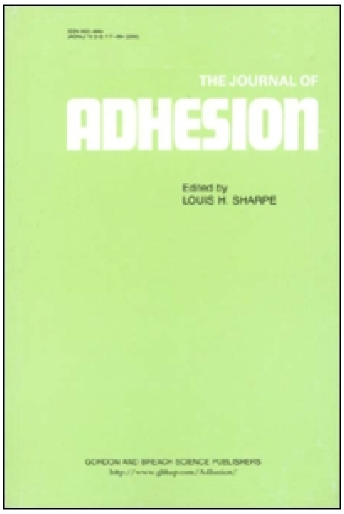

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Parvatareddy, H. , Dillard, J. G. , McGrath, J. E. and Dillard, D. A.(1999) 'Solvent Effects on High Temperature Polyimides and their Bonded Joints', The Journal of Adhesion, 69: 1, 83 — 98
To link to this Article: DOI: 10.1080/00218469908015920
URL: http://dx.doi.org/10.1080/00218469908015920

J. Adhesion, 1999, Vol. 69, pp. 83–98
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Solvent Effects on High Temperature Polyimides and their Bonded Joints

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(Received 19 December 1997; In final form 3 June 1998)

Environmental stress crazing/cracking (ESCR/C) of adhesives under organic solvent exposure is a subject of great practical importance to adhesive end-users, especially in dealing with structural applications. In the past, the mechanical properties of several adhesive systems have been shown to degrade considerably after both prolonged and momentary exposure to solvents under a state of stress. In this study, the solvent resistance of three structural polyimide adhesives was studied, with respect to organic solvents that may come in contact with the adhesives during their service life.Initially, dog-bone samples of the resin systems were prepared, according to ASTM Standard D638-91a, and these were soaked in the solvents to obtain equilibrium solvent mass uptake curves. The solvents used in the study included acetone, methyl ethyl ketone (MEK) and ethylene glycol, among others. The equilibrated samples were then tested in a miniature tensile testing machine, to obtain stress-strain characteristics. Secondly, samples equilibrated in the solvents were held in a vacuum environment at 150°C (which is below the glass transition temperature of the adhesives) to desorb the solvent, and these were then tested to obtain residual properties.To study the durability of bonded joints under solvent exposure, Ti-6Al-4V/adhesive bonds were prepared and wedge tests were performed on them for periods up to several days in solvent baths. Based on the measured crack lengths, the strain energy release rate due to solvent-induced environmental stress cracking (G_{ESC}) was computed as a function of crack growth rate. The G_{ESC} measurements help quantify the durability of the bonded joints on exposure to the various solvents, and further help in ranking the adhesives in terms of solvent resistance.

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Keywords: Environmental stress cracking (ESC); solvent sensitivity; wedge test; FM-5 polyimide; VT Ultem™ polyimide; REGULUS™ polyimide

INTRODUCTION

Environmental stress cracking (ESC) of polymers is a failure phenomenon of great practical significance which was first noted in polyethylene in the 1950s [1]. Since the 1970s, several researchers [2–4] have found that many thermoplastic adhesives and polymers, mechanically loaded and immersed in certain kinds of fluids, undergo failure by crazing or cracking. The loads required for the failure of specimens exposed to solvents are significantly less than those required for failure in air. Failures like these are called environmental stress crazing (ESCR) and environmental stress cracking (ESC). The mechanisms for ESC/CR are not fully understood to date; however, several reasons for this phenomena have been suggested by researchers who have worked in this area. Some of the most common reasons suggested for ESC behavior are plasticization of polymer material [2], solubility parameter differences between polymer and solvent [5], hydrogen bonding [6], reduced crystallinity [7] and residual stresses [8].

Parvatareddy *et al.* [9] showed that high performance composites exhibited ESC when exposed to common organic solvents used in the aircraft industry. Recent studies by Dillard *et al.* [10] and Clifton [11] showed that even high-performance polyimide adhesives may be sensitive to organic solvents and aircraft fluids. In light of these observations, it is essential to study the solvent sensitivity of high-performance structural adhesives in the context of the solvents which may come into contact with the adhesive and/or joint during the service life.

In the present study the phenomenon of ESC is investigated in three high-performance polyimide adhesives, FM-5, VT Ultem™, REGULUS™, and their adhesively-bonded joints. The solvents used in this research included acetone, methyl ethyl ketone (MEK), toluene, jet fuel, hydraulic fluid, and ethylene glycol. The FM-5 adhesive system is being currently investigated to study its feasibility for application in a future supersonic civil transport aircraft. Thus, this study is of relevance to the aircraft industry because some of the solvents used in this study are currently used as degreasers and paint strippers in the aircraft industry [12].

