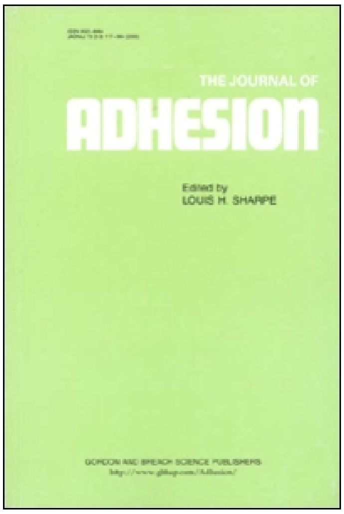

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Aging characterization of advanced polymer systems

K. A. Simmons[a]; K. I. Jacob[a]; W. S. Johnson[b]
[a] School of Polymer, Textile and Fiber Engineering, Georgia Institute of Technology, Atlanta, GA, USA
[b] School of Material Science & Engineering and G. W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, USA

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AGING CHARACTERIZATION OF ADVANCED POLYMER SYSTEMS

K. A. Simmons
K. I. Jacob
School of Polymer, Textile and Fiber Engineering,
Georgia Institute of Technology, Atlanta, GA, USA

W. S. Johnson
School of Material Science & Engineering
and G. W. Woodruff School of Mechanical Engineering,
Georgia Institute of Technology, Atlanta, GA, USA

Aging of three advanced polymer systems used as adhesives in the aerospace industry is characterized by Fourier transform infrared spectroscopy (FTIR) with attenuated total reflectance (ATR-FTIR), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). Since significant changes in mechanical properties were observed for AF191, FM®73, and FM®5 bonded joints, the purpose of this work was to identify whether there is any chemical and physical degradation for the adhesives used in these joints.

Each of the adhesives has been evaluated after exposing to Hot/Wet and Hot/Dry environments for 5000 h. They were also thermally cycled in conditions that represent subsonic and supersonic cruise. Hot/wet exposures demonstrated a greater amount of possible degradation than hot/dry or thermally cycled exposures. The hot/wet aging condition resulted in more pronounced O–H, C–H, and N–H infrared absorptions, reduced glass transition temperature of adhesives, and reduced tensile and fracture properties of corresponding bonded systems. Overall, these adhesives were chemically very stable under the environments to which they were exposed, even though some of the joints showed reduced fracture toughness due to the exposure. Additional work is needed to understand the mechanism causing the change in joint properties when exposed to these environments.

Keywords: Adhesive bonding; Environmental exposure; Durability; Chemical degradation; Attenuated total reflectance; X-ray photoelectron spectroscopy

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Address correspondence to W. S. Johnson, G. W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, GA 30332-0245, USA. E-mail: steve.johnson@mse.gatech.edu

INTRODUCTION

Long-term durability of aircraft structures depends partly on the durability of adhesively bonded systems. Durability is a measure of the resistance to mechanical and thermal fatigue and to environmental degradation. Although principles of fracture mechanics can be applied to monitor mechanical degradation due to long-term thermal aging and thermal cycling [1], characterization of chemical degradation on various adhesive bonded systems will assist in our understanding of their mechanical performance and will also assist in designing adhesive structures for future aircrafts and for maintaining the airworthiness of the aging aircraft fleets.

An adhesive bonded "system" is comprised of an adhesive, adherends, appropriate surface pretreatment to the adherends, and the interphase/interface regions resulting between the first three components. The overall durability of this system is determined by the least durable component, which generally is the adhesive [1]. In most cases the adhesive is not one simple entity but a combination of several monomers, polymers, reactants, additives, and fillers; each of these entities within the adhesive has a specific role with respect to the integrity of the adhesive. During aging, additional crosslinks may be formed between these components, while other chemical changes and degradation processes could take place in the material [2]. The purpose of this investigation is to understand the changes in the chemical structure and physical behavior of the adhesives caused by environmental exposure.

The adhesives studied are: (1) FM® (Cytek Industries, W. Patterson, NJ, USA), a polyimide used in bonding metal for the wings and fuselage of the proposed high speed civil transport (HSCT); (2) AF191 (3M Co., St. Paul, MN, USA), a modified epoxy used to bond composites for use as control surfaces on the F-22 fighter; and (3) FM®73 (Cytek), a toughened epoxy used to bond composite patches to cracked aluminum structure in aged aircraft like the C-141 [3].

