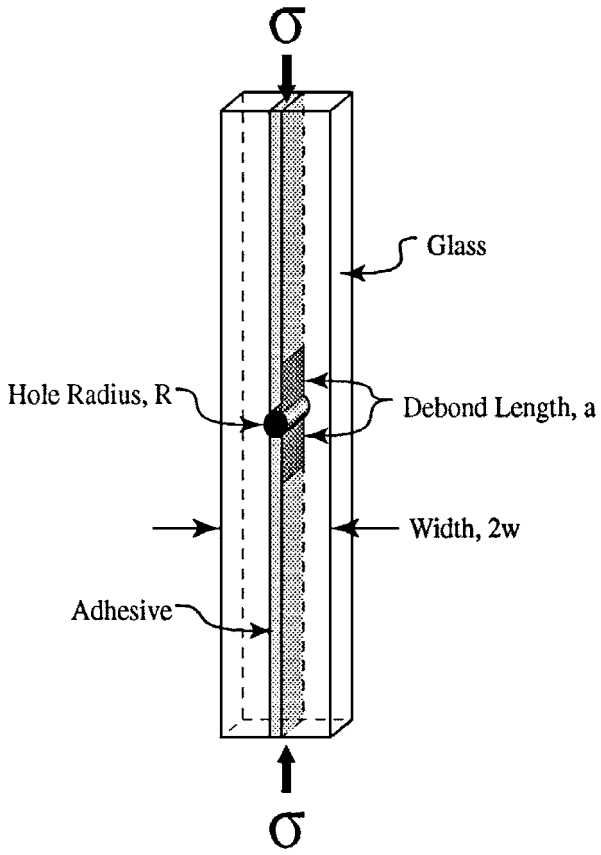

Figure 1 Schematic of the fracture mechanics double cleavage drilled compression (DCDC) specimen.

it was fully reacted with the resin. To adduct the rubbers, each was proportionally mixed with the resin and placed in a 110°C oven for 1.5 hours. Both modified resins were then cured in the same manner as the HSE. The HSE was chosen because the plastic zone size was thought to be smaller that that of the LSE. The 1300X31 yielded large particles (HSELP) ranging nominally from 10–40 μm and the 1033X13 yielded small particles (HSESP) ranging nominally from 1–2 μm upon curing.

The DCDC specimen geometry is a rectangular beam (about $6.0 \times 6.0 \times 60$ mm) with a hole (0.79 mm radius) drilled into the center (see Fig. 1). For the epoxy/glass sandwich specimens, two beams of glass ($3.0 \times 6.0 \times 60$ mm) were cut from plates. To establish an interfacial pre-crack (about 3 mm) in the epoxy/glass specimens, a thin layer of chrome followed by a thin layer of gold (each about 3 nm thick) were 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/H_2SO_4, rinsed in acetone, methanol, and distilled water, before drying in a nitrogen chamber. To silanize the glass surface, the glass beams were soaked for 5 min. in a 0.1 M aqueous solution of the silane coupling agents 3-APES or mixture of 3-APES/PES. These silane coupling agents were obtained from Fluka Chemical Corp. The silanized beams were bonded together with the desired epoxy adhesive by pressing the bonded beam between stops that controlled the adhesive thickness at 40 μm (± 10 μm). The epoxy was cured by placing the specimens in a 50°C oven for 3 hours. After 3 hours the temperature was raised to 20°C above the T_g of the epoxy and post-cured for 3 additional hours. The T_g for the HSE and LSE are 145 and 60°C, respectively [14]. After curing, the edges of the specimens were polished to eliminate any excess adhesive that had squeezed out between the glass beams. The ends were polished using a squaring fixture. A diamond core drill (radius 0.79 mm) was used to drill a hole through the center of each specimen.

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 [15] shows that the energy release rate G for a monolithic glass specimen is given by:

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

where σ is the compressive stress, R is the hole radius, a is the crack length, $2w$ is the specimen width, and $\bar{E}$ is equal to $E/(1-\nu^2)$ where E is elastic modulus and ν is Poisson's ratio. Since the adhesive layer is thin, G for the epoxy/glass sandwich is approximately equal to that of the monolithic glass specimen [16] and the phase angle for the epoxy/glass interface, given by the asymptotic solution of Suo and Hutchinson [16], is $-11°$. This negative phase angle tends to deflect the interface crack into the epoxy, however, such defection cannot occur because of the relatively high toughness of the epoxy, thus, allowing interfacial crack growth at the interface even though the adjoining glass has a considerably lower fracture toughness.

