**ACCELERATED AGING OF
POLYIMIDE/TITANIUM ADHESIVE BONDS
USING THE NOTCHED COATING ADHESION
TEST**

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ABSTRACT

The effect of elevated temperature aging on the interphase of a polyimide adhesive and a titanium substrate has been investigated. An interfacially debonding adhesive test was applied, and the adhesive/substrate interphase was characterized through an analysis of the failure surfaces. To facilitate the aging study, an “open-faced” adhesive geometry was used. Use of this adhesive geometry allows an acceleration of diffusion-related aging phenomena by up to two orders of magnitude, as compared to a traditional “sandwiched” bond. The failure surfaces were characterized using x-ray photoelectron spectroscopy and optical microscopy. Bulk adhesive properties were investigated using differential scanning calorimetry, infrared spectroscopy, and solvent uptake. Although there was evidence of polyimide degradation within the interphase, only minor changes in the bulk polyimide properties were detected. This indicates that the adhesive may be degrading preferentially in the interphase region.

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INTRODUCTION

When bonded joints are subjected to harsh environmental conditions, failures tend to occur near the interface (1-5). Therefore, the long-term durability of adhesive joints is critically dependent on the three-dimensional adhesive/substrate interphase. Although changes in adhesive performance after aging are measured routinely, the interaction of an adhesive with the substrate during aging is not well understood (6). As depicted by Drzal *et al.* (7), the interphase exists from the point in the substrate where the local properties begin to differ from the bulk, through the interface, and into the adhesive until the properties equal those in the bulk. Figure 1 is based on Drzal's schematic representation of the interphase as it applies to metal/adhesive bonds. The thickness of the interphase can vary greatly, with estimates ranging from a few nanometers to a few thousand nanometers (7, 8).

Analysis of the adhesive-substrate interphase is essential in the study of the durability of high-performance adhesives. A current area of adhesive durability research is the development of critical technologies for elevated temperature aerospace applications. High performance polymeric adhesives are needed for bonding titanium in structural components of aircraft. These joints have been designed to withstand a temperature of 177°C for 60,000 hours while maintaining desirable mechanical properties (9).

LaRC™ PETI-5 (10-18), a phenylethynyl-terminated polyimide adhesive, was developed for potential use in high-temperature aircraft applications. The structure of the PETI-5 precursor, which undergoes chain extension and crosslinking of the end groups during

cure, is illustrated in Figure 2. Prior to cure, the molecular weight of PETI-5 used in the current study is 5,000 g/mol. After an elevated temperature cure, the lightly crosslinked, amorphous polyimide has a glass transition temperature of 260°C. FM-5, developed by Cytec Fiberite, Inc., Havre de Grace, MD, is a blended adhesive based on PETI-5. It has a slightly lower glass transition temperature, 250°C. Details regarding the blend components are proprietary. The potential for use of PETI-5 or FM-5 in the aerospace industry has prompted numerous investigations of the durability of these adhesive joints with Ti-6Al-4V (14, 18, 19), an alloy of 90% titanium, 6% aluminum, and 4% vanadium.

In one such study, Parvatareddy *et al.* (19) investigated thermal aging of double cantilever beam (DCB) specimens of FM-5 adhesive bonded to chromic acid anodized (CAA) Ti-6Al-4V. Specimens were aged at 177°C or 204°C in air. The failure surfaces of DCB specimens, as-received and aged for 12 months, are shown in Figure 3. Prior to specimen aging, the bonded samples fail cohesively, through the centerline of the adhesive. Following 12 months of aging at 177° or 204°C, there are two distinct failure modes. The central portions of the specimens continue to fail cohesively. However, the edges of the specimens, upon visual inspection, appear to have failed at the adhesive/substrate interface.