These polymer-based systems were characterized using dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and X-ray photoelectron spectroscopy (XPS). These characterization tools can help to identify the chemical and physical changes in the polymer structure due to environmental exposure. DMA can identify the changes in the T_g of each polymer resin due to damage/degradation, while TGA can show whether environmental effects will impinge on the adhesives' decomposition temperature and will help identify changes in the degree of crosslinking in the polymer adhesive. ATR-FTIR can provide spectrographic signatures of the adhesives and can detail the formation or destruction of any specific functional groups within the polymer chains. Finally, XPS could confirm ATR-FTIR results by presenting quantitative information about chemical composition of the surface of the polymer-based structural adhesives.

BACKGROUND

Structural adhesives have been under investigation for many decades. The requirements that structural adhesives must meet are far simpler to describe than to achieve. They must be suitable for joining ceramics, composites, metals, films, and their combinations, and maintain bonding under various conditions. Whether structural adhesives are in aircraft, space vehicles, automobiles, bridge components, microchips, or missiles, they are required to resist deformation and environmental degradation at various temperatures, often for long periods of time under various loads.

Just how stable the adhesive needs to be depends solely on the application. In microelectronics, the polymer must adhere to the substrate during various processing cycles where the temperature may reach 400°C in an inert environment. Missiles require mechanical performance for less than a minute, but at temperatures that exceed 540°C. Aircraft structures, which are the focus of this research, demand the material to be stable for tens of thousands of hours at temperatures up to 230°C [4].

Durability of Bonded Joints

Recently, Butkus, Lubke, and Johnson [5–10] investigated four basic bonded structures and quantified the effects of environmental exposure on the fracture and fatigue behavior of these systems. The first two systems were aluminum-bonded to aluminum using FM®73 (a modified epoxy) (Cytek Industries, Havre de Grace, MD, USA) and aluminum bonded to a boron epoxy composite with FM®73, in connection with the repair patches on the U.S. Air Force's C141 fleet. Due to its use on control surfaces for the F-22 fighter, AF191 (a modified epoxy) bonding between graphite-fiber–reinforced bismaleimide was also investigated. Finally, FM®5 (a polymide) bonding titanium parts (supplied by Boeing, Seattle, WA, USA) was studied due to their possible use in the High Speed Civil Transport aircraft.

Under Butkus and Johnson's investigation [7], the Graphite-Bismaleimide/AF191/Graphite-Bismaleimide (*Gr-BMI*/*AF191*/*Gr-BMI*) system was aged for 10,000 h at 104°C (220°F) and at 71°C (160°F)/ > 90% relative humidity (RH). This system was also thermally cycled between −54°C (−65°C) to 104°C (220°F) for 100 cycles representing temperature changes from subsonic cruise and super sonic operational conditions of the F-22. Cycle times correspond to operating characteristics of the components on C-141, F-22, and HSCT aircrafts, where these adhesives were planned to be used.

The cycles are 12°C/min average ramp rate for FM®73, 6°C/min for AF-191, and 7°C/min for FM®5. Lubke *et al.* [10] present data that shows a dramatic decrease in mode I fracture toughness after this exposure. Figure 1 shows the mode I fracture toughness for this material as a function of aging and test temperature.

The Ti/FM®5/Ti system [3] was aged for 10,000 h at 177°C (350°F) and at 71°C (160°F)/ > 90% RH. This system was also cycled between −54°C (−65°F) and 163°C (325°F) for 250 cycles, representing temperature changes from subsonic cruise and supersonic operational conditions of the supersonic commercial transport. The various aging conditions did not reduce the fracture toughness of this system dramatically in spite of the high temperature exposures.

In order to address issues related to repairing cracks in aged aircraft, the boron–expoxy/FM®73/Al system and the Al/FM®73/Al system were aged for 10,000 h at 71°C (160°F) and at 71°C (160°F)/ > 90% RH [9]. Both systems were also thermally cycled between −54°C (−65°F) and 71°C (160°F) for 100 cycles, representing temperature changes from subsonic cruise and hot runway conditions. Fracture

