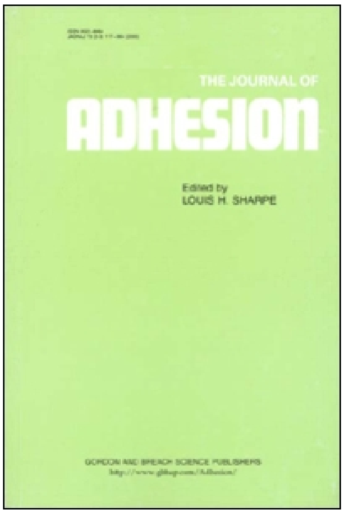

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This study was conducted to investigate the performance of the Ti-6Al-4V/FM-5 adhesive bonded system for potential applications on high-speed aircraft. The long-term environmental aging effects on Ti-6Al-4V/FM-5 bonded joints and neat FM-5 and PETI-5 resin specimens were investigated. Dynamic mechanical analysis (DMA) and uniaxial tensile testing using dogbone samples were performed on neat FM-5 and PETI-5 resin specimens before and after high-temperature aging in both ambient and reduced pressure environments. Mode I fracture testing was also performed on beam specimens fabricated with mat-scrim-cloth-supported films of FM-5 adhesive bonding titanium adherends prior to and after environmental aging. Experimental results revealed that both physical aging, which is reversible, and irreversible chemical aging took place simultaneously in the adhesive systems, and both types of aging could contribute to loss in adhesive bond performance. Furthermore, the properties of several different Ti–6Al-4V/FM-5 systems, prepared using different

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surface pretreatment methods and different supportive matrices of FM-5 resin, were compared in this study, and the effect of mode-mixity on the fracture toughness of the adhesive-bonded systems was also evaluated by conducting double cantilever beam (DCB), end-notched flexure (ENF), and mixed-mode flexure (MMF) tests. The creep behavior of the Ti/FM-5 bonded joint was also investigated by performing thick adherend shear tests.

Keywords: Durability; Adhesive bonds; Physical aging; Chemical aging; Strain energy release rate; Creep; Polyimade; Titanium

INTRODUCTION

Adhesively bonded structures are increasingly used in aerospace and other applications because of their many advantages over traditional, mechanically fastened assemblies. These advantages include improved fatigue and corrosion resistance, reduced weight, and lower manufacturing costs. Epoxy-based adhesives, with their high moduli and enhanced load-bearing abilities, are commonly used in subsonic aircraft structures. However, for certain applications, including supersonic aircraft, more advanced adhesives are required for long-term structural bonds exposed to elevated temperatures. Thermoplastic and thermosetting polyimides have been synthesized for such applications, and they offer useful properties that are necessary for such structures, including high toughness and thermo-oxidative stability [1–4]. Of particular interest here is the study of the durability of high performance adhesives that might be required for structural components of high speed aircraft.

PETI-5, a polyimide developed at NASA Langley (Langley, VA, USA) [3], has been the basis not only for a composite resin but also for several adhesive products that have been considered for different bonding applications on high speed aircraft. FM-5, a formulated version of PETI-5, was developed by Cytec Industries Inc. (Havre de Grace, MD, USA). The potential use of PETI-5 or FM-5 in high-speed aircraft has stimulated investigations of the properties and durability of these adhesives and their bonded joints.

The high-speed civil transport (HSCT) was envisioned as the next level of competition in the aviation industry, the long range, economical, environmentally acceptable, second-generation supersonic passenger transport [5]. In aircraft such as the HSCT, the structural adhesive bonds could be required to withstand temperatures of 177°C or more for a potential service life of 60,000 h while maintaining adequate mechanical properties. Physical aging and chemical aging of the adhesive material could be of great concern and must be taken into account for predicting the durability of such adhesive joints. Physical aging is the slow evolution of a polymer toward thermodynamic equilibrium by time-dependent changes in volume, enthalpy, entropy and mechanical properties [6–8]. Physical aging is a thermo-reversible process. On the other hand, chemical aging is generally an irreversible process, involving the breaking of chemical bonds, reduction in molecular weight, loss in weight associated with the outgassing of lower molecular weight gaseous species [9], or other chemical changes. Both physical and chemical aging can have significant effects on the durability of these adhesive bonded systems.

An adhesively bonded joint is a complex system, composed of an adhesive, adherends, adherend surface pretreatment, and the interphase and interface regions between the adhesive and the adherends. The behavior of each of these components may affect the durability of the adhesive joint. In the present study, a Ti-6Al-4V alloy was selected as the adherend material. Titanium metal in general has a high strength to weight ratio, a high melting point, and excellent corrosion resistance [10]. With the addition of aluminum and vanadium, the Ti-6Al-4V alloy shows good formability and good cold and hot strength [11], making it an excellent material for high-performance structures. A good surface pretreatment method employed on the metal adherends is significantly important to form a strong, durable bond. Several surface pretreatment methods, which can be categorized into mechanical, chemical, and anodization treatments, have been introduced for titanium metal [12–16] to improve the strength and durability of the adhesive bonds. In this project, two kinds of pretreatment methods were used on the titanium substrates. Chromic acid anodization (CAA) [17] was used in the first portion of this project, which addressed the effects of thermal aging on the properties of FM-5 resin and the durability of CAA-pretreated Ti-6Al-4V bonded with FM-5 on a woven scrim [18]. This article covers more recent work on an aliphatic sol-gel surface pretreatment [19] that was used as an alternative to chromic acid anodization.

In this work, the mechanical properties of FM-5 and PETI-5 resin coupons were studied, comparing the glass transition temperature, ultimate stress, and strain to failure for specimens aged for up to 30 months at elevated temperatures in both ambient air and reduced pressure environments. The performance of aliphatic sol gel Ti/FM-5 bonded joints was also investigated prior to and after environmental aging, and the mechanical performance of several different Ti–6Al-4V/FM-5 systems were compared. The creep behavior of the Ti/FM-5 bonded joint was investigated by performing thick adherend shear tests.

MATERIALS AND SURFACE PRETREATMENTS

To study the effects of aging on FM-5 and the base resin PETI-5, neat resin coupons were prepared and tested. Four plaques (sheets, $150 \times 150 \times 1.5$ mm) of PETI-5 were supplied by NASA Langley. The PETI-5 adhesive was molded from Imitec (Schenectady, NY, USA) imide powder (lot number 062–100) by sandwiching about 48 g of powder between Kapton® films in a stainless steel mold that was then heated to 371°C for 1 h. When the temperature reached 350°C, a pressure of 1.03 MPa was applied and maintained throughout the cure process. The FM-5 adhesive was supplied by Cytec in two forms: as polymer film supported on a fiberglass cloth and as an unsupported film. Both mat scrim cloth and woven scrim cloth were used in this study. The supported film was used to bond titanium adherends to conduct fracture tests. The unsupported film was used to conduct the material characterization tests such as dynamic mechanical analysis and stress-strain tests.