These failure regions were analyzed by x-ray photoelectron spectroscopy (XPS) (20). Titanium was detected on the metal failure surface but not on the adhesive failure surface, indicating that the failure did not occur in the metal oxide layer. Evidence of FM-5 adhesive (carbon, oxygen, and nitrogen at the known binding energies) was detected on both failure surfaces. This indicates that the failure occurred through the

adhesive interphase, close enough to the titanium substrate that the titanium could be detected within the penetration depth of the XPS, typically 5 to 10 nm. This type of failure occurred only around the edges of the bond. Therefore, it appears that degrading species, presumably oxygen, diffused through the edges of the bonded specimen during elevated temperature aging in air, and this degradation led to failure in the interphase.

The primary objective of the current research has been to investigate the effect of thermal aging on the interphase region of PETI-5 and FM-5 bonded to chromic acid anodized titanium substrates. From Parvatareddy's work (19, 20), it appears that degradation is occurring when the adhesive is simultaneously exposed to the adherend, elevated temperatures, and air. While previous work has focused on changes in adhesive strength and bulk polymer properties as a function of aging time, the current study will focus on changes in the adhesive adjacent to the substrate surface as a result of elevated temperature aging. The polyimide/Ti-6Al-4V interphase was investigated using an interfacially debonding adhesive test, the notched coating adhesion test (21). The adhesive joints were aged at elevated temperatures for up to 3 months in air.

An additional objective of the present study is to evaluate the use of the NCA test for durability characterization of other adhesive-substrate systems. As is observed in the example of Parvatareddy's study, the interphase is subject to environmental attack in many adhesive systems, particularly when metal adherends are used (22). Thus, there is a great need for methods of assessing the durability of this region of the adhesively bonded joint.

Notched Coating Adhesion Test

In the present work, adhesive performance was measured using the NCA test (21, 23). A schematic of an NCA specimen during testing is shown in Figure 4. The NCA test is based on self-delamination theory (24), the phenomenon of delamination of a sufficiently thick coating from a substrate, caused by residual stresses within the coating. In the NCA test, the stresses within the coating are increased by applying a tensile load to the NCA specimen. A debond between the adhesive and the substrate is initiated by notching the adhesive coating. The specimen is pulled in tension until the initial adhesive debond propagates. The strain at which the debond propagation occurs, the critical strain, is used to calculate the critical strain energy release rate, G_c , of the system. This is a measure of the adhesive/substrate system's resistance to fracture. Assuming the steady-state condition, according to Dillard *et al.*,²³ Equation 1 is used to calculate G_c , where

$$G_c = \frac{h}{\hat{E}} \left\{ \left[\sigma_o^2 + \sigma_o \hat{E} \varepsilon_c \right] (1 - \nu) + \frac{1}{2} (\varepsilon_c \hat{E})^2 \right\} \quad \text{Equation 1}$$

and h is the adhesive thickness, E is the modulus of the adhesive, ν is Poisson's ratio of the adhesive, σ_o is the sum of all residual stresses within the adhesive, and ε_c is the critical strain to cause debond propagation.

There are two major advantages of the NCA test in this study. First, the “open-faced” adhesive geometry may allow aging to occur more quickly than in traditional adhesive bonds due to the shortened diffusion path. In a traditional adhesive bond geometry, the adhesive is sandwiched by two substrates, so diffusion of species in the environment can

only occur through the edges of the adhesive bond. The diffusion path length, therefore, is half the width of the adhesive specimen, generally 6 to 12 mm. In an NCA specimen, the diffusion path length is the thickness of the adhesive, generally less than 1 mm. Since diffusion time is proportional to the diffusion distance squared, the total time for a specimen to reach equilibrium with the environment may be decreased by up to two orders of magnitude. The second advantage of the NCA test is the incorporation of two modes, or mixed mode I and II, that drives the failure toward the interface. This allows surface characterization of the area of interest in this investigation, the interphase region, at all stages of the durability study.