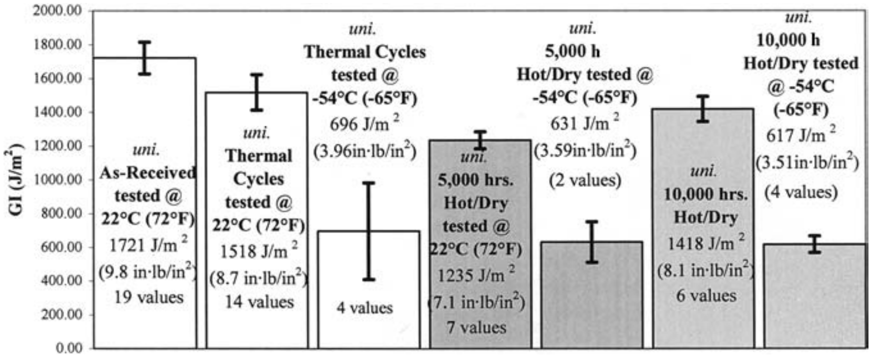


FIGURE 1 Effect of the combination of environmetal exposure and testing at various temperatures on unidirectional double cantilever beam (DCB) Gr-BMI/AF-191/Gr-BMI [10].

toughness values from double cantilever beam (DCB) specimens are shown in Figure 2.

It was evident that the hot/wet (71°C [160°F], >90% RH) condition was the most degrading environment and caused some reduction in the tensile and fracture toughness properties of the adhesive and in the bonded systems containing FM®73. The FM-73 also appeared to be unable to recover the "as-received" toughness by "drying out" the bonded system at room temperature. Because this hot/wet condition may have been too severe to represent actual exposures, more realistic outdoor rooftop exposures were performed by Lubke *et al.* [9] that exemplified reduced fracture toughness of the adhesive joints, but not as much as the hot/wet exposures. Furthermore, Johnson *et al.* [3] reported that toughness of both the Ti/FM®5/Ti and Gr-BMI/AF191/Gr-BMI systems are reduced under long-term exposure to hot/dry environments, the AF-191 more so than the FM-5. Lubke *et al.* [9] expanded on these findings by combining cold temperature testing (−54°C [−65°F]) with environmental exposure and reported more significant effects on the fracture toughness. This can be seen in Figure 1 for the AF-191 adhesives. Thermally cycled joints showed

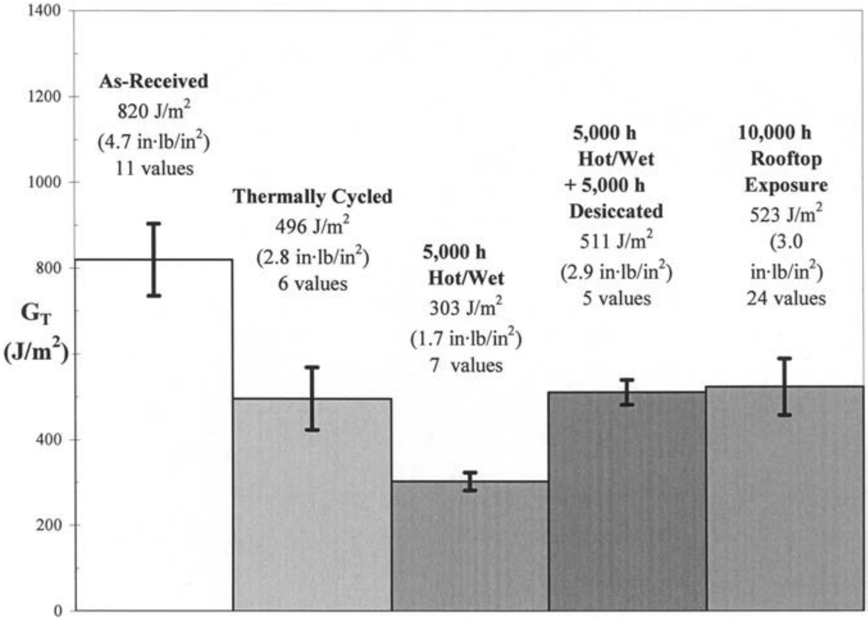


FIGURE 2 Fracture toughness data for FM-73 DCB specimens subjected to various exposures [9].

limited reduction of fracture toughness. All of these findings on mechanical properties along with issues of fatigue crack growth set the background for this present research work. It was the goal of this work to identify chemical and physical changes in the adhesives due to environmental exposure and to investigate whether these changes have any direct relationship with changes in the tensile, fracture, and fatigue properties of adhesive films and bonded joints.

EXPERIMENTAL

Materials

Three different adhesives were examined; two epoxy-based adhesives (FM®73 and AF-191) and one polyimide-based adhesive (FM®5). These adhesives underwent chemical and thermal analysis and were used previously to bond structural joints for tensile and fracture toughness properties [3]. A summary of exposure conditions for each of the samples is given in Table 1. As the exact structure of some of the adhesives cannot be disclosed, a sample epoxy is shown in Figure 3.