EXPERIMENTAL

Materials

The FM-5 adhesive is based on a polyimide originally developed at NASA Langley Research Center (LaRC PETI-5) [13] and then modified and supplied by Cytec Engineered Materials, Inc., Havre de Grace, Maryland USA. The molecular weight of the adhesive used in this study was 5000 g/mole. The adhesive was supplied in two forms: as polymer film supported on a woven fiberglass cloth and as an unsupported film. The supported film contained 85% polymer by weight. This supported film also contained approximately 4% by weight of the solvent *N*-methyl-2-pyrrolidinone (NMP). The supported film was used to bond titanium adherends to conduct wedge tests. The unsupported film had less than 0.5% by weight of the solvent and was used to conduct the solvent uptake and desorption tests and the tensile tests. The adhesive was cured at a temperature of 250°C for 30 minutes, followed by a hold for 60 minutes at 350°C while maintaining a curing pressure of 75 psi (0.518 MPa). The glass transition temperature, T_g, of the cured adhesive was approximately 250°C.

VT Ultem [14] is a thermosetting polyimide based on General Electric's Ultem and synthesized at Virginia Tech. The molecular weight of the VT Ultem material used in this study was 3000 g/mole. The VT Ultem material was also supplied as a scrimmed adhesive film with approximately 85% polymer by weight. The bonding procedure used for making wedge specimens with the VT Ultem is as follows: 250°C for 30 minutes under no pressure, followed by a hold for 90 minutes at 380°C while maintaining a pressure of 75 psi (0.518 MPa). The T_g of the cured adhesive was found to be around 240°C.

REGULUS^{TM} is a thermoplastic polyimide produced by Mitsui Toatsu Chemicals, Inc., Japan. For this study, the REGULUS^{TM} adhesive was supplied by the Boeing Company, Seattle, WA, USA.

The molecular weight of the adhesive was 5000 g/mole. The adhesive was bonded to titanium metal for conducting the wedge tests using the following cure cycle: 2 hours hold at 150°C under contact pressure, followed by a 10-minute cure at 400°C under a pressure of 300 psi (2.07 MPa). The T_g of the adhesive was reported to be 250°C. Table I summarizes the material properties and the cure schedules of the three adhesives used in the study.

The adherends used in the study were cut from Ti-6Al-4V plates, having dimensions of 200 ×25 ×3.175 mm, and supplied by President Titanium Company, Hanson, MA. The adherends were surface pretreated with chromic acid anodization (CAA) before bonding with the adhesive.

Solvent Uptake and Desorption

Solvent uptake tests were performed on unsupported FM-5 and REGULUS^{TM} films. Dog-bone specimens, 0.5 mm thick, were prepared in accordance with ASTM D638M-91a [15] for testing. The solvents used in the study included acetone, MEK, toluene, jet fuel, ethylene glycol, hydraulic fluid and water. Ten dog-bone specimens of each resin were immersed in each of the solvents (in scintillation vials of 20 ml volume) and the samples periodically weighed using a Mettler AE200 microbalance to obtain equilibrium solvent mass

TABLE I Material properties and cure schedules of the three adhesive systems used in this study

Adhesive	*Mol. wt. (g/mole)*	T_g *(°C)*	*% by wt. of NMP solvent in adhesive*	*Cure schedule*
FM-5	5000	250	4	250°C for 3 mins (no pressure), 350°C for 60 mins under 75 psi(0.518 MPa)
REGULUS^{TM}	5000	250	–	250°C for 30 mins (no pressure), 380°C for 90 mins under 75 psi (0.518 MPa)
VT-Ultem	3000	240	–	150°C for 120 mins (no pressure) 400°C for 10 mins under 300 psi (2.07 MPa)

uptake data. Before each weight measurement, the surface of the sample was carefully wiped to eliminate any residual solvent. When the measurements were completed, the specimens were promptly put back in their respective vials, the entire weighing process taking 20–30 seconds per specimen. Data was collected on the specimens in excess of 1200 hours. The experimental variability for the solvent uptake in the FM-5 films was around 0.3 mass%, while it was 0.1 mass% in the case of the REGULUS^{TM} films. Following saturation of the various solvents in the adhesive specimens, five equilibrated specimens from each solvent were wiped and dried in a vacuum oven at 150°C for 60 minutes, to desorb the solvent. This temperature was chosen for desorption as it was above the boiling point of most of the solvents used in this study, but far below the T_g of the three adhesive resins.