EXPERIMENTAL

Materials

Adhesives

The focus of this study involves the behavior of two polyimide adhesives, Cytec Fiberite™ FM-5 and LaRC™ PETI-5. FM-5 was used as received from Cytec Fiberite Inc.™, Havre de Grace, MD, and consisted of a polyimide adhesive supported by a glass scrim cloth arranged in a 0°/90° plain weave. As received, FM-5 contained approximately 4% N-methyl pyrrolidinone (NMP) by weight. Upon cure, FM-5 is an amorphous thermoset with a T_g of 250°C. PETI-5 was received from Imitec,™ Schenectady, NY, as an amic acid solution at 35% solids (w/w) in NMP. The calculated molecular weight of uncured PETI-5 was 5,000 g/mol. Upon cure, PETI-5 is a thermoset with a T_g of 260°C.

FM-5 adhesive tape, supported by a glass scrim cloth, was used as received in the fabrication of adhesive specimens. PETI-5 adhesive tape was fabricated and subsequently used in the preparation of adhesive specimens. An E-glass scrim cloth, 0.08 mm thick with A1100 finish arranged in a 0°/90° plain weave, was stretched onto a frame and dried at 150°C for one hour prior to application of the adhesive. The cloth was impregnated with adhesive by applying PETI-5 as a poly(amic acid) solution in NMP using a natural bristle paintbrush. Each coat of PETI-5 solution was dried for one hour at 175°C. Several coats were applied to the glass cloth until the desired thickness of 0.30 mm was obtained. Further drying cycles up to 250°C were performed to reduce the volatile content of the tape to less than 2.5%.

Substrates

The substrates of all adhesive specimens were Ti-6Al-4V. Substrates were received from President Titanium Co., Hanson, MA. The substrates used with the FM-5 adhesive measured $121 \times 12.7 \times 1.78$ mm, and those used with the PETI-5 adhesive were $203 \times 12.7 \times 1.78$ mm.

Following degreasing of the substrates, they were anodized in chromic acid at 5.0 V and 0.2 amps for 20 minutes. After drying in a 60°C oven, the PETI-5 coupons were primed using a 16% solids solution of PETI-5 amic acid in NMP. The primed coupons were dried at 225°C for 1 hour. The FM-5 coupons were not primed, and were bonded within 48 hours of anodization.

Adhesive Bonding Conditions

The FM-5 adhesive samples were manufactured in a hot press using a bonding pressure of 690 kPa at 350°C for one hour. Two plies of FM-5 adhesive in scrim cloth were used, and bondlines were controlled to 0.76 mm.

The PETI-5 adhesive samples were manufactured in an autoclave under vacuum using a bonding pressure of 690 kPa at 350°C for 30 minutes and 371°C for 30 minutes. Two plies of adhesive in scrim cloth were used, and bondlines were controlled to 0.25 mm.

The modifications in the PETI-5 cure cycle, application of a vacuum and a higher final cure temperature, were necessary to eliminate residual volatiles and crystallinity. The use of primer on the PETI-5 titanium coupons was recommended to protect the chromic acid anodized titanium surface. These modifications more accurately mimic the processing conditions that would be used commercially, however, the changes prevent one from making a direct comparison between the FM-5 and PETI-5 adhesive systems. Regardless, the observed trends during elevated temperature aging of the two adhesive systems were the same, as expected.

Aging Conditions

FM-5 adhesive specimens were aged for 1 to 90 days in air at 177°C. PETI-5 adhesive specimens were aged for 30 days at 177°C in either air or nitrogen. Atmospheric pressure was maintained in all ovens. Unaged specimens were stored in a vacuum desiccator at room temperature until testing was performed.

Characterization

Adhesive / substrate debonding

FM-5 adhesive specimens

A pre-crack was made between the adhesive and substrate by notching the center of the specimen with a hacksaw. The notch created an area of localized debonding. Ten NCA specimens were tested for each aging condition. The specimens were tested on an Instron 4505 machine under control of a Lab View program. A 100 kN load cell was used. A 25.4-mm gauge length extensometer was used to monitor strain. The strain rate used was 10 mm/min.