FM® 73

FM®73 is a toughened epoxy developed and manufactured by CYTEC Engineered Materials, Inc. (Havre de Grace, MD). The manufacturer-sepcified maximum service temperature is 82°C (180°F). It is currently being used for bonding composite patches to cracked metallic

TABLE 1 Summary of Exposure Conditions Applied to Each Adhesive

Adhesive	Exposure	Exposure conditions
AF191	as received	—
	thermally cycled	–54°C (–65°F) to 104°C (220°F), 500 cycles
	hot/dry	104°C (220°F), 0% RH
	hot/wet	71°C (160°F), $>$ 90% RH
FM®73	as received	—
	thermally cycled	–54°C (–65°F) to 71°C (160°F), 100 cycles
	hot/dry	71°C (160°F), 0% RH
	RT/wet	22°C (72°F), $>$ 90% RH
	hot/wet	71°C (160°F), $>$ 90% RH
FM®5	as received	—
	thermally cycled	–54°C (–65°F) to 163°C (325°F), 500 cycles
	hot/dry	177°C (350°F), 0% RH
	hot/wet	71°C (160°F), $>$ 90% RH

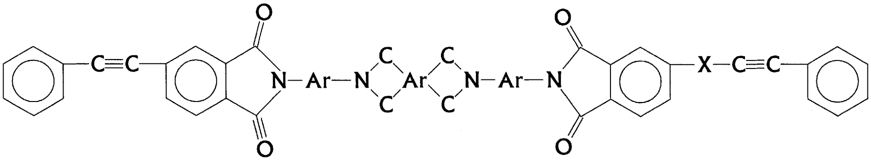


FIGURE 3 Example of a typical epoxy structure.

airplanes on the C-141, where the most severe condition is 71°C (160°F) and >90% RH [11].

The cured sheets of the FM®73 adhesive had a nominal weight of 290 g/m^2 (0.06 lb/ft^2) and an approximate thickness of 0.25 mm (10 mils). The cured FM®73 is translucent and has a yellow-orange color.

Samples of this adhesive were aged for 5000 h at 71°C (160°F), 5000 h at 22°C (72°F), and at 71°C (160°F)/>90% RH (hot runway conditions). It was also cycled between −54°C (−65°F) to 71°C (160°F) for 100 cycles representing temperature changes from subsonic cruise and supersonic operational conditions. Neat resin coupons were obtained from the cured sheets of neat resin.

AF-191

AF-191 is a modified epoxy adhesive [12] manufactured by 3M Corporation (St. Paul, MN, USA). The maximum service temperature is 177°C (350°F) for this adhesive, as specified by the manufacturer. This adhesive will be used on the F-22 Raptor in areas where the temperature could reach as high as 104°C (220°F) during supersonic flight [13, 14].

Cured sheets were referenced to have a nominal weight of 260 g/m^2 (0.05 lb/ft^2) with an approximate thickness of 0.25 mm (10 mils). The cured AF-191 film is pale yellow in color and in translucent as a single layer. This adhesive was aged for 5000 h at 104°C (220°F) and at 71°C (160°F)/>90% RH. It was also cycled between −54°C (−65°F) and 104°C (220°F) for 100 cycles, representing temperature changes from subsonic cruise and supersonic operational conditions. Neat resin coupons were cut from the cured sheets and characterized.

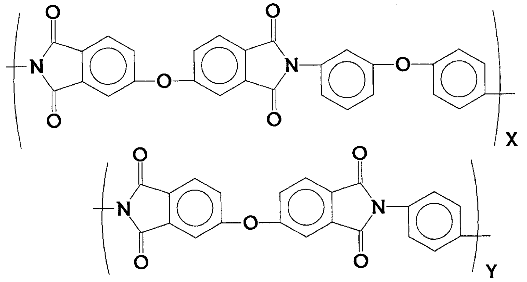
FM®5

FM®5 is a semicrystalline polyimide (manufactured by CYTEC Engineered Materials, Inc., Havre de Grace, MD) blend of approximately 70% PETI-5 (from CYTEC) and 30% LaRC™-IAX (a NASA Langley product, VA) resins [15]. This adhesive was considered for wing and fuselage structures on the High Speed Civil Transport [16] where temperatures may approach 177°C (350°F), close to the maximum use temperature as specified by the manufacturer. The chemical structures of the components for FM®5 are shown in Figure 4.