The Ti/FM-5 bonded joints used in the first portion of the program were made at Virginia Tech. The 3.2 mm thick Ti-6Al-4V plates were first cut to the dimensions of 200×25 mm and then pretreated by CAA before bonding [18]. On the other hand, the aliphatic sol-gel Ti-6Al-4V/FM-5 adhesive bonded joints were manufactured and supplied by the Boeing Commercial Airplane Group (Seattle, WA, USA). Large aliphatic sol-gel–pretreated Ti-6Al-4V panels with dimensions of $200 \times 200 \times 3.2$ mm were first bonded with the FM-5 adhesive, and then sliced into several specimens with dimensions of 200×25 mm in length and width, respectively.

In addition to fracture testing on the Ti-6Al-4V/FM-5 adhesive bonded joints, some thick adherend creep tests in shear mode were also conducted on the adhesive bonded joints. The thick adherend specimens were manufactured and supplied by Boeing and were made from 6.35 mm thick Ti-6Al-4 V titanium alloy plates pretreated by aliphatic sol-gel at the bonding area and bonded with mat-scrimmed FM-5 polyimide adhesives supplied by Cytec. The specimens had an overlap length of 12.7 mm and a nominal width of 25.4 mm, and they are illustrated in Figure 1.

ENVIRONMENTAL AGING CONDITIONS

Typical temperatures expected to be encountered by the aircraft during flight are around 177°C. In order to simulate HSCT conditions, the Ti-6Al-4V/FM-5 bonds and neat resin samples were aged at 177°C and 204°C. Neat FM-5 and PETI-5 resin samples were conditioned in

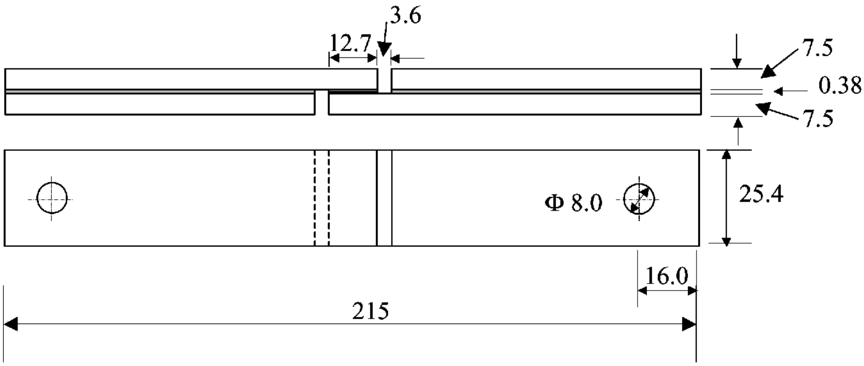

FIGURE 1 Illustration of thick adherend specimen (dimensions in mm).

aging ovens for periods of up to 30 months, and selected samples were periodically removed and tested. The aging temperature for DMA samples was 204°C at ambient pressure. For stress-strain dogbone samples, the aging environments included ambient atmospheric air at 204°C, ambient atmospheric air at 177°C, and reduced air pressure of 13.8 Kpa (2 psi) air at 177°C. The reduced air pressure condition was to simulate pressure at the intended service altitude. The Ti-6Al-4V/FM-5 bonded joints were conditioned at 177°C and 204°C in ambient atmospheric air, respectively.

ENVIRONMENTAL AGING EFFECTS ON THE THERMAL PROPERTIES OF NEAT FM-5 AND PETI-5 RESINS

To study the effects of thermal aging on the glass transition temperature (T_g) of the FM-5 and PETI-5 resin, a TA Instruments 2980 Dynamic Mechanical Analyzer (DMA: TA Instruments, New Castle, DE, USA) was used in fixed-frequency mode. The T_g was taken to be the peak of the loss modulus, E'', for the purposes of this article. The specimen sizes in the test were: $17 \times 13 \times 1$ mm for FM-5 resin and $17 \times 13 \times 1.4$ mm for PETI-5 resin. Specimens were tested in single cantilever mode at a fixed frequency of 1 Hz and were ramped between room temperature and 350°C at 1°C/min to obtain the glass transition behavior.

The DMA results obtained from the PETI-5 and FM-5 samples aged at 204°C are summarized in Table 1. Two samples were tested for each condition, and the difference between T_g values obtained from the two samples at each condition, was less than 1°C. As can be observed from the table, the DMA-based T_g values remained relatively constant up to

TABLE 1 DMA Measurements of the Glass Transition Temperature, T_g, of FM-5 and PETI-5 Resin Samples Following Aging at 204°C in Air at Ambient Pressure

Aging time	FM-5	PETI-5
As-received	237°C	256°C
2 weeks	241°C	257°C
2 months	241°C	257°C
6 months	252°C	265°C
30 months	250°C	262°C

2 months of aging for either material system. After 6 months of aging, however, the T_g values had increased significantly. A similar phenomenon was also observed on FM-5 resin by Parvatareddy *et al*. [18]. In their study, FM-5 samples were aged up to 12 months. They observed a considerable increase in T_g of FM-5 in the first 6 months of aging. Following additional aging between the 6 and 12 month period, however, only a slight increase in the T_g of the FM-5 resin sample was noted. Their study suggested that the increase in T_g of these two polyimide materials could be attributed to physical aging of both materials. To investigate the thermal changes of PETI-5 and FM-5 resin at even longer times, DMA samples of both bulk materials were aged up to 30 months and then tested in this study. It is interesting to note from Table 1 that the T_g of both resins decreased slightly following the longest aging time. One possible reason for this phenomenon may be attributed to chemical aging in the adhesive resins, which dominates over physical aging at longer aging time [18]. Chemical aging can cause chain scissioning, which creates more free chain ends, thereby leading to greater mobility and a lower T_g.