PETI-5 adhesive specimens

An initial debond was made between the adhesive and substrate of the NCA specimens by driving a razor blade into the interface. Specimens were then placed in a hand-held three-point-bend fixture and bent so that the adhesive coating was in tension. The razor-induced debond propagated to form a sharp-tipped debond between the adhesive and the substrate. Following initiation of the pre-crack, specimens were fully debonded by gripping the substrate and pulling the specimens in tension at a strain rate of 2.5 mm/min. This was accomplished on a 9 kN Instron test frame equipped with a System 4000 data acquisition system. Ten specimens were tested for each aging condition.

X-ray photoelectron spectroscopy

To determine the atomic concentration of elements on the failure surfaces of NCA specimens, XPS was performed using a Perkin Elmer model 5400 spectrometer. A Mg K α x-ray source operated at 14 kV (300 watts) of power was used to analyze a spot size of 1.0 – 3.0 mm on the specimen surfaces. Typical sampling depths are 5 to 10 nm, and the detection limits of the instrument reflect an atomic concentration of approximately 0.2%. Both failure surfaces of two specimens were analyzed for each aging condition of FM-5 and PETI-5 specimens. For all reported binding energies, spectra were standardized to the hydrocarbon portion of the spectrum at 285.0 eV.

Optical Microscopy

Optical micrographs of failure surfaces were obtained using an Olympus BH-2 optical microscope. All failure surfaces, adhesive and metal failure sides, were analyzed.

Differential scanning calorimetry

DSC was performed on a DuPont Instruments 910 Differential Scanning Calorimeter at a heating rate of 10°C per minute. Initial scans were from room temperature to 300°C. Samples were then quenched to room temperature and scanned to 450°C. The T_g was taken at the half-height of the change in slope of the baseline. One to three replicates were analyzed in all cases.

Infrared spectroscopy

Diffuse reflectance infrared spectra were obtained using a Nicolet Magna-750 Infrared Spectrometer equipped with a KBr beamsplitter. Polymer samples were ground with a metal file and mixed with ground KBr. Spectra were collected against a KBr background. Prior to collection of spectra, the chamber was purged with dry nitrogen. At a spectral resolution of one cm^{-1} , 128 sample scans were collected. Spectra were analyzed with Nicolet's OMNIC software package.

Solvent Uptake

The weight uptake of FM-5 upon exposure to NMP at room temperature was measured. Pieces of debonded adhesive from the FM-5 NCA specimens were cut using a Dewes-Gumbs Die Company manual press. They were weighed on an analytical balance, immersed in NMP, and re-weighed periodically. Excess solvent was removed from the samples with a Kimwipe prior to weighing. The error in the technique is estimated to be ± 0.2 mg, with a typical sample mass of 150 mg. Five replicates were tested for each aging condition.

RESULTS AND DISCUSSION

Adhesive Specimens

Average critical strain energy release rates (G_c) for FM-5 specimens, as a function of aging time at 177°C , are presented Figure 5. At a 95% confidence level, the G_c values are the same for the unaged samples and those aged for one and seven days. However, the

50% to 70% drop in G_c of samples aged for 30 or 90 days is statistically significant compared to the unaged value. In a previous study of the same adhesive, substrate, and surface treatment, a 25% decrease in adhesive strength was seen in DCB samples that had been aged for one year at the same aging conditions used here (20). This illustrates the acceleration in aging that is associated with the decreased diffusion distance of the NCA specimens. The implication here is that degradation of the bond strength is due in part to the diffusion of species, presumably oxygen, to the adhesive/substrate interface. This does not eliminate the contribution of non-diffusion related degradation mechanisms, such as physical aging, however it is apparent that diffusion contributes significantly to the aging process. As mentioned previously, the adhesive geometry used in this work can lead to a significant acceleration in aging. Therefore, these results indicate probable long-term aging behavior of this adhesive/substrate system.