The compressive load was applied in a servo-hydraulic Instron testing machine (Model 1321) that applied 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 the cyclic tests was set at 130 N, corresponding to a G_{min} of about 0.008 J/m^2. All tests were carried out in a moist environment at 24°C by enclosing the test fixture with a plastic envelope and then piping in moist air with >95% R.H. For the elevated temperature test, hot air was pumped into the envelope. After establishing a pre-crack 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 with television monitor (see Fig. 2). An analysis of this data using the finite difference between data points then gave the crack velocity as a function of the applied G.

3. Results and discussion

3.1. Neat epoxies

Fig. 3 shows the cyclic fatigue crack growth rate as a function of the maximum G of the loading cycle, G_{max}, for the 100% 3-APES bonded non-rubber-toughened epoxy/glass interfaces. The cyclic fatigue behavior of the interfaces involving the neat epoxies with the controlled material properties (HSE and LSE) show little difference with respect to each other within the experimental scatter. However, the cyclic fatigue resistance,

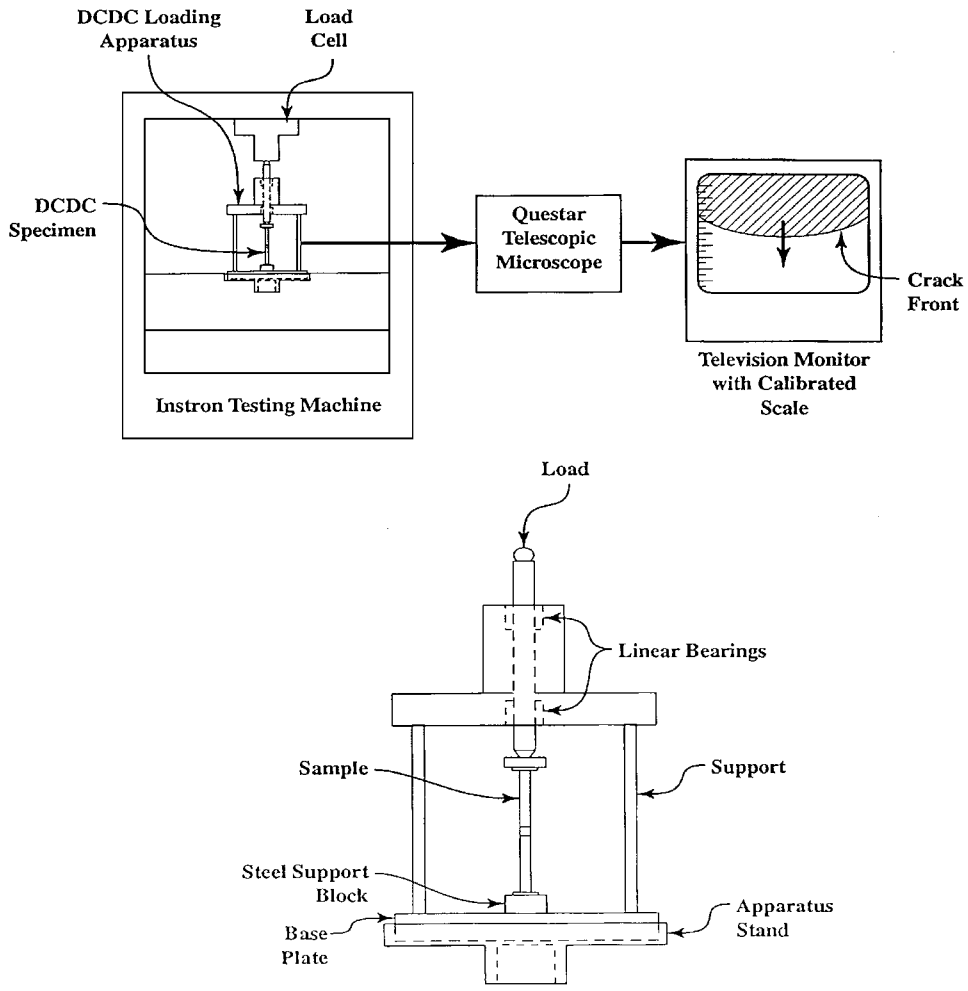

Figure 2 Schematic of the DCDC test and loading fixture.