ENVIRONMENTAL AGING EFFECTS ON THE STRESS-STRAIN PROPERTIES OF NEAT FM-5 AND PETI-5 RESINS

Tensile dogbone stress-strain specimens (ASTM D-638) of neat FM-5 and PETI-5 were prepared using a Tensiukut unit (Maryville, TN) from neat resin plaques that were supplied by the Boeing Company and NASA Langley, respectively. Two sets of FM-5 dogbone samples made from the same unsupported FM-5 adhesive film were aged and tested at different periods. The first set of FM-5 samples were initially placed into ovens and aged at 177°C and 204°C, in both ambient pressure and 13.8 KPa air environments. Selected samples were periodically removed and tested following aging times of various lengths. A second set of FM-5 dogbone samples and a set of PETI-5 samples were prepared some time later and aged at 204°C in ambient air. Tensile testing was performed on a 4505 Instron machine (Canton, MA, USA) at a crosshead displacement rate of 1 mm/min. The stress and strain values were recorded for all the specimens using an axial extensometer to acquire strain data.

Table 2 shows the stress-strain results from the first set of FM-5 samples aged at both 177°C (in air and 2 psi air) and 204°C for periods up to 24 months. The overall trend is that the failure stress and the failure strain decrease significantly as aging time increases under various aging conditions, although a slight increase in stress and strain can be observed for specimens aged for 18 months at 177°C. The greatest drop in material properties occurred for the samples aged at 204°C. Following 24 months of aging at 204°C, the failure stress decreased to 53 MPa from an initial value of 107 MPa, a decrease of about 50%; the strain value decreased from 6.3% to 1.32%, a reduction of 79%. By comparing the results for samples aged at 177°C in different air atmospheres (air pressure and 13.8 KPa air) shown in Table 2, we can see that aging in the reduced-pressure atmosphere leads to a less-pronounced reduction in the stress and strain. The significant conclusions from the above results are that the greatest drop in material properties occurs for the samples in atmospheric air at 204°C, and that the lower air pressure, and

TABLE 2 Tensile Stress-Strain Results on the First Set of FM-5 Neat Resin Samples for Various Aging Times, Temperatures, and Pressures

Aging condition	# Spec	Failure stress, MPa (Std. Dev.)	Failure strain (Std. Dev.)
As-received	10	107 (11)	0.063 (0.0027)
3 months in air at 177°C	4	111 (2.8)	0.0585 (0.0051)
6 months in air at 177°C	4	88 (2.2)	0.0355 (0.0033)
12 months in air at 177°C	4	71 (2.1)	0.0189 (0.0015)
18 months in air at 177°C	3	83 (15)	0.0237 (0.0052)
24 months in air at 177°C	2	80.3 (1.4)	0.0233 (0.002)
6 months 13.8 KPa at 177°C	4	108 (3.6)	0.0412 (0.0042)
12 months 13.8 KPa at 177°C	3	103 (19)	0.0347 (0.0105)
18 months 13.8 KPa at 177°C	2	106 (21)	0.0381 (0.0136)
3 months in air at 204°C	4	95 (2.2)	0.0478 (0.0064)
6 months in air at 204°C	8	84 (7.9)	0.0304 (0.0022)
12 months in air at 204°C	3	67 (8.2)	0.0195 (0.0043)
18 months in air at 204°C	3	54 (7.2)	0.014 (0.0017)
24 months in air at 204°C	3	53 (10.6)	0.0132 (0.0032)

therefore the lower the concentration of oxygen in the aging environment, the smaller the drop in material properties. The failure stress and the failure strain as a function of aging time for each aging condition are shown in Figures 2–4, with error bars denoting plus and minus one standard deviation. Lines have been curve fitted through the mean strength and strains for convenience, but they are not meant to imply actual trends.

The stress strain behavior results for the second set of FM-5 specimens, as well as PETI-5 dogbone samples, are shown in Table 3. These samples were aged at 204°C for periods of up to 30 months. For the FM-5 samples, the results exhibit very similar trends to those seen for the first set of FM-5 samples. The failure stress and failure strain continued to decrease as the aging time increased. Following 30 months of aging, the tensile strength dropped by 70% to 36 MPa from an initial value of 120 MPa, and the failure strain decreased dramatically from the initial value 10% to 0.8%. The PETI-5 samples retained relatively stable strength even after 12 months of aging. However, after 30 months of aging, the tensile strength of PETI-5 exhibited a reduction of around 50%, from the initial value of 124 MPa to 69 MPa. The failure strains of the PETI-5 specimens showed a decreasing

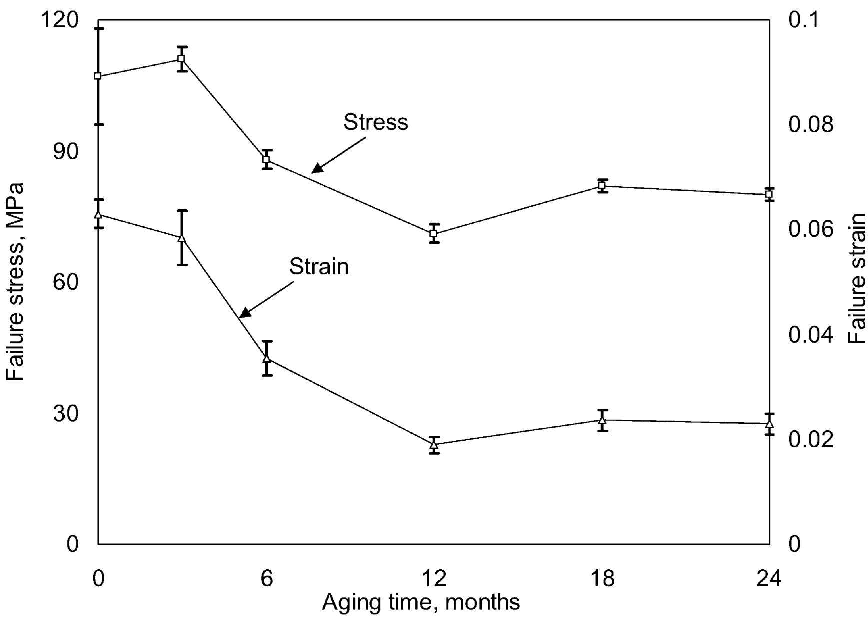

FIGURE 2 Failure stress and failure strain as a function of aging time for FM-5 resin samples aged at 177°C in air at ambient pressure.

FIGURE 3 Failure stress and failure strain as a function of aging time for FM-5 resin samples aged at 177°C in 13.8 KPa air.