PETI-5 NCA specimens were aged for 30 days in either air or nitrogen at 177°C. This aging time was selected based on the FM-5 data, in which a significant drop in the critical strain energy release rate of a similar system occurred after 30 days.

Quantitative strain energy release rates were not obtained for the PETI-5 NCA samples due to difficulties in obtaining accurate critical strain values. However, a qualitative assessment of bond strength was made by initiating a debond between the adhesive and substrate. The relative difficulty in initiating this debond indicates that samples aged in air at 177°C have much lower bond strengths than unaged samples. In contrast, strengths of samples aged in nitrogen at 177°C are not noticeably different from unaged samples. The effect of aging in air versus nitrogen is consistent with data reported by Parvatareddy

(20) for a similar adhesive/substrate system. He found that the bond strength degrades more quickly during aging at elevated temperatures in air at atmospheric pressure, compared to aging in a reduced air pressure environment.

Failure Surface Analysis

By visual inspection, all debonds of NCA specimens appeared to be interfacial. That is, only the titanium substrate was visible to the naked eye on the metal failure side of the bond, and only polymer was visible on the adhesive failure side. However, when the failure surfaces of unaged NCA specimens were analyzed using XPS or optical microscopy, titanium dioxide and polyimide adhesive were detected on the adhesive and metal failure surfaces. After aging the FM-5 specimens for 30 days or longer at 177°C in air, no titanium is detected on the adhesive failure surfaces by XPS. The atomic concentrations of titanium on the adhesive failure surfaces are presented in Figure 6 as a function of aging time.

Observing the FM-5 adhesive failure surfaces with optical microscopy, the same trend is seen. Representative optical micrographs for each aging time are presented in Figure 7. In the micrographs, the dark colored regions are adhesive and the lighter regions are titanium oxide. Essentially no titanium is observed on the failure surface of the sample aged for 90 days, and very little on the sample aged for 30 days. (Note: the 30-day sample displayed in Figure 7 is the only 30-day sample on which titanium was observed by optical microscopy; no titanium was observed on the 30-day samples analyzed by XPS.) It is apparent from the micrographs that the failure propagated alternately through

two distinct regions. Where titanium is visible on the adhesive failure surface, the failure propagated through the titanium oxide layer of the substrate. Where adhesive is visible, failure occurred in the adhesive layer adjacent to the substrate, or the adhesive interphase. After aging the FM-5 specimens for 30 days or longer at 177°C in air, there is little or no titanium on the adhesive failure surfaces. Thus, as the aging time increases, failure through the adhesive interphase dominates failure through the titanium oxide layer.

A similar trend is observed on the adhesive failure surfaces of PETI-5 NCA specimens. High titanium concentrations were detected on failure surfaces of unaged specimens, by XPS and optical microscopy. This is illustrated in Figure 8 and Figure 9, respectively. No differences from the unaged samples are observed after aging for 30 days in nitrogen at 177°C. After aging in air rather than nitrogen, however, the titanium concentration by XPS has dropped by almost 50% on average. Simultaneously, coverage of titanium oxide as detected by optical microscopy has visibly decreased.

Failure through the oxide layer of the FM-5 and PETI-5 specimens, indicated by high concentrations of titanium on the adhesive failure surface, corresponds to strong adhesive specimens. The FM-5 adhesive specimens lost approximately 50% of their original adhesive strength at the same aging time, 30 days, at which the titanium coverage on the adhesive failure surface decreases substantially. In addition, the air-aged PETI-5 NCA specimens were qualitatively determined to be weaker than the unaged and nitrogen-aged specimens, which had correspondingly higher proportion of failure through the titanium oxide layer.