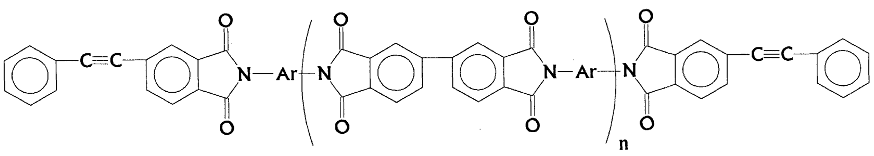
The nominal weight of the cured FM®5 was 515 g/m^2 (0.10 b/ft^2), and it had an approximate thickness of 0.34 mm (13 mils). The color of the FM®5 film is dark brown and is opaque as a single layer. This adhesive was aged for 5000 h at 177°C (350°F) and at 71°C (160°F)/ > 90% RH. It was also cycled between −54°C (−65°F) and 163°C (325°F) for 500 cycles, representing temperature changes from subsonic cruise and supersonic operational conditions. Neat resin coupons were cut from the cured sheets and characterized.

Environmental Exposure Equipment

Long-term isothermal exposures were performed on the adhesives by using a Thermotron (Holland, MI) model OV-12 circulating air oven. The RH was monitored by a humidistat placed in each oven or chamber. For room temperature/wet exposure, the humidity apparatus was removed from the oven.



Repeat units of ***LaRC-IAX*** where X ranges from 75 to 90 mole%, and Y ranges from 10 to 25 mole%.



Repeat unit of ***PETI-5*** polyimide.

FIGURE 4 FM®5 is a blend of approximately 70% PETI®-5 and 30% LaRC™-IAX.

Thermal cycling was performed using a dual-chamber thermal cycling apparatus located at the Warner Robins Air Logistics Center, Robins AFB, GA, manufactured by Russell's Technical Products (Holland, MI, USA). Cured adhesive sheets were placed on a tray and cycled and held for a period of time between hot chamber (using electric heating elements) and a cool chamber (using circulated air and injected liquid nitrogen). A summary of the aging on each adhesive type is listed in Table 1.

Characterization Techniques

To understand the effects of environmental exposure on the structure, composition, and behavior of AF191, FM®73, and FM®5, the material was characterized before and after the exposure with a number of techniques. A brief description of the different characterization techniques used is given in the following sections.

DMA Test

DMA is a technique that characterizes the viscoelastic properties of materials. DMA generally measures the modulus (stiffness) and the damping (energy dissipation) properties as a material deforms under periodic stresses, from which the storage modulus (E′), loss modulus (E″), and the phase angle, δ, can be evaluated [17].

To study the effects of environmental exposure on the T_g of each of the neat resins, a Seiko DMS210 Dynamic Mechanical Analyzer (Selko Instruments, Nasaka, Japan) was used in fixed-frequency mode. The T_g was taken as the peak of $\tan\delta$. Test specimens were approximately $20.0 \times 10.0 \times 0.25$ mm (for FM®5 it was $20.0 \times 10.0 \times 0.38$ mm). Samples were aged in environmental chambers prior to testing. Specimens were tested at 10°C/min and at a fixed frequency of 10 Hz between the temperatures of 25°C and 350°C for AF191, 25°C and 200°C for FM®73, and 100°C and 400°C for FM®5.

TGA Measurements

A SEIKO thermal analysis system (RDC 220, Paramus, NJ, USA) is used for all TGA analysis, which quantitatively measures weight change with respect to time or temperature for a sample subjected to increasing temperature in a thermal chamber. The thermnal stability and thermal decomposition studies of AF191, FM®73, and FM®5 were performed over a temperature range of 50°C to 600°C, using a Seiko "SSC 5200-TG/DTA 320" in an air environment at a heating rate of 20°C/min. Samples were tested in an aluminum sample pan and the decomposition temperatures were calculated.

ATR-FTIR

FTIR of each neat resin film was performed on a Brukner Vector 22 Infrared spectrophotometer (Bruker Optics, Inc., Billerica, MA, USA). This instrument was fitted with a Miracle single reflection horizontal ATR that utilizes a spherical germanium ATR crystal as the sampling surface.

The ATR-FTIR spectra were collected at $4\,\text{cm}^{-1}$ resolution over 32 scans. The sampling depth of penetration was approximately $1\,\mu\text{m}$. By using the ATR-FTIR spectrum, chemial bonds and the molecular structure of organic compounds can be identified [18].