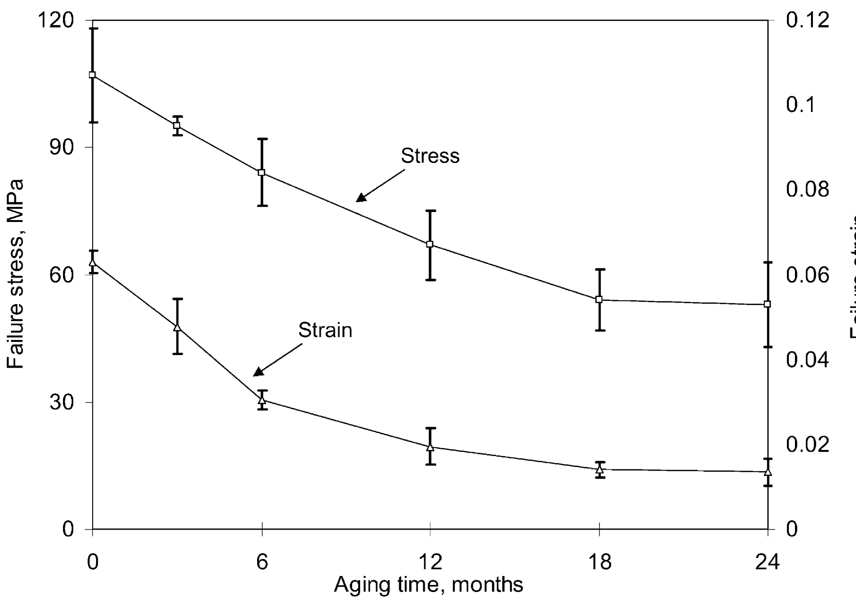

FIGURE 4 Failure stress and failure strain as a function of aging time for FM-5 resin samples aged at 204°C in air at ambient pressure.

TABLE 3 Tensile Stress-Strain Results on the Second Set of FM-5 and PETI-5 Neat Resin Samples as a Function of Aging Time

	Aging Condition	# Spec.	Failure Stress, MPa (1 Std. Dev.)	Failure Strain (1 Std. Dev.)
PETI-5	As-received	6	124 (1.7)	0.4*
	6 months in air at 204°C	3	132 (1.5)	0.074 (0.0088)
	12 months in air at 204°C	3	135 (0.6)	0.068 (0.0004)
	31 months in air at 204°C	3	69 (8.5)	0.0184 (0.003)
FM-5	As-received	6	120 (0.8)	0.1 (0.01)
	6 months in air at 204°C	3	60 (15)	0.015 (0.004)
	12 months in air at 204°C	3	57 (5)	0.013 (0.002)
	31 months in air at 204°C	3	36 (1.4)	0.00842 (0.0017)

*Maximum strain estimated at the necking region (outside of the extensometer gage length).

trend with increased aging, and after 30 months of aging the failure strain decreased to 1.8% from 40%, which was obtained on the as-received PETI-5 samples. These results suggest that significant thermal degradation of the adhesive resin and embrittlement have occurred as a result of thermal aging. These dramatic changes in ultimate strength, failure strain, and toughness of the FM-5 and PETI-5 resins raise significant concerns about using these resins at elevated temperatures for extended periods of time.

COMPARISON OF CAA TI/WOVEN SCRIM FM-5, SOL-GEL TI/WOVEN SCRIM FM-5, AND SOL-GEL TI/MAT SCRIM FM-5 JOINTS

Mode I, mode II, and mixed-mode fracture tests were conducted to compare the properties of different adhesive joints. In this study, double cantilever beam (DCB, mode I), end notch flexure (ENF, mode II) and mixed-mode flexure (MMF, mixed-mode;) (see Figure 5) fracture specimens were utilized to evaluate the critical strain energy release rates of the adhesive bonded systems. Prior to testing, a sharp precrack was made in each fracture specimen by hitting a stainless wedge inserted into one edge of the sample. For more details concerning the test principle and test methods, interested readers are referred to Parvatareddy and Dillard [21]. The adhesive joints under investigation were CAA Ti/woven scrim FM-5 bonds (designated as FM-5 in the figures), sol-gel Ti/woven scrim FM-5, and sol-gel Ti/mat scrim FM-5 (designated as FM-5M in the figures). Some sol-gel Ti/mat scrim FM-5 joints with considerable porosity were initially supplied by

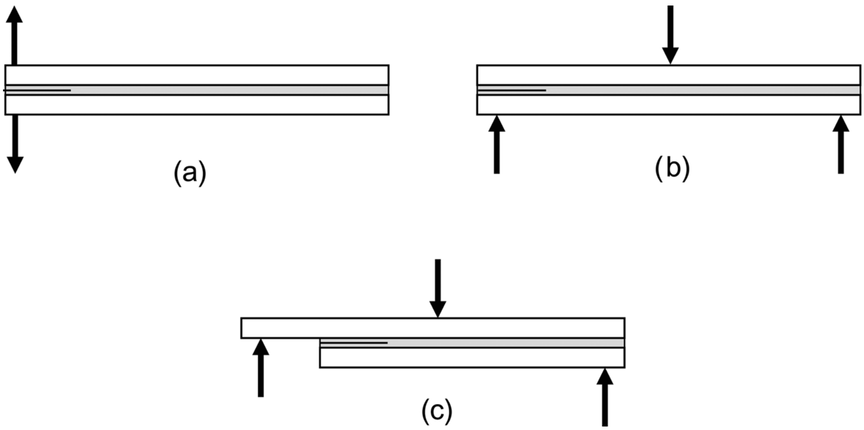

FIGURE 5 Schematic of fracture specimen geometries: (a) symmetric DCB, pure mode I; (b) end-notched flexure (ENF), pure mode II; (c) mixed-mode flexure (MMF), 57% mode I and 43% mode II.

Boeing and tested. Later on, Boeing supplied some new sol-gel Ti/FM-5M specimens with improved quality (reduced porosity) as a replacement for the porous joints. Results obtained on both porous sol-gel Ti/FM-5M joints and those with reduced porosity are presented for comparison purposes although the cause of the porosity is unknown to us.

Figure 6 shows the DCB results for as-bonded aliphatic sol-gel Ti/woven scrim FM-5 and aliphatic sol-gel Ti/mat scrim FM-5 joints. For comparison purpose, test results for as-bonded CAA Ti/woven scrim FM-5 bonds, which were given in Parvatareddy *et al.* [18], are also shown in the figure. The error bars in the figure denote plus and minus one standard deviation, and they are obtained from multiple fracture energy values (at least eight data points) obtained on a single DCB specimen. As can be observed from the figure, the fracture energy of sol-gel Ti/FM-5 and sol-gel Ti/FM-5M with reduced porosity is comparable with that of CAA Ti/FM-5 under mode I loading condition, although the arrest value for sol-gel Ti/FM-5M is somewhat lower than the other two material systems. However, for the porous sol-gel Ti/FM-5M joints, which were initially supplied by Boeing, the fracture energy is much less than that for other adhesive joints. This verifies that porosity significantly affects the property of these bonds and also suggests that one must be very careful in making the adhesive joints to reduce porosity.