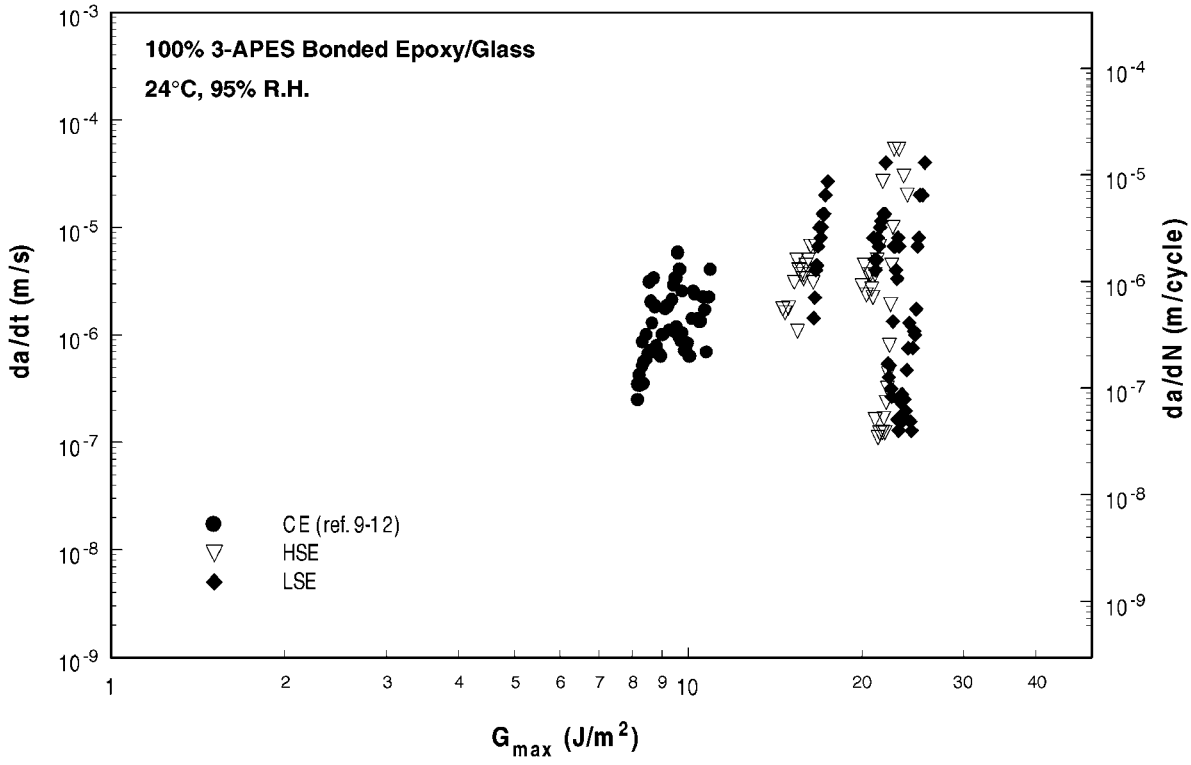

Figure 3 Comparison of the cyclic fatigue crack growth rate results for the 100% 3-APES bonded epoxy/glass interfaces using the various non-rubber-toughened epoxies.