XPS

In XPS, the specimen surface is irradiated with X-rays of known energy (most commonly 1486 or 1254 eV), causing electrons to be ejected from the surface. The kinetic energy of these so called "photoelectrons" is measured using a hemispherical analyzer. The escape depth of these electrons is around 10 atomic layers, and so the technique is extremely surface specific. The binding energy is characteristic of both the electronic shells and the oxidation state of the atom from which the electron was ejected. Therefore, XPS is used for both elemental and chemical analysis of the sample surface.

XPS was performed on a Surface Science Laboratories Model SSX-100 Small Spot Spectrometrer (Surface Science Instruments, Mountain View, CA, USA) in the Microelectronics Research Laboratory at Georgia Tech. Base pressure of the instrument was maintained at $\leq 2.0 \times 10^{-9}$ Torr. The operating pressure was 3.0×10^{-8} Torr. Low-resolution experiments were applied to yield detailed chemical information about the surface of the adhesives.

Microscopy

Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) were used to observe microcracking initiated by environmental exposure. Optical micrographs were developed on a Reichert MeF3a optical microscope (Leica Microsystems, Bannockburn, IL, USA) and Olympus OV100NM microscope (Olympus, Melville, NY, USA) at magnifications of 200× and 1000×. Scanning electron micrographs were taken on a LEO Stereoscam 2430 and analyzed with the LEO SRV32 software system (Leo Electron Microscopy, Thornwood, NY, USA). All SEM samples were gold sputter coated using an Edwards Six Scancoat (Activac Technology, Wilmington, MA, USA), and micrographs were taken on the SEM to a magnification of 1000×.

RESULTS AND DISCUSSION

Visual inspection of the adhesives after they were environmentally exposed showed some color changes. AF191, which initially was pale yellow turned to a pale brownish color after being exposed to hot/dry dry conditions, turned to a pale butter color after being exposed to hot/wet environments and remained the same after thermal cycling. FM®73, which was yellowish-orange in the "as-received" state, did not experience a major color change, just as FM®5 did not change from its dark brown color.

DMA Test

Changes in the glass transition temperature T_g, of AF191 neat resins were monitored following exposure in various environments. These resluts are summarized in Table 2. For AF191, the "as-received" glass transition temperature is measured to be 223°C from the tan δ *versus* temperature peak. Upon exposure to hot/wet conditions and hot/dry conditions, the T_g reduces to 219°C and 209°C, respectively (Table 2). This may suggest some chain scission, and increase of chain mobility, especially in the hot/dry conditions, but other techniques are needed to confirm this conclusion. For the thermally cycled specimen, the T_g was approxiamtely 220°C, indicating that not much change has occurred during cycling. Since mechanical properties could not be measured for the sample, it is unclear whether the change in glass tranistion temperature is due to chain scission or simply due to changes in molecular configuration resulting in different free volume distribution. Although none of these changes are significant, the least change is observed for thermal cycling. Nothing conclusive could be deduced from this observation.

TABLE 2 Glass Transition Temperatures of Adhesives at All Exposures, as Calculated by DMA

	Peak of tan δ					
Adhesive	REF	As received	Thermally cycled	Hot/dry	Hot/wet	rt/wet
AF191	230°C	223°C	220°C	209°C	219°C	
FM®73	100°C	101°C	93°C	101°C	96°C	102°C
FM®5	250°C	263, 325°C	261, 332°C	265, 320°C	259, 321°C	

T_gs are taken from the maximum peak of the tan δ *versus* temperature plot.

FM®73 gives a single tan δ peak identifying 101°C as the T_g of the "as-received" sample. As seen in Table 2, the T_gs of the thermally cycled and hot/wet exposed specimens decreased to 93°C and 96°C, respectively, yet remained the same for hot/dry and RT/wet conditions, indicating that no major structural changes had taken place at these conditions. This is consistent with Johnson, *et al.*'s tensile, fracture, and fatigue measurements [3]. Among all the environmental conditions, thermal cycling seems to have a significant effect on the glass transition temperature, which has not directly translated into any significant change in mechanical properties. Thus, it is likely that the changes in glass transition are due to changes in free volume alone, rather than any changes in the molecular weight of the polymer chains.