Figure 7 summarizes the fracture energies of the aliphatic sol-gel Ti/scrim FM-5M adhesive-bonded system under mode I, mode II,

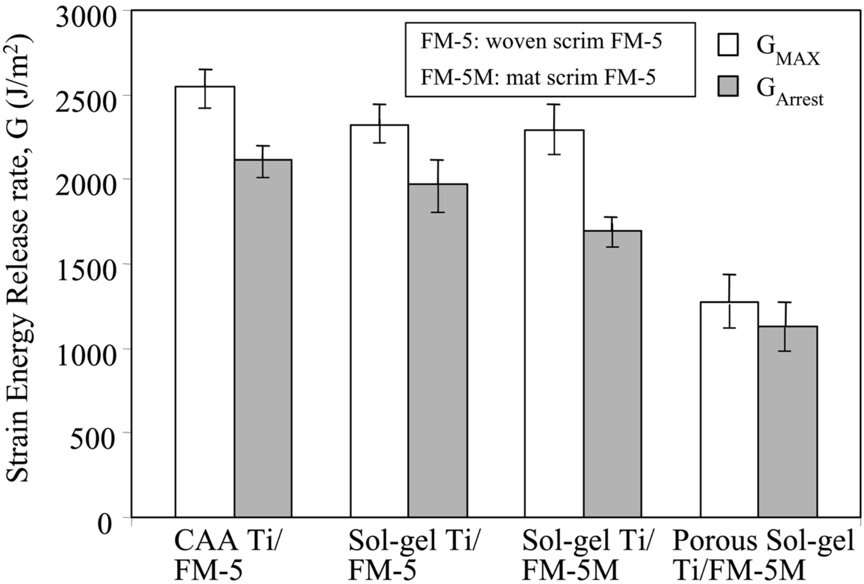

FIGURE 6 DCB test results for different adhesive-bonded systems.

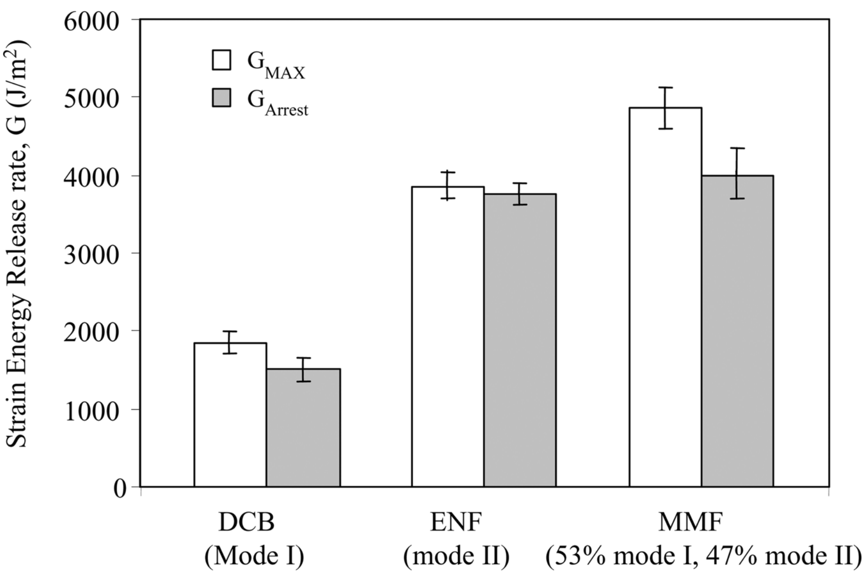

FIGURE 7 Strain energy release rate values under mode I, mode II and mixed mode loading for the aliphatic sol-gel Ti/FM-5M adhesive bonded system.

and a combination of mode I and mode II loading conditions. The error bars in the figure denote plus and minus one standard deviation. Two specimens were tested for each condition, and approximately ten loading cycles per specimen were obtained. One point that should be mentioned here is that the maximum fracture energies under mode I and mixed-mode loading were the ones calculated with the maximum load value, while the maximum energy value under mode II loading corresponded to the load point at which load *versus* displacement traces began to deviate from linear load deflection behavior, which indicates that the crack starts propagating, and may have underestimated the maximum fracture energy of the adhesive bond under Mode II loading. The reason for different criteria in the tests is that plastic deformation in the substrates was evident in the mode II testing when the samples were loaded to the maximum value, as might be expected because of the lower fracture efficiency for the ENF geometry [20]. To avoid permanent deformation in the substrates due to overloading, the crosshead was held immediately after load *versus* displacement traces deviated from linearity. For mode I and mixed mode tests, no plastic deformation was observed in the substrates even when the load reached the maximum value. From Figure 7, it can be observed that the energy values measured under mode II and mixed-mode loading are considerably higher than those obtained under mode I conditions for the sol-gel–pretreated Ti/mat scrim FM-5 adhesive bonds. Furthermore, visual observations of the fracture surfaces of sol-gel–pretreated Ti/mat scrim FM-5 suggest that adhesive joints tested under mode I, mode II, and mixed-mode loading conditions all exhibited cohesive failure, near the middle of the adhesive layer. One possible explanation for the great difference in the fracture energies under different loading modes is that under mode II loading, as well as mixed-mode loading, the two fractured surfaces may have come in contact near the crack tip during crack propagation and resulted in some friction, giving rise to greater energy dissipation and a higher fracture energy, while under mode I loading the two fractured surfaces separated from each other during loading and thus could reduce the friction between the fractured surfaces of the adhesive joint.

The results obtained on the aliphatic sol-gel Ti/scrim FM-5M joint are quite different from those observed on CAA Ti-6Al-4V/FM-5 bonds in the previous work [21]. For the CAA Ti-6Al-4V/FM-5 adhesive bonded system, the mode I fracture energy was much greater than the mode II and mixed-mode fracture energies. This unusual behavior was attributed to the observation that mode I loading produced failures along the scrim cloth region, where fiber tear-out, fiber bridging, and a tortuous failure path led to increased fracture toughness [22].