This indicates that, prior to aging, the strength of the adhesive is comparable to that of the titanium oxide layer, with failure propagating through both regions of the interphase. As the overall bond strength decreases during elevated temperature aging, failure through the adhesive in the interphase dominates failure in the titanium oxide. Weakened adhesive at the interphase, therefore, appears to be responsible for the overall loss of bond strength during elevated temperature aging in air.

Degradation of the adhesive at the interphase could be occurring concurrently with changes in the bulk adhesive. Alternatively, degradation in the interphase may be enhanced by interaction with the surface of the titanium substrate. To determine the source of degradation, the bulk properties of the polyimide adhesives were investigated.

Bulk Adhesive Characterization

It is clear that the adhesive in the interphase region is affected by elevated temperature aging in air. To determine whether aging is also affecting the bulk adhesive, the debonded adhesive from the NCA specimens was analyzed using DSC, infrared analysis, and a solvent uptake study.

Differential scanning calorimetry

DSC was performed on the debonded FM-5 and PETI-5 films from NCA specimens. Glass transition temperatures for all aging conditions are presented in Table 1 and Table 2. No significant changes in glass transition temperatures of FM-5 or PETI-5 were observed after aging the specimens. In addition, there was no evidence of physical aging from the DSC data, as observed by the lack of a characteristic physical aging

endothermic peak at the glass transition. First heat DSC thermograms of PETI-5 are illustrated in Figure 10.

Infrared spectroscopy

Diffuse reflectance infrared spectroscopy was performed on PETI-5 adhesive films, debonded from titanium substrates, that were ground and mixed with KBr. Spectra of unaged PETI-5 and PETI-5 aged in air at 177°C for 30 days are presented in Figure 11. Major peaks are identified in Table 3 (25). No differences were detected between the aged and unaged samples. Diffuse reflectance IR was also performed directly on the failure surface of the adhesive, in an attempt to chemically characterize the adhesive interphase region. Spectra of the failure surface indicated that there was no significant difference between the surface and the bulk material. However, the penetration depth of IR, approximately one micron, may be much greater than the thickness of the interphase region. Therefore, the bulk material may dominate the spectra of the failure surface.

Solvent Uptake

Debonded adhesive films were immersed in NMP to qualitatively determine if chemical changes such as crosslinking or chain scission had occurred during aging. After 1200 hours of exposure, equilibrium had not been reached in weight uptake, as seen in Figure 12. However, hypotheses concerning degradation mechanisms can be made from the sorption curves.

The sorption by films from NCA specimens that were aged for one day was within 0.1% of the sorption by unaged films. After seven days of aging, there was 25% less solvent absorbed after 900 hours. This may be the result of thermally induced crosslinking. At longer aging times, however, the sorption increased. Absorbed solvent in films that were aged for 30 days is greater than that of films aged for seven days, and weight uptake in films aged for 90 days was much greater than in any other films. This increase in sorption could be a result of chain scission or microcracking; these are both related to embrittlement of the adhesive. The trend of an initial decrease in weight uptake of NMP at short aging times, followed by an increase in weight uptake at longer aging times, implies that there are two competing mechanisms, one that dominates at short aging times and one that becomes important at longer aging times.

The inference from this data, that adhesive embrittlement dominates at aging times of 30 days or longer, is consistent with the G_c data from the NCA test and the change in failure location determined by XPS and optical microscopy. Embrittlement of the adhesive at the interphase would decrease the adhesive joint's resistance to fracture. This would lower the G_c of the adhesive/substrate system and simultaneously force the failure to occur within the weakened adhesive, rather than at the adhesive/substrate interface.

CONCLUSIONS

After aging NCA specimens of FM-5 or PETI-5 bonded to chromic acid anodized Ti-6Al-4V at 177°C for 30 days or longer in air, the adhesive bond strength decreases

significantly. Simultaneously, a greater percentage of the failure is propagating through the adhesive in the interphase region. No differences were observed between unaged adhesive samples and those aged in nitrogen rather than air. Thus, the weakening of the adhesive at the interphase appears to be related to components of the air-aging atmosphere, presumably oxygen.