Minimat Tensile Testing

The solvent-saturated and re-dried specimens were tested in a miniature tensile testing machine according to ASTM D638M-91a [15] to obtain stress-strain characteristics. In all cases, moduli, strains to failure, and yield stresses were computed, and comparisons made with unexposed control specimens.

Wedge and DCB Testing

To study the durability of bonded joints under solvent exposure, Ti-6Al-4V/adhesive wedge specimens were prepared and tests performed for several hours in solvent baths. Based on the measured crack lengths, the strain energy release rate due to environmental stress cracking (G_{ESC}) was computed as a function of crack growth rate [16]. The G_{ESC} measurements help to quantify the durability of the bonded joints on exposure to the various solvents, and further help in ranking the solvent resistance of the adhesive. Five wedge specimens were exposed to each of the solvents and the results reported in a later section are average values from the five tests. Anodized Ti-6Al-4V/FM-5 DCB specimens were also prepared and these specimens soaked in several solvents (2 specimens per solvent) for one month. Following the soak period, the samples were tested in accordance with the procedure described in Reference [17].

RESULTS AND DISCUSSION

Solvent Uptake and Desorption

Figure 1 shows equilibrium solvent mass uptake curves for dog-bone specimens of neat FM-5 resin. Ten specimens each were exposed to seven different solvents for over 1200 hours. The highest solvent uptake occured in MEK (~6%). Jet fuel and toluene had similar uptakes (~4%). Acetone was next with around 3% uptake, followed by hydraulic fluid, ethylene glycol, and water (~1%). Diffusion coefficients were evaluated for the FM-5 system for the different solvents used in this study. These values were calculated from the slopes of the linear uprising portion of the solvent uptake curves (see Tab. II). For the FM-5 polymer, the highest diffusion rate was seen

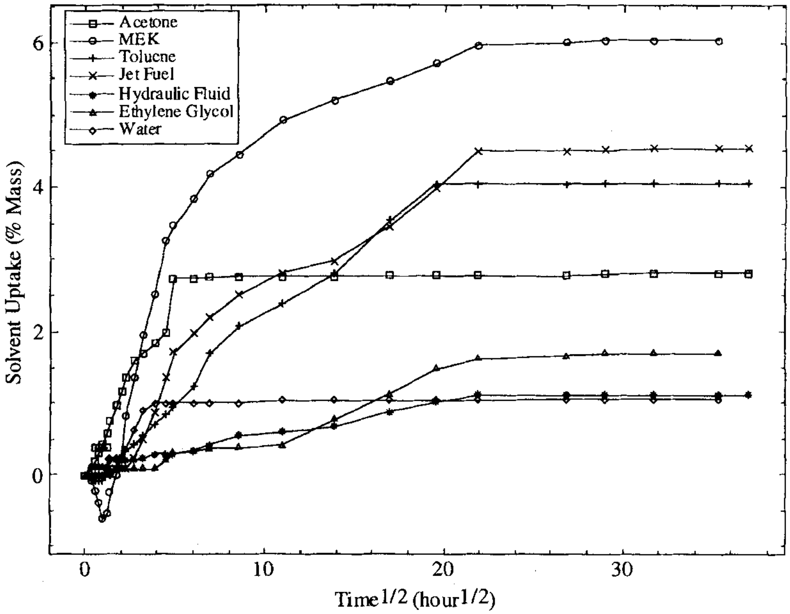

FIGURE 1 Solvent mass uptake curves for FM-5 neat resin specimens.

TABLE II Calculated diffusion coefficients for FM-5 and REGULUS^{TM} resins in the different solvents

FM-5 adhesive		*REGULUS^{TM} adhesive*	
Solvent	*Diffusion coefficient (cm^2/sec)*	*Solvent*	*Diffusion coefficient (cm^2/sec)*
Acetone	1.29 E−7	Acetone	1.17 E−7
MEK	8.25 E−8	MEK	1.20 E−7
Toluene	2.55 E−8	Toluene	1.54 E−7
Jet Fuel	9.93 E−9	Jet Fuel	1.58 E−7
Hydraulic Fluid	5.74 E−9	Hydraulic Fluid	5.79 E−8
Ethylene Glycol	1.28 E−8	Ethylene Glycol	1.46 E−9
Water	2.32 E−8	Water	3.07 E−9

with acetone, followed by MEK and toluene, while the lowest diffusion rate was seen with ethylene glycol. Following the solvent uptake tests, 5 of the specimens from each solvent were dried in a vacuum oven at 150°C for 60 minutes. The results from the desorption study are summarized in Figure 2. As seen in this figure, except