TABLE 4 Failure Mode of the Aliphatic Sol-gel Ti/scrim FM-5M Joint and the CAA Ti-6al-4v/FM-5 Joint

	DCB	ENF	MMF
Sol-gel Ti/scrim FM-5M	Cohesive	Cohesive	Cohesive
CAA Ti-6Al-4V/FM-5	Cohesive	Interfacial	Mixed mode

On the other hand, mode II loading induced the debond to propagate near the interface where less energy could be dissipated by the propagating debond. Visual observations of the fracture surfaces of sol-gel–pretreated Ti/mat scrim FM-5 and CAA-pretreated Ti-6Al-4V/woven scrim FM-5 reveal that the two material systems exhibited different failure modes (See Table 4). Under mode I loading, the CAA Ti-6Al-4V/woven scrim FM-5 joint showed cohesive failure, similar to the aliphatic sol-gel Ti/scrim FM-5M joint, and the fracture energies are similar for both adhesive joint systems. However, under mode II and mixed-mode loading, the CAA Ti-6Al-4V/FM-5 samples exhibited an interfacial failure under mode II loading and a mixed-mode failure under mixed-mode loading, while the aliphatic sol-gel Ti/ FM-5M joint displayed a pure cohesive failure, all based on visual observations. The different failure modes between CAA Ti-6Al-4V/FM-5 and aliphatic sol-gel Ti/ FM-5M joints may suggest that the adherends pretreated with sol-gel may produce stronger, more durable bonds than those pretreated with CAA. Further investigation, however, is needed to explore the roles these factors could play in the adhesive bond strength.

ENVIRONMENTAL AGING EFFECTS ON SOL-GEL TI/MAT SCRIM FM-5 JOINTS

Sol-gel Ti/mat scrim FM-5 DCB joints were tested prior to and after aging at 177°C and 204°C, following the test procedure described in ASTM D 3433–99 [23]. Two specimens were tested for each condition, and approximately ten loading cycles per specimen were obtained. As can be seen in Figure 8, the fracture energy of the adhesive system showed a significant decrease in both maximum and arrest values of the critical strain energy release rates following 22 months of aging. For samples aged at 177°C, the G_{MAX} decreased to 1220 J/m^2 from an initial value of 1830 J/m^2, a reduction of about 34%, and the G_{Arrest} fell to 970 J/m^2 from 1506 J/m^2, a decrease of approximately 36%. For samples aged at 204°C, the decrease of the fracture energy is more remarkable. The G_{MAX} decreased to 340 J/m^2, which is only 19% of

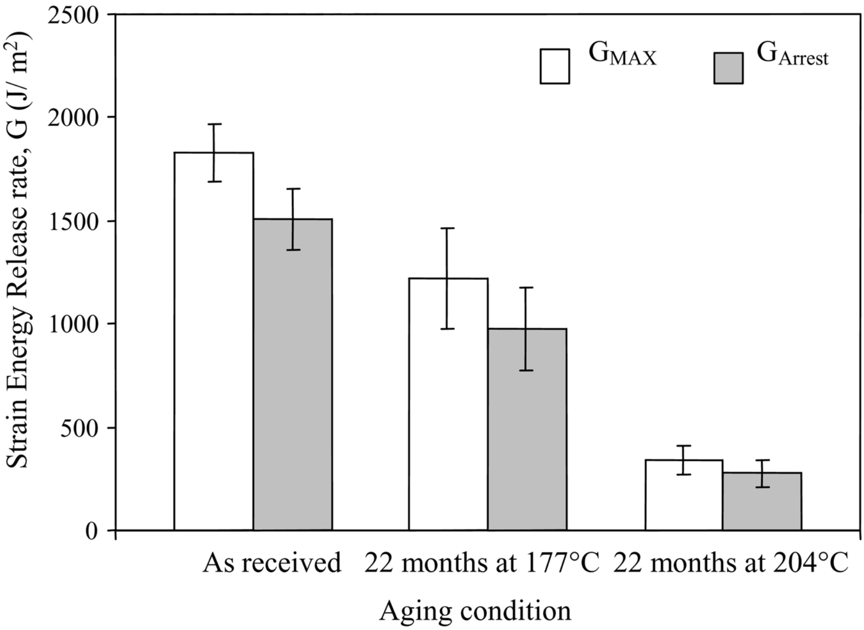

FIGURE 8 Static DCB test data on as-received and aged aliphatic sol-gel Ti/FM-5M adhesive bonded joints.

the initial fracture energy, and the G_{Arrest} fell to 270 J/m^2, which is only 18% of the initial value. Higher aging temperature could accelerate the thermal degradation process of the adhesive joint and cause reduction in the fracture toughness at a faster rate. The typical fracture surfaces of the as-received joints and aged joints are shown in Figure 9. As can be observed from the figure, the as-received joint exhibited pure cohesive failure. Following aging, however, the samples showed some interfacial failure (visual observation) at the adhesive/adherend interface around the outer edges of the specimens. This transition from cohesive failure to interfacial failure at the outer edges may suggest chemical degradation at the interfacial regions. The degradation of Ti/FM-5 bonds with time is of great concern, and significant improvements may be required before these material systems could safely be used in high-speed aircraft.

THICK ADHEREND (TA) CREEP TESTS

To investigate the creep behavior of the Ti-6Al-4V/FM-5 bonded system, creep tests were conducted on the thick adherend specimens