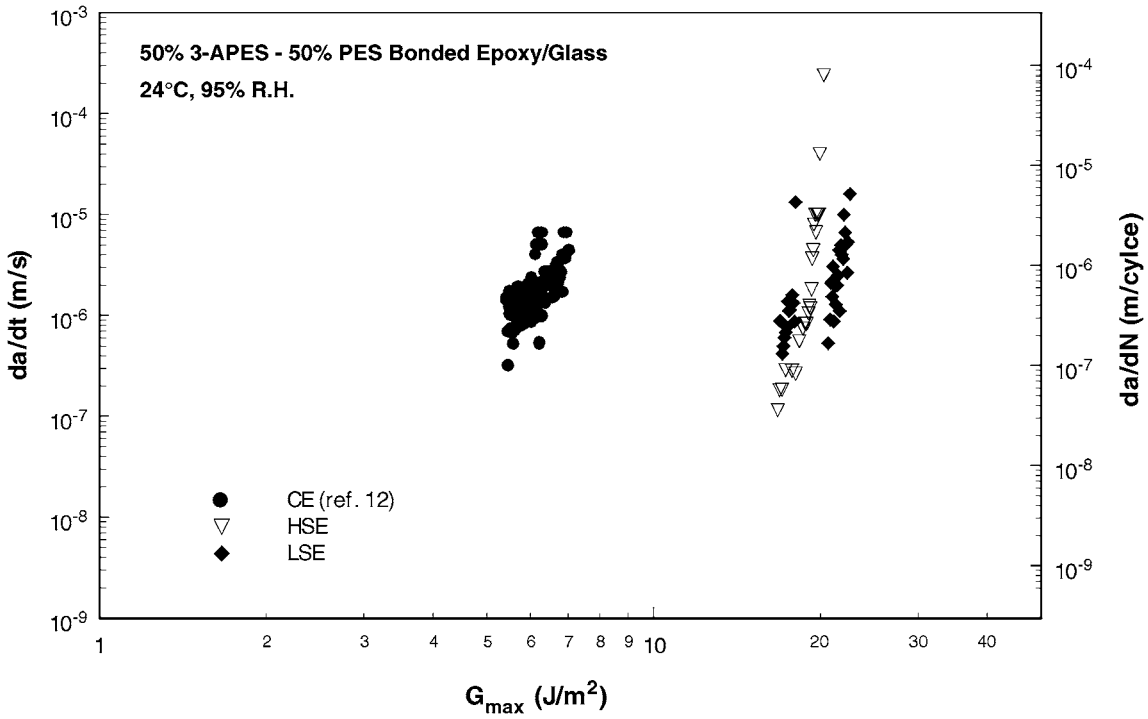

Figure 4 Comparison of the cyclic fatigue crack growth rate results for the 50% 3-APES – 50% PES bonded epoxy/glass interfaces using the various non-rubber-toughened epoxies.

as measured by $G_{\max}$, of the interfaces using these epoxies is about twice as great as those from our previous research [9–12] using the commercial epoxy (CE). Due to the high $G_{\max}$ needed to drive the crack at the interfaces involving the HSE and LSE, the crack frequently kinked into the glass before data could be recorded. For the HSE, fourteen DCDC tests were run and data was recorded from only three. With the remaining eleven tests, the crack either kinked into the glass or the specimen failed from a flaw at the ends of the glass before measurements were taken. The ratio of successful tests to non-successful tests for the LSE was 4 : 12. Therefore, the data used to calculate the $G_{\max}$ needed to drive the crack may be biased, with data from only the weakest interfaces being recorded. It should be noted that the tendency of the interfacial crack to kink out of the interface and form a glass chip has previously been observed in metal-ceramic interfaces [17] and occurs when the crack encounters a preexisting flaw in the glass surface at the interface.

Due to the high propensity for the crack to deviate into the glass substrate, an attempt was made to weaken the adhesion of the interface by decreasing the number of primary bonds between the epoxy and glass. This decrease was accomplished by silanizing the glass with a solution of 50% 3-APES and 50% PES [12]. It was also thought that any influence due to differences in the plasticity of the HSE and LSE epoxies may become more pronounced with the decrease in the number of silane bonds. Fig. 4 shows the cyclic fatigue crack growth rate results for the 50% 3-APES-50% PES bonded epoxy/glass interfaces using the various non-rubber-toughened epoxies. The fatigue resistance for the HSE and LSE is about 3 times greater than that for CE [12]. However, any differences that exist between the HSE and LSE are still well within experimental scatter. Note that the interfacial crack still had a tendency to deviate into the glass since the G_{max} values are still high and not significantly different from the results of the 100% 3-APES (Fig. 3). The ratios of successful to non-successful DCDC tests for the HSE and LSE using 50% 3-APES – 50% PES were 1 : 5 and 2 : 2, respectively.

3.2. Effect of silane

Fig. 5 shows the cyclic fatigue crack growth rate results for the various silane-bonded epoxy/glass interfaces using the HSE. The HSE was tested with a silane ratio of 25% 3-APES –75% PES because of the crack's continued tendency to kink into the glass, however the LSE was not tested at this ratio since differences in the fatigue resistance of the interfaces using the two epoxies were not seen previously. As seen in the figure, there is no dependence of the fatigue resistance on the degree of primary bonding between the epoxy and glass, contrary to our previous research [12]. Our previous research [11] showed that the fatigue crack propagated through the silane interphase region, thereby, involving primarily the rupturing of Si–O–Si bonds through the combined influence of cyclic stressing and moisture. Thus, the maximum energy dissipated from the breaking of bonds, G_b, is thought to be no greater than that required for moisture-assisted crack growth through monolithic glass, ~2–3 J/m^2 for a velocity of 10^{-6} m/s [11]. This represents about 30% of the total $G_{\max}$ to drive the crack in the case for the 100% 3-APES bonded CE/glass interface [11]. Assuming that the 100% 3-APES bonded HSE interface in this research exhibits a similar G_b, it is now seen that G_b now represents only about 10–15% of the $G_{\max}$ to drive the crack. Thus the G_b contribution to energy dissipation is now dwarfed by the plastic and inelastic dissipation and, therefore, varying the G_b