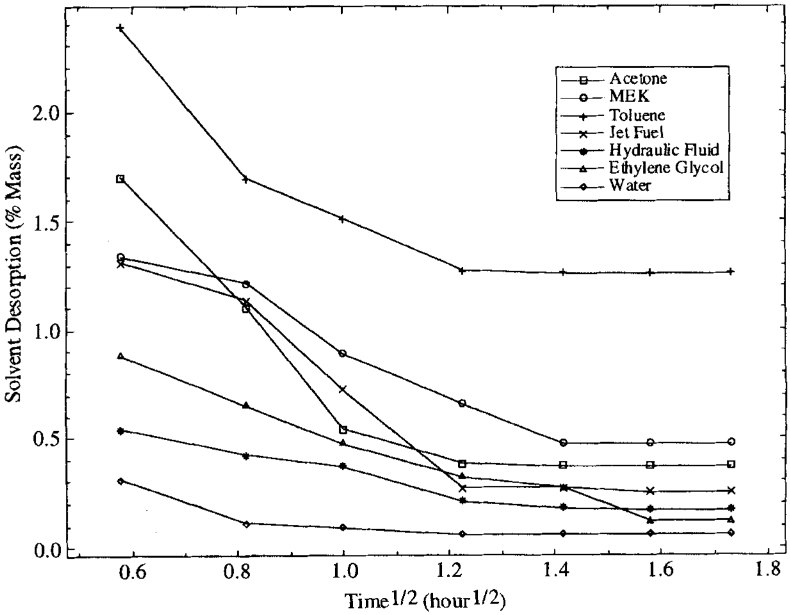

FIGURE 2 Desorption curves for FM-5 neat resin specimens.

for the specimens soaked in toluene, which retained around 1.5% by mass of the solvent, the other specimens lost most of the absorbed solvent.

Figure 3 shows the solvent uptake data for REGULUS^{TM} films exposed to the same solvents as the FM-5 resin. For this adhesive material the highest solvent uptake was seen in acetone, MEK, and toluene (~1.5%) and the least in water and hydraulic fluid. The diffusion rates calculated for this adhesive system, as seen in Table II, are the highest with jet fuel, while the lowest diffusion rate was seen with hydraulic fluid. Upon drying, all the specimens lost most of the absorbed solvent, and the residual solvent in the films was less than 0.1 mass% (see Fig. 4). The drying procedure used was similar to that described for the FM-5 system in that the specimens (5 out of the 10 saturated specimens per solvent) were dried in a vacuum oven at 150°C for 60 minutes.

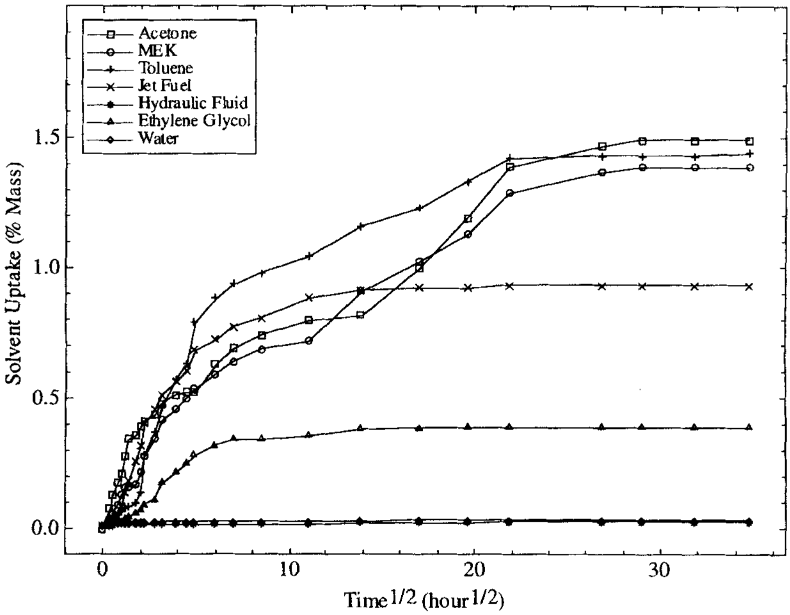

FIGURE 3 Equilibrium solvent mass uptake curves for REGULUS^{TM} neat resin specimens.