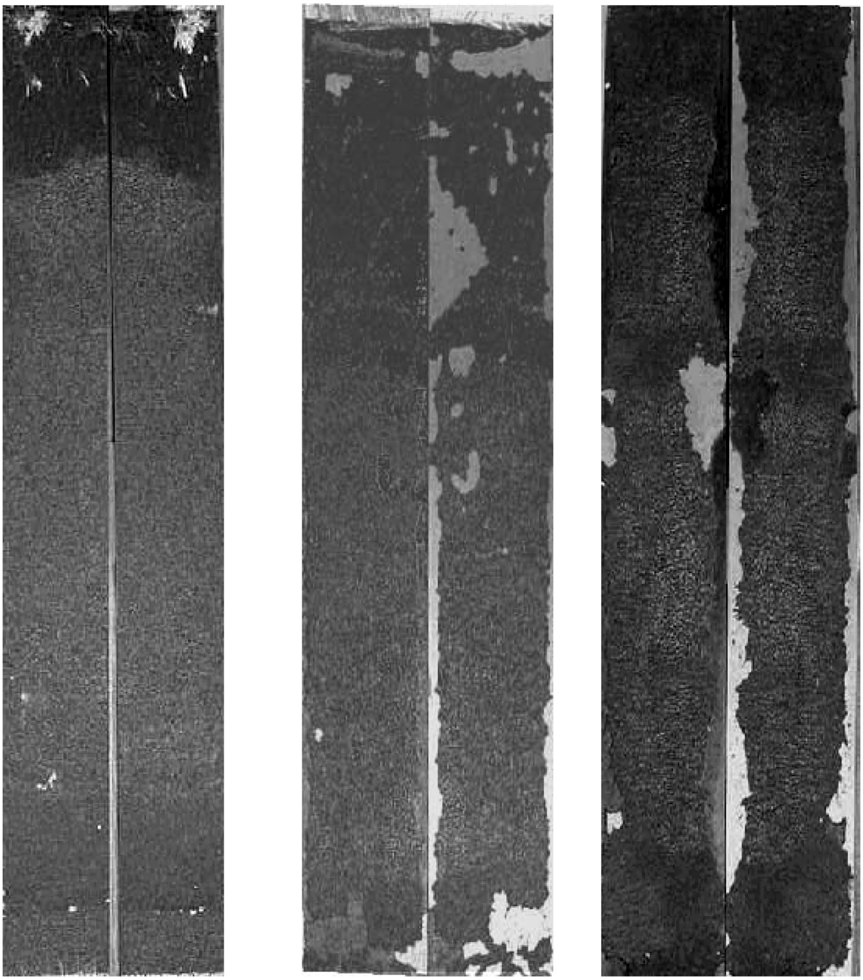

FIGURE 9 Fractured surfaces of DCB specimens, both as-received and following aging at 177°C and 204°C for 22 months.

loaded in a tensile creep frame. Specimens were instrumented with Iosipescu strain gage rosettes (Micromeasurements A2P-08-C085C-500, Raleigh, NC, USA) that consist of $\pm 45^\circ$ elements. Because these gages are sized appropriately for straddling the bondline, they are believed to represent an improvement over the use of other rosettes [24]. The tests were undertaken at a series of temperatures, from RT to about 150°C. At each temperature, the specimen was loaded for an hour, followed by another hour in the unloaded state to recover the creep deformation. Then the specimen was heated to the next test temperature for one more hour to accelerate the recovery. Applied loads in the creep test were 20, 40 and 50% of the shear strength of TA specimens, respectively, which is around 41 MPa (6000 psi) as obtained by conducting ramp-to-failure tests at room temperature. Two specimens were tested for the 20% loading level to verify the repeatability of the measurement, and one specimen was tested for the other two loading levels through all of the designated temperatures.

Figure 10 shows the trace of strain-time relationship at different temperatures for both the loading and recovering stage under a load of 20% of the shear strength. From this figure, one can find that the adhesive joint shows significant creep behavior even at room temperature and under a relatively low loading condition (20% of shear strength). This was somewhat unexpected, as the polymer is well below its glass transition temperature. As the test temperature goes up, the creep behavior tends to be more evident. Figure 11 shows master curves for creep compliance obtained using the creep curves at different temperatures under applied loads of 20, 40, and 50% of the shear strength. A master curve can be obtained by shifting each creep curve horizontally relative to a curve obtained at a reference temperature. As can be observed from the figure, the compliance curves under loads of 20% of the shear strength and those of 40% of the shear strength basically exhibit the same trend, while for the creep test

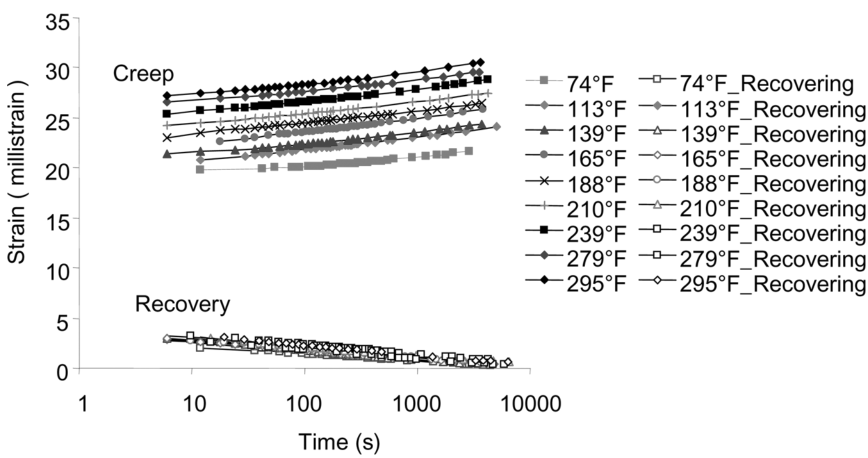

FIGURE 10 Creep strain of TA specimen under 20% shear strength.

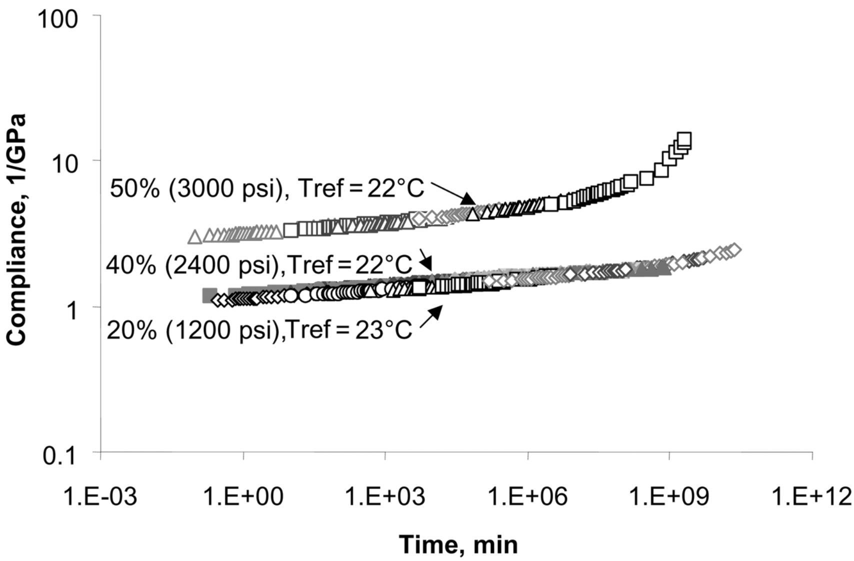

FIGURE 11 Creep compliance master curves of thick adherend specimens under different loading levels.

loaded at 50% of the shear strength the compliance values are apparently higher than the values obtained under loads of 20 and 40% of the shear strength. The significant increase of compliance magnitude when the specimen was loaded with 50% of shear strength may suggest that nonlinear viscoelastic behavior has occurred under this loading condition.