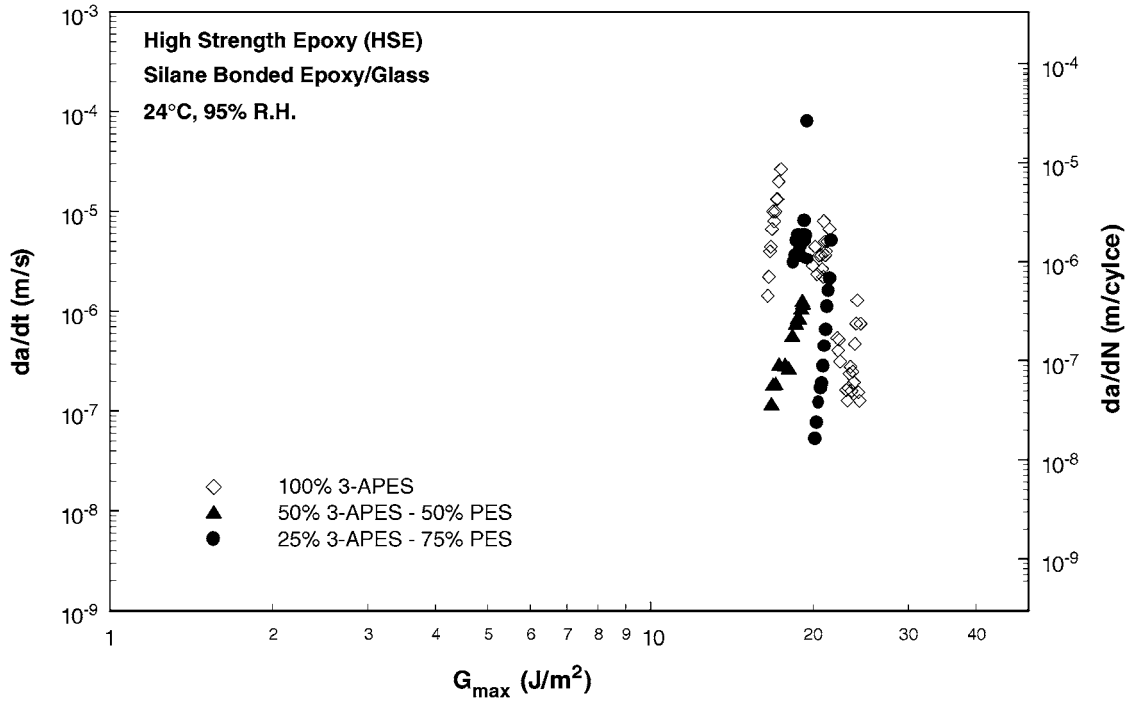

Figure 5 Comparison of the cyclic fatigue crack growth rate results for the various silane-bonded HSE/glass interfaces.

term through using different ratios of 3-APES to PES is lost in the experimental scatter.

3.3. Effect of temperature

To determine the influence of temperature on the epoxy of a silane-bonded epoxy/glass interface, tests were conducted at a temperature of 60°C. The HSE was used because its glass transition temperature ($T_g = 145°C$) was sufficiently higher than the test temperature. All specimens were silanized with the 25% 3-APES −75% PES solution to minimize the chance of the crack kinking into the glass. The successful to non-successful tests ratio was 2 : 2. Fig. 6 shows the cyclic fatigue crack growth rate results for the 25% 3-APES −75% PES bonded epoxy/glass interface using the HSE at room temperature and $T = 60°C$. The interfaces tested in the high temperature environment were more resistant to fatigue crack growth than those tested at room temperature. The G_{max} needed to grow the crack at 10^{-6} m/s in the elevated temperature environment is about 26 J/m^2 and is about 33% greater than at room temperature ($G_{max} = 20$ J/m^2). This appears to be statistically significant, and is thought to be related to the lower yield strength of the epoxy at 60°C.