Since FM® is a semicrystalline polyimide blend of approxiamtely 70% PETI-5 and 30% LaRC™-IAX, two transitions are noted as expected (Figure 5). Thr peaks for tan δ occur approximately at 263°C and around 325°C. These two peaks stem from the composition of PETI-5 and LaRC™-IAX and their wide-ranging glass transition temperatures. PETI-5's glass transition temperature varies with its annealing temperature, ranging from 210°C at an annealing temperature of 250°C, up to a T_g of 270°C for an annealing temperature of 350°C. LaRC™-IAX behaves in a similar fashion, ranging from a T_g

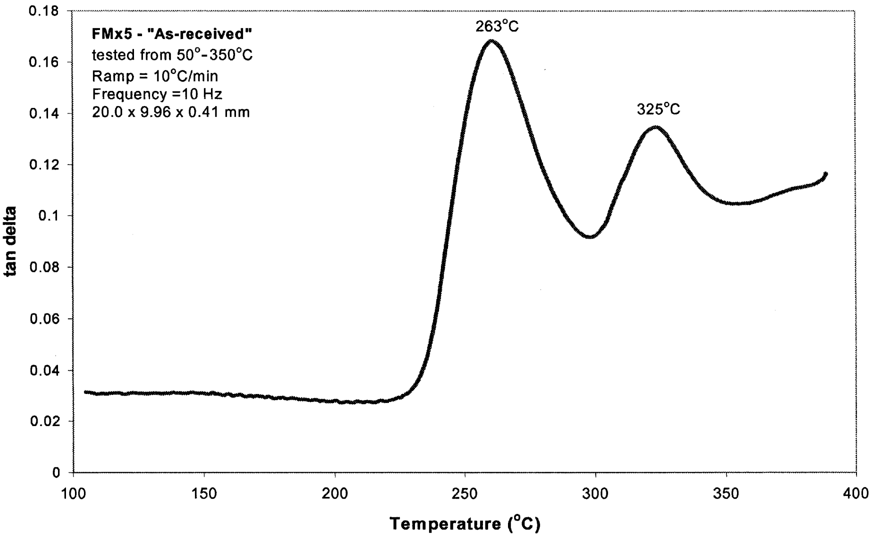


FIGURE 5 DMA thermogram of "as-received" FM®5. $T_g \sim 263°C$.

of 236.8°C at a cure temperature of 300°C up to a T_g of 268.0°C at a cure temperature of 400°C.

The adhesive exposed to hot/wet environments demonstrated a decreased T_g of four degrees, whereas the thermally cycled specimens showed a reduction of two degrees, while hot/dry conditions increased the T_g by two degrees. None of the exposures demonstrate any major chain restructuring, yet the hot/wet condition needs be examined by other techniques to gain more insight into any structural changes.

TGA

Information provided by TGA regarding the weight loss in the AF191 sample surrounded by air as a function of temperature is shown in Figure 6. It is clear from the figure that a double-stage decomposition process is evident, and the decomposition under air left negligible residues.

For AF191, the first-stage degradation begins at 382°C and stops between the range of 440°C and 450°C, whereas the second appears between the same range of 440–450°C and ends approximately around 570°C. This small difference in spectra above 450°C may suggest slight chain reformation, but other techniques are needed to verify and quantify this initial conclusion. TGA does not show any significant behavior for the samples due to various environmental treatments.

Percentage of weight loss in the sample as a function of temperature is seen in Figure 7 for FM®73. It is obvious again that a double-stage

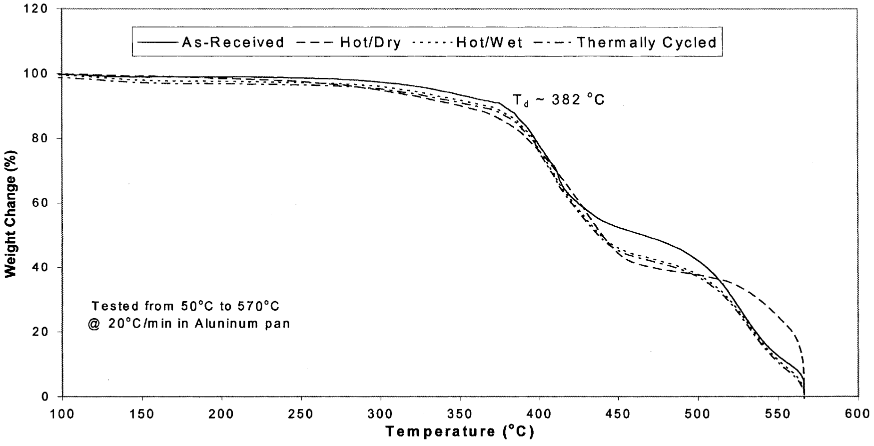


FIGURE 6 TGA Thermogram of AF-191 at various environmental exposures.