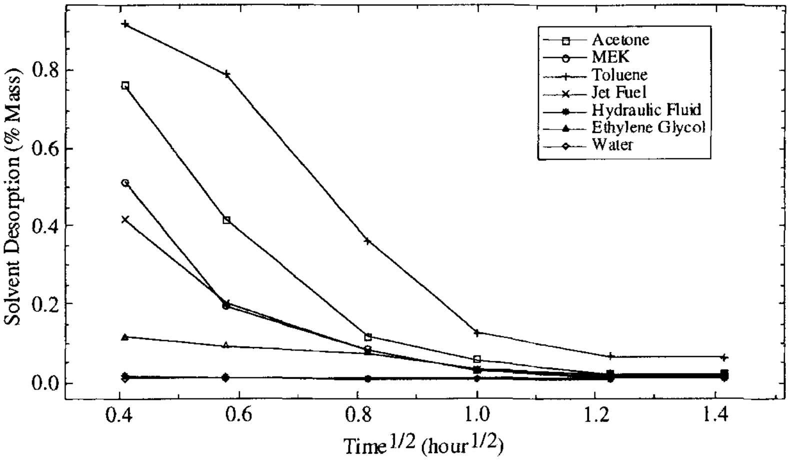

FIGURE 4 Desorption curves for REGULUS™ neat resin specimens.

Tensile Test Results

Following the desorption tests, all specimens, both saturated with the solvents and re-dried were tested in a tensile testing machine. The stress-strain curves obtained from these tensile tests for the FM-5 specimens are summarized in Figure 5. Samples saturated with acetone, MEK, and toluene were plasticized, as evidenced by the lower yield stresses and the higher strains to failure. However, on drying the specimens, irrespective of the solvent to which the samples were exposed, all the stress-strain curves resembled that obtained for the as-received specimen. This finding indicates that there may be minimal residual effects of the solvents on the FM-5 resin. The results for the REGULUS™ resin system are summarized in Figure 6. Samples saturated with toluene and jet fuel were plasticized, yielding very high strain-to-failure values. However, similar to the results obtained for the FM-5 resin, upon drying of the REGULUS™ specimens and re-testing, all the stress-strain curves, except those from specimens exposed to toluene, approached the stress-strain characteristics obtained on as-received specimens. The samples that were exposed to toluene and tested after re-drying showed a slightly lower modulus and yield stress value, compared with specimens that were

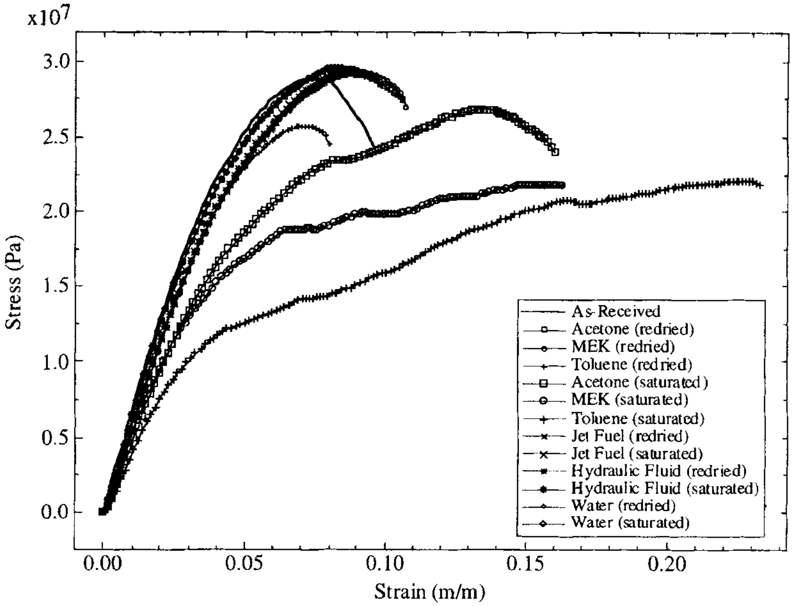

FIGURE 5 Stress–strain curves from solvent-saturated and re-dried FM-5 neat resin specimens.