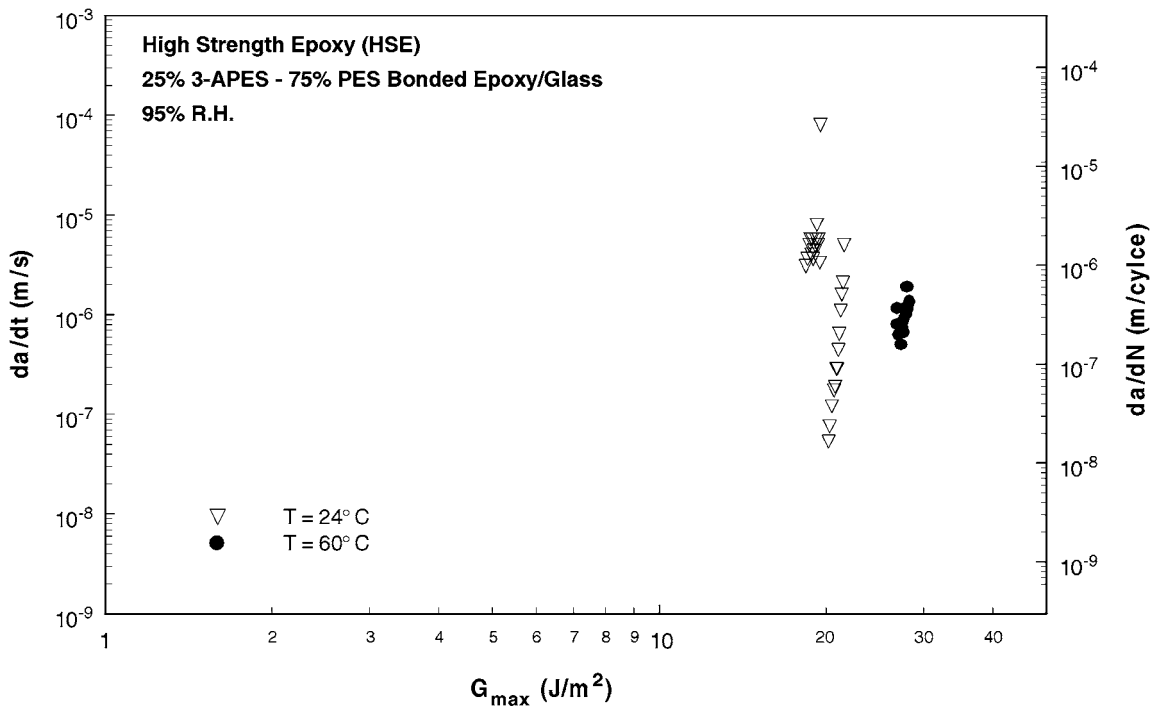

Figure 6 Comparison of the cyclic fatigue crack growth rate results for the 25% 3-APES − 75% PES bonded HSE/glass interface at room temperature and $T = 60°C$.

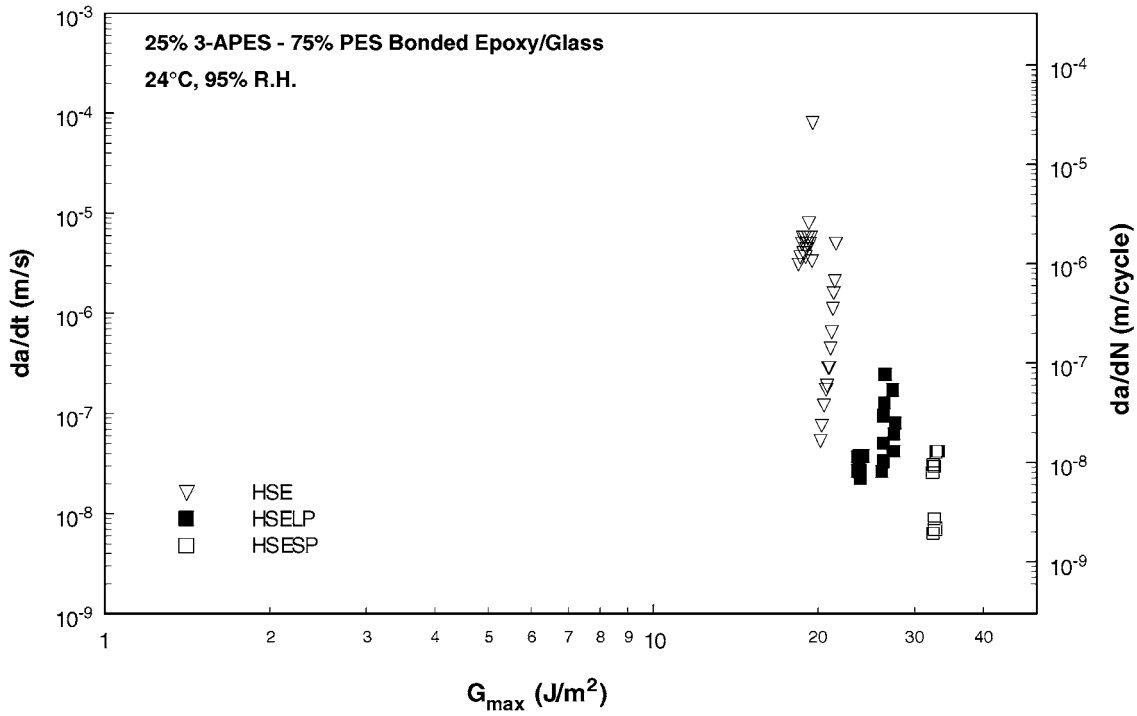

Figure 7 Comparison of the cyclic fatigue crack growth rate results for the 25% 3-APES −75% PES bonded HSE/glass interface to that of the rubber-modified HSELP and HSESP interfaces.