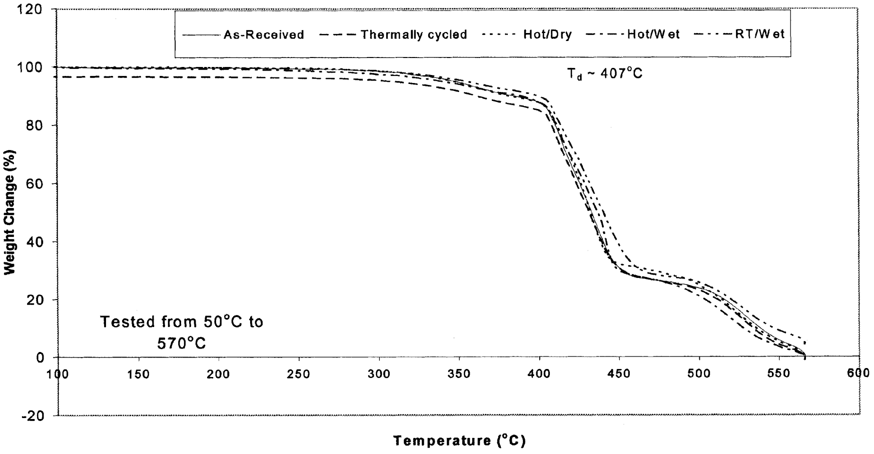


FIGURE 7 TGA Thermogram of FM®73.

decomposition process takes place, which also leaves negligible residues. The first stage of the degradation reaction was observed to begin around 407°C and stop at 450°C, where the second stage of degration for FM®73 appears between 445°C and 565°C. It is clear that all exposed samples are thermally very stable and showed little difference in TGA.

For the FM®5 adhesive, the TGA results were different from the other two adhesives, demonstrating excellent thermal stability up to 563°C. Since platinum test pans were unavailable, aluminum test pans were used, which limited the maximum testing temperature to 600°C. In comparison, it can be seen from Figure 8 that the degradation temperature for FM®5 does not change significantly for any exposure conditions, suggesting no major changes in the degree of crosslinking. For AF191 clear differences are observed during the second stage of degradation. It should be noted that for FM®5 hot/dry and hot/wet conditions did not produce any difference in moisture absorption.

ATR

The ATR-FTIR spectra obtained for AF191 at varied exposures are essentially equivalent to the "as-received" spectra. Figure 9 shows no major chemical shift induced because of exposure, and no major appearance or diappearance of any characteristic FTIR absorption bands. In the as-received sample, the two peaks observed at 2916 and 2844 cm^{-1}are due to C–H stretching bands, and it can be noted

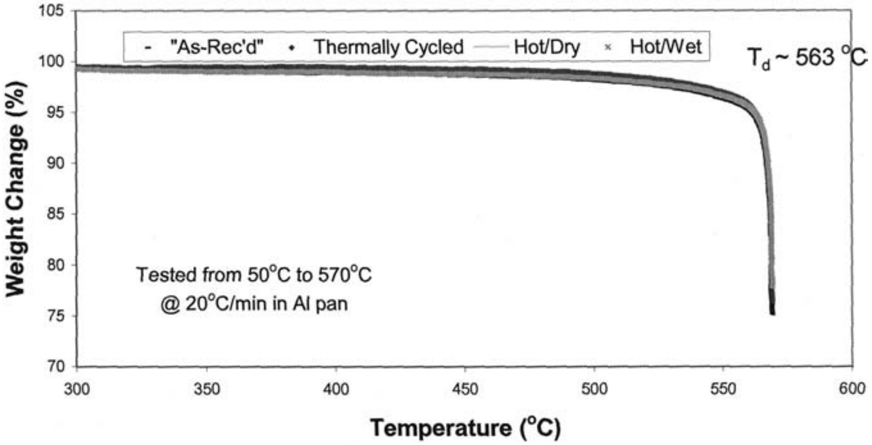


FIGURE 8 TGA Thermogram of FM®5.

that the O–H stretching appears around 3350 cm^{-1}. The small wave of a peak at 2314 cm^{-1} suggests weak alkyne stretching (C$\equiv$C). The ATR band resulting from C–N bending is seen as a doublet around 1500 cm^{-1}. The crowded fingerprint region (1400 cm^{-1} and below)