Changes in bulk FM-5 or PETI-5 were not observed by DSC or IR spectroscopy, although evidence of adhesive embrittlement was observed by sorption of NMP. While this embrittlement may be responsible for the increase in failure propagating through the adhesive interphase, degradation in that region may be enhanced by interaction with the substrate surface. The interaction of PETI-5 with titanium dioxide is currently under investigation.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Center for Adhesive and Sealant Science at Virginia Tech and the Adhesive and Sealant Council Education Foundation for financial support. In addition, we would like to thank several members of the Composites and Polymers Branch, NASA Langley Research Center. We thank Terry St. Clair for providing materials and research facilities, and Mia Siochi and Jeffrey Hinkley for valuable discussions. Finally, we would like to thank Sandia National Laboratories for support of the preparation of this manuscript. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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Table 1: Glass transition temperatures, by DSC, of FM-5 before and after an initial heat to 300°C. Samples shown are aged for the indicated time at 177°C in air.

Aging time, days	Glass transition temperature, °C	
	First heat	Second heat
0	241	248
1	238	247
7	242	249
30	240	248
90	241	249

Table 2: Glass transition temperatures, by DSC, of PETI-5 before and after an initial heat to 300°C. Samples shown are aged at 177°C at the indicated time and atmosphere.

Aging time, days	Aging atmosphere	Glass transition temperature, °C	
		First heat	Second heat
0	none	252	254
30	nitrogen	249	252
30	air	251	252

Table 3: PETI-5 infrared spectrum peak identification (25).

Wavenumber, cm^{-1}	Peak identification
3065, 1590, 1506, 1487	Aromatic C-H
1776, 1726	Imide
2184	Phenylethynyl

Figure 1: Schematic representation of the components of the three-dimensional interphase between adhesive and substrate, after Drzal (7).

Figure 2: Structure of PETI-5 before cure. $\langle M_n \rangle = 5,000$ g/mol.

Figure 3: Failure surfaces of double cantilever beam specimens of FM-5 adhesive bonded to chromic acid anodized Ti-6Al-4V. Samples shown are as received, aged in air at 177°C for 12 months, and aged in air at 204°C for 12 months.

Figure 4: Schematic of a notched coating adhesion specimen during testing.

Figure 5: Critical strain energy release rate, G_c , for Ti/FM-5 joints aged at 177°C in air. Error bars represent the 95% confidence intervals.

Figure 6: Atomic concentration of titanium on FM-5 NCA adhesive failure surfaces, by XPS. Samples were aged at 177°C in air.

Figure 7: Optical micrographs of FM-5 adhesive failure surfaces from NCA specimens. Aging times at 177°C in air are indicated below each micrograph.

Figure 8: Atomic concentration of titanium on PETI-5 NCA adhesive failure surfaces, by XPS. Samples were aged for 30 days at 177°C in the indicated atmosphere.

Figure 9: Optical micrographs of PETI-5 adhesive failure surfaces from NCA specimens. Specimens were aged for 30 days at 177°C in the indicated atmosphere.

Figure 10: First heat DSC thermograms of PETI-5 adhesive samples removed from titanium substrates. Samples shown are unaged, aged for 30 days at 177°C in nitrogen, or aged for 30 days at 177°C in air.

Figure 11: Infrared spectra of unaged PETI-5 and PETI-5 aged 30 days in air at 177°C.

Figure 12: Weight uptake of debonded FM-5 adhesive films upon exposure to NMP. Samples were aged for the indicated times at 177°C in air. Error bars represent the standard error of the mean, based on the pooled error of each sample for all sorption times.

Atomic Concentration of Titanium

No Aging

Nitrogen-Aged

Air-Aged

25 μm

Weight Uptake with NMP Exposure