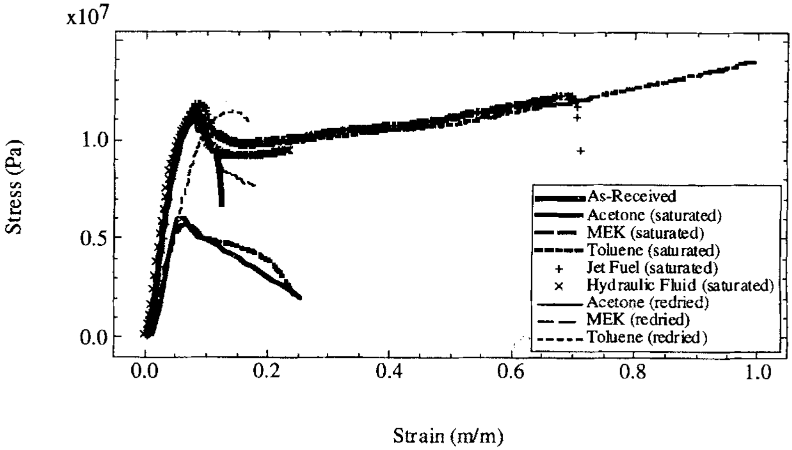

FIGURE 6 Stress–strain curves from solvent-saturated and re-dried REGULUS^{TM} neat resin specimens.

dried after exposure to other solvents. One possible explanation for this behaviour is the fact that there was still enough residual toluene in the polymer after re-drying to act as a plasticizer. These results further confirm that upon adequate drying of the REGULUS^{TM} films after solvent exposure, there is very little residual effect of the various solvents on the adhesive material.

Wedge and DCB Test Results

To study the effect of solvent exposure on adhesive bond durability, Ti-6Al-4V/adhesive bonded specimens treated with CAA were immersed in solvents for periods up to 168 hours. Five specimens each were immersed per solvent and crack length data collected as a function of exposure time. Results from these wedge tests obtained on the Ti-6Al-4V/FM-5 system are summarized in Figures 7 and 8. Data shown are average values obtained from the 5 test specimens per solvent. As can be seen from Figure 7, the longest crack growth was obtained from samples immersed in boiling water, while the least was seen in the samples immersed in room temperature water. The rest of the solvents had a certain ranking in terms of the crack length obtained following exposure of the bonded joint. In terms of ascending

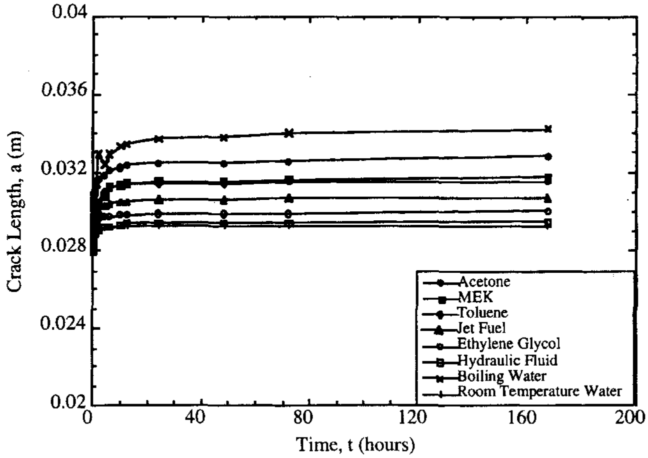

FIGURE 7 Wedge crack length *versus* exposure time curves for FM-5 bonded specimens in different solvents. Data were collected for 168 hours.

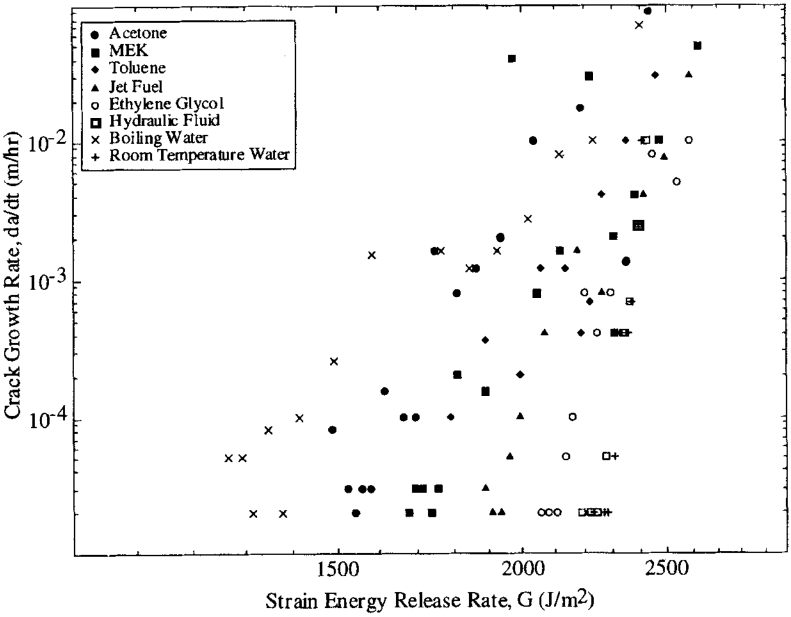

FIGURE 8 Wedge crack growth rate *versus* fracture energy for FM-5 bonded specimens exposed to different solvents. Data were collected for 168 hours.