SUMMARY AND CONCLUSIONS

This work was initiated to evaluate the durability of Ti-6Al-4V/FM-5 adhesive joints for applications in high-speed aircraft. Through this study, some important conclusions may be drawn, as follows:

Thermal aging effects took place in the Ti-6Al-4V/FM-5 bonded joints and neat FM-5 and PETI-5 resin specimens upon exposure to high temperature, affecting the durability of the material systems.

The tensile test results on both neat FM-5 and PETI-5 resin samples revealed that significant thermal degradation of the adhesive resin and embrittlement have occurred as a result of thermal aging, which resulted in significant loss in strength and failure strain.

Fracture tests conducted on both woven scrim and mat scrim FM-5 adhesive bonds suggest that there are no significant differences for as-bonded specimens between these two different-scrimmed FM-5 adhesive bonds. However, porosity in the adhesive joints can greatly affect bond toughness. The fracture energy measured with the porous adhesive joints is significantly less than for specimens with reduced porosity.

Several important differences between aliphatic sol-gel–pretreated Ti-6Al-4V/mat scrim FM-5 adhesive bonds and CAA-pretreated Ti-6Al-4V/woven scrim FM-5 adhesive joints were observed in this study. For aliphatic sol-gel Ti-6Al-4V/FM-5M adhesive bonds, the fracture energies of mode II and mixed mode are about twice and three times that for mode I, respectively. However, for CAA-pretreated Ti-6Al-4V/woven scrim FM-5 adhesive joints, the mode I fracture energy is about twice and 1.5 times that of the mode II and mixed-mode fracture energies, respectively. In addition, for aliphatic sol-gel Ti-6Al-4V/FM-5M samples, the failure under mode II and mixed mode is cohesive, while the CAA Ti-6Al-4V/FM-5 samples exhibit interfacial failures and mixed-mode failures, respectively.

Results obtained from this work suggest that both the bulk polyimide adhesives and their joints can significantly degrade upon exposure to high-temperature conditions. As potential materials to be used in high-speed aircraft, these materials and their joints might be subjected to temperatures on the order of 177°C for 60,000 h. This study suggests that significant improvements might be required before these material systems could safely be used under such conditions.

Thick adherend creep test results show that the Ti-6Al-4V/FM-5 adhesive joint exhibits evident creep behavior even under relatively low loading (20% of shear strength) and at room temperature. At higher loading conditions, the compliance amplitude shows a significant increase, and nonlinear viscoelastic behavior could have occurred. The evident creep behavior of this adhesive system may also be of concern for applications in high-speed aircraft.

For future work, it is necessary to conduct further investigations on the durability of Ti/FM-5 bonds with different scrim cloth and surface treatment and identify the adhesive bond with the best scrim cloth and surface treatment for HSCT applications. Thermal fatigue and humidity tests may also be important to understand the performance of the adhesive bonds under these environmental conditions that could be encountered in simulated HSCT flight conditions.

REFERENCES

[1] St. Clair, T. L. and Progar, D. J., *J. Adhesion* **47**, 67–82 (1984).

[2] Hendricks, C. L. and Hill, S. G., In: *Polyimide: Synthesis, Characterization, and Applications*, K. L. Mittal, Ed., (Plenum Press, New York, 1984), Vol. 2, pp. 1103–1115.

[3] Smith, J. G. and Hergenrother, P. M., *Polym. Prepr*. **35**, 353–355 (1994).
[4] Falcone, A., Pate, K. D., Cao, T. Q., Hsu, F. F., and Rogalski, M. E., In*: Proc. 41st Int. SAMPE Symp*., Anaheim CA, (1996), pp. 1035–1046.
[5] Haggerty, J. J., *Spinoff*, Washington, D. C. (1994); (National Aeronautics and Space Administration, Office of Space Access and Technology Transfer Division, 10, 1992).
[6] Struik, L. C. E., *Polymer* **30**, 815–830 (1989).
[7] Sullivan, J. L., Blais, E. J., and Houston, D., *Composite Sci. Technol*. **47**, 389–403 (1993).
[8] Wang, J. Z., Pavatareddy, H., Chang, T., Iyengar, N., Dillard, D. A, and Reifsnider, K. L., *Composite Sci. Technol*. **54**, 405–415 (1995).
[9] Emaniel, N. M. and Buchachenko, A. L., *Chemical Physics of Polymer Degradation and Stability* (VNU Science Press, Utrecht, 1987).
[10] Cotton, F. A. and Wilkinson, G., *Basic Inorganic Chemistry* (John Wiley and Sons, Inc., New York, 1976).
[11] Brick, R. M., Pense, A. W., and Gordon, R. B., *Structure and Properties of Engineering Material*s, 4th ed. (Mc-Graw Hill Book Company, New York, 1977).
[12] Mahoon, A., In: *Durability of Structural Adhesives*, A. J. Kinloch, Ed. (Applied Science Publishers, London, 1983).
[13] Allen, D. R. and Allen, A. S., *SAMPE J*. **3**, 64–73 (1967).
[14] Ditchek, B. M., Breen, K. R., Sun, T. S., and Venables, J. D., *25th National SAMPE Symp*. 13–19 (1980).
[15] Filbey, J. A. and Wightman, J. P., *J. Adhesion* **28**, 1–22 (1989).
[16] Brown, S. R., *27th National SAMPE Symp.* 363–370 (1982).
[17] Allen, K. W., Chan, S. Y. T., and Armstrong, K. B., *Int. J. Adhesion Adhesives* **2**, 239–256 (1981).
[18] Pavatareddy, H., Dillard, J. G., McGrath, J. E., and Dillard, D. A., *J. Adhesion Sci. Technol*. **12,** 615–637 (1998).
[19] Arnold, J. R., Sanders, C. D., Bellevou, D. L., Martinelli, A. A., and Gaskin, G. B., *SAMPE J.* **34**, 11–14 (1998).
[20] Lai, Y. H. and Dillard, D. A., *Int. J. Solids Structures*, **34**(4), 509–525 (1997).
[21] Parvatareddy, H. and Dillard, D. A., *Int. J. Fracture*, **96**, 215–228 (1999).
[22] Chen, B., Dillard, D. A., Dillard, J. G., and Clark, R. L. Jr., *Int. J. Fracture*, **114**, 167–190 (2002).
[23] American Society for Testing Materials, ASTM D3433–99, Standard test method for fracture strength in cleavage of adhesives in bonded metal, In: *Annual Book of ASTM Standards* (American Society for Testing and Materials, West, Conshohocken, PA, 1999).
[24] Tsai, N. Y., Morton, J., and Oplinger, D. W., *Exper. Mech.*, **36**, 297–304 (1996).