3.4. Rubber-toughened epoxies

Fig. 7 shows the cyclic fatigue crack growth rate results for the 25% 3-APES −75% PES bonded epoxy/glass interface for the high strength epoxy (HSE), high strength epoxy–large particles (HSELP), and high strength epoxy–small particles (HSESP). This silane ratio was chosen to minimize the kinking of the crack into the glass. Resistance to fatigue crack growth increased with the addition of the large particles (10–40 μm) and increased further with the addition of the small particles (1–2 μm). The addition of the large particles to the epoxy increased the resistance to crack growth at the interface by about 30% compared the HSE/glass interfaces. Addition of the small particles increased resistance by over 75% compared to HSE/glass interfaces. No attempt was made to reach the crack velocities at and above 10^{-6} m/s. Consequently, the ratio of successful to non-successful test was greatly improved to 4 : 0

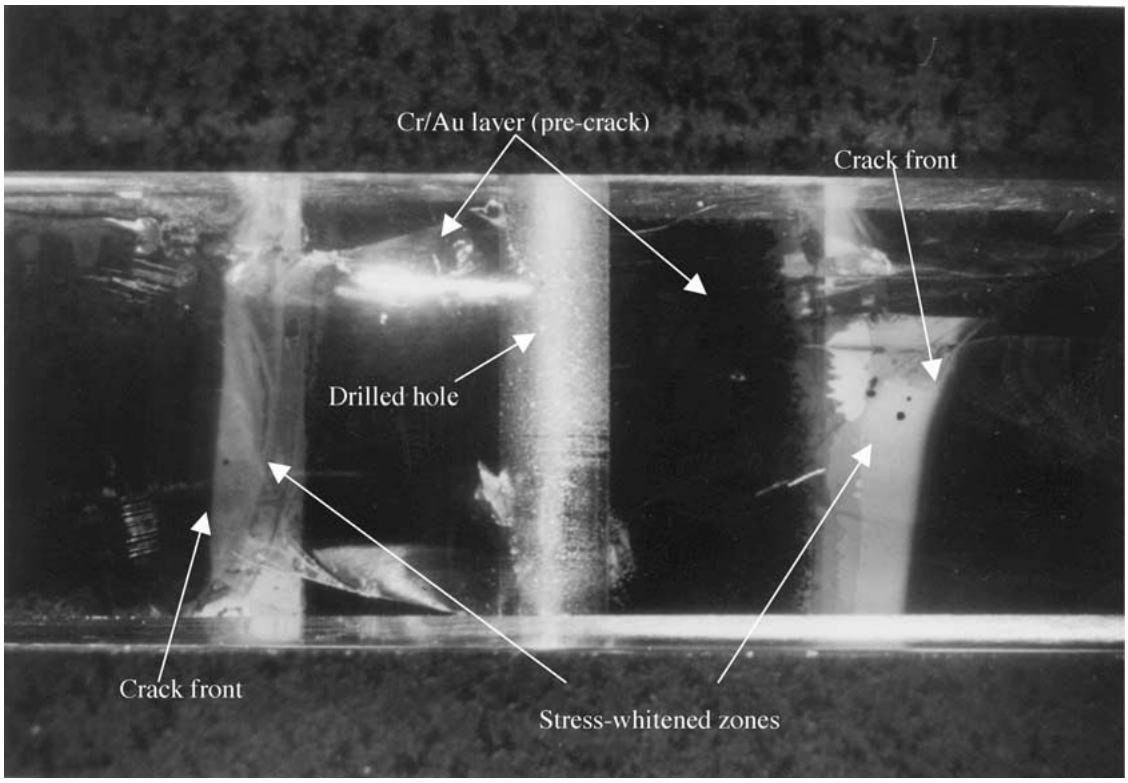

Figure 8 Stress-whitened zone in wake of crack in a HSESP specimen.

and 2 : 2 for the HSELP and HSESP/glass interfaces, respectively, despite the high G levels needed to drive the crack.