durability, as can be seen from the arrest fracture energy values (Fig. 8) the ranking order was: acetone, MEK, toluene, jet fuel, ethylene glycol, hydraulic fluid, and room temperature water. The crack growth showed mixed-mode failure characteristics in the boiling water, while it was cohesive in the rest of the solvents. As seen from Table II the diffusion rate of acetone into the FM-5 system is the highest, followed by MEK and toluene. Also, the fracture data in Figure 8 shows that acetone, MEK and toluene (in that order) are the solvents that are most detrimental to the performance of the Ti-6Al-4V/FM-5 joints. In light of these observations, extreme care should be taken to avoid or minimize contact between the above mentioned bonded system, during service, with the three solvents mentioned above. Figure 9 summarizes the DCB test results obtained on the T-6Al-4V/FM-5 bonds after the bonded specimens were soaked in different solvents for 1 month and tested. The data shown is an average from 2 specimens per solvent condition. While jet fuel and hydraulic fluid have no effect on the mode I fracture toughness, a 10–15% drop in fracture toughness was

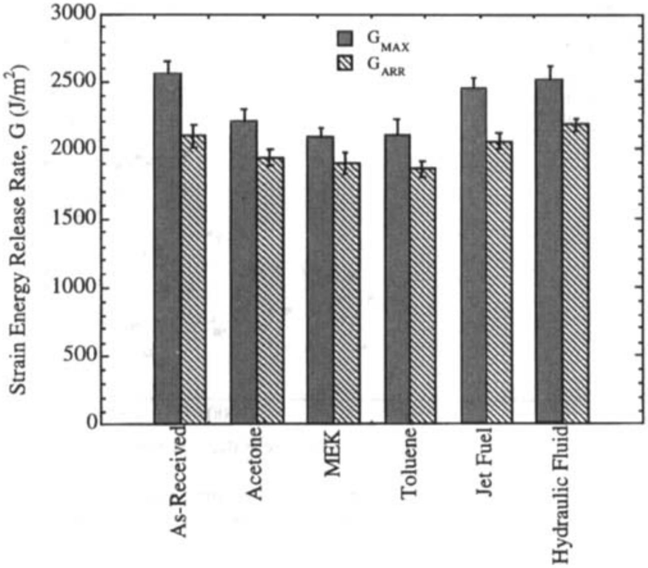

FIGURE 9 DCB test data on chromic acid anodized (CAA) titanium/FM-5 bonds immersed in different solvents for 1 month.

noted in MEK, acetone and toluene solvents. This drop in toughness is rather small considering that the bonded samples were submerged in the solvents for a month. Further it must be noted that it is highly unlikely that the adhesive bonds would be submerged in acetone, MEK or toluene, for a 1-month period during actual service. Also, it is encouraging to note that there was no drop in toughness following the continued exposures to jet fuel and hydraulic fluid. There is a greater probability that the above two solvents may come into contact with a bonded aircraft structure for a prolonged period of time during service.

Figure 10 summarizes the results obtained from wedge tests conducted on CAA-treated Ti-6Al-4V/REGULUS^{TM} bonds following the interaction of the bonded joints with different solvents over a 168-hour period. While the bonded joints immersed in boiling water showed the least durability based on the arrest energy release rates that were calculated, the best durability was seen in the samples immersed in hydraulic fluid. The arrest fracture energies for this bonded system were considerably lower than for the Ti-6Al-4V/FM-5 bonded system

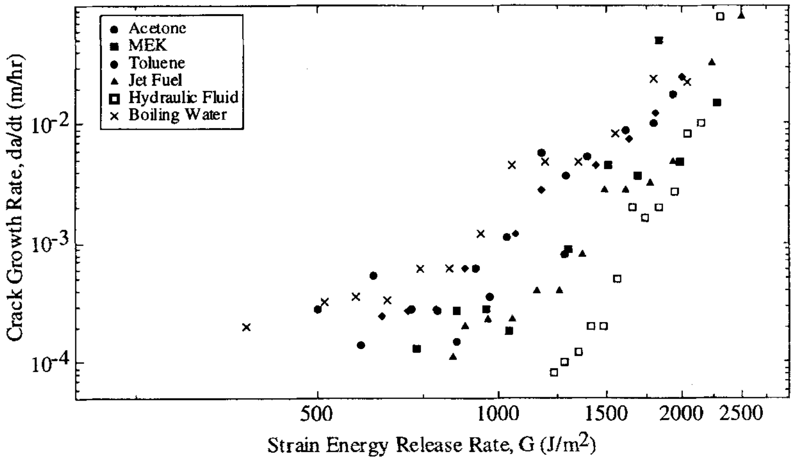

FIGURE 10 Wedge crack growth rate *versus* fracture energy for REGULUS^{TM} bonded specimens exposed to different solvents. Data were collected for 168 hours.

over a similar exposure period to exactly the same solvents. Trends similar to those observed with the titanium/REGULUS^{TM} bonds were seen in the CAA-treated Ti-6Al-4V/VT Ultem bonded specimens. These results are summarized in Figure 11.