Upon examination of the DCDC specimens made with both the HSELP and HSESP, stress whitened zones, as seen by Pearson and coworkers [5–7] during crack propagation in monolithic rubber-toughened epoxy, were also observed in our interfacial crack growth specimens. Fig. 8 is a photo of the specimen showing the stress-whitened zone for a HSESP/glass specimen. This zone is caused by scattering of light from the voids formed by the cavitated rubber particles. Thus, it is believed that the increase in the fatigue resistance of these rubber-toughened epoxy/glass interfaces is due to the additional energy absorbed by cavitation and shear yielding. The stress-whitened zone in the HSELP specimens were less intense (more transparent) than the HSESP specimens, indicating less cavitation and shear yielding. These results would indicate that the plastic zone ahead of the interfacial crack tip is larger than 1–2 μm but is smaller that 40 μm. This is consistent with the size estimated from the finite element analysis [18].

4. Conclusions

Cyclic fatigue resistance of silane-bonded epoxy/glass interfaces is influenced by the epoxy's ability to dissipate energy through plastic and other inelastic deformations. Adjustment of the material properties of two epoxies with similar chemical structures by manipulation of the molecular weight between cross-links, M_c, shows little difference in the cyclic fatigue resistance of the interface within experimental scatter. However, the fatigue resistance of these interfaces formed from epoxies with controlled networks is significantly greater that that from a commercial epoxy [9–12]. Incorporation of rubber particles smaller than the plastic zone size found ahead of the propagating crack gives a significant improvement in the cyclic fatigue resistance of the interfaces through the additional energy absorbing mechanisms of cavitation and shear yielding. Smaller sized particles give the greatest improvement, over 75% greater resistance than the non-toughened epoxy. For the HSE and LSE, adjustment of the number of silane bonds between the epoxy and glass shows little effect on the fatigue resistance of the epoxy/glass interface. It is believed that energy absorbed though the breakage of bonds, G_b, accounts for only about 10–15% of the total G_{max} necessary to drive the crack. Therefore, this term becomes negligible compared to the energy dissipated though plastic deformation and other inelastic mechanisms, and any systematic variability of G_b is lost in experimental scatter. Testing at elevated temperature (60°C) significantly increased the fatigue resistance of the HSE/glass interface.

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References

1. A. BAGCHI and A. G. EVANS, *Interface Science* **3** (1996) 169.
2. J. W. SMITH, E. J. KRAMER and P. J. MILLS, *J. Polym. Sci (Polym. Phys.)* **32** (1994) 1731.
3. J. W. SMITH, E. J. KRAMER, FEI XIAO and CHUNG-YUEN HUI, *J. Mater. Sci.* **28** (1993) 4234.
4. A. F. YEE and R. A. PEARSON, *ibid.* **21** (1986) 2462.
5. R. A. PEARSON and A. F. YEE, *ibid.* **21** (1986) 2475.
6. *Idem.*, *ibid.* **24** (1989) 2571.
7. *Idem.*, *ibid.* **26** (1991) 3838.
8. H. R. AZIMI, R. A. PEARSON and R. W. HERTZBERG, *ibid.* **31** (1996) 3777.
9. J. E. RITTER, J. R. FOX, D. I. HUTKO and T. J. LARDNER, *ibid.* **33** (1998) 4581.
10. J. E. RITTER, J. C. LEARNED, G. S. JÁCOME, T. P. RUSSELL and T. J. LARDNER, in "Materials Reliability in Microelectronics IX," edited by C. S. Volkert, A. H. Verbruggen and D. D. Brown, Mater. Res. Soc. Proc. (Pittsburgh, PA, 1999). **563** p. 291.
11. *Idem.*, *J. Adhesion* **76** (2001) 401.
12. J. E. RITTER, G. S. JÁCOME, J. R. PELCH, T. P. RUSSELL and T. J. LARDNER, *J. Electronic Packaging*, to be published 2002.
13. E. CRAWFORD and A. J. LESSER, *Pol. Engng. Sci.* **39** (1999) 385.
14. *Idem.*, *J. Polym. Sci. (Polym. Phys.)* **36** (1998) 1371.
15. M. Y. HE, M. R. TURNER and A. G. EVANS, *Acta Met. Mater.* **43** (1995) 3453.
16. Z. SUO and J. W. HUTCHINSON, *Mater. Sci. Eng.* A **107** (1989) 135.
17. A. G. EVANS, M. RUHLE, B. J. DALGLEISH and P. G. CHARALAMBIDES, *Mater. Sci. and Eng.* A **136** (1990) 53.
18. S. S. CHAKRAVARTHY, M. S. thesis, Mechanical and Industrial Engineering Department, University of Massachusetts, 2000.

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