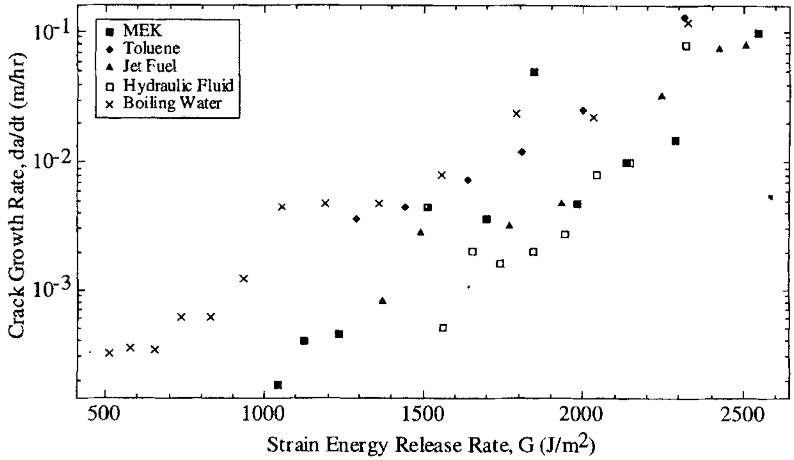

FIGURE 11 Wedge crack growth rate *versus* fracture energy for VT Ultem bonded specimens exposed to different solvents. Data were collected for 168 hours.

SUMMARY AND CONCLUSIONS

This study was undertaken to gain an understanding of the important issue of solvent sensitivity and environmental stress cracking in the FM-5 adhesive and its titanium bonded joints. The Ti-6Al-4V/FM-5 adhesive bonded system is currently being evaluated for application in a future supersonic aircraft. It is common knowledge that adhesives used in aerospace structures often come into contact with organic solvents and aircraft fluids during their service life. Past studies with high-performance polymers have shown them to be susceptible to organic solvents under load, therefore making it imperative to study the behaviour of the titanium/FM-5 bonds in certain organic solvents and aircraft fluids. As a part of this study, the performance of the FM-5 adhesive in different solvents was also compared and contrasted with two other polyimide adhesives, VT Ultem and REGULUS^{TM}.

Tensile tests conducted on neat FM-5 specimens, both saturated with solvent and re-dried, showed no cracking or crazing of the polymer. Under the saturated condition some of the solvents appeared to have a plasticization effect on the polymer. However, upon drying of these specimens, most of them behaved in a normal fashion similar to the as-received samples. To study the interaction of the solvent and stress on the bonded joints, wedge tests were conducted on the titanium/FM-5 system. The wedge bonds were submerged in different solvents for a week and crack-length measurements taken over this period of time. These cracklength measurements helped rank the different solvents in terms of their detrimental effect on the bonded system. If carried out for longer periods of time, this test could serve as a very good durability test for any adhesive bonded system exposed to different solvents. As well, the arrest fracture energies that can be calculated from this test can prove useful for design purposes.

The one notable conclusion that can be drawn from this study is that the FM-5 adhesive material is fairly resistant to the solvents that were used in the research. This augurs well for the future application of this adhesive to aircraft structures. It must also be mentioned here that the VT Ultem and REGULUS^{TM} adhesives were chemically resistant to the solvents used in this study. The one difference between the FM-5 and REGULUS^{TM} resins in terms of performance was that the arrest fracture energies obtained from the wedge tests on the

REGULUS^{TM} bonds were considerably lower than for the FM-5 material.

Acknowledgements

The authors would like to acknowledge the financial support of the Boeing Commercial Airplane Company for conducting this research. The authors would also like to acknowledge Cytec Engineered Materials, Inc., for supplying the FM-5 resin and The Boeing Company for providing the REGULUS^{TM} resin. The authors would like to thank Brian Williams for help with some of the experiments and Paul Hergenrother of NASA Langley Research Center for helpful discussions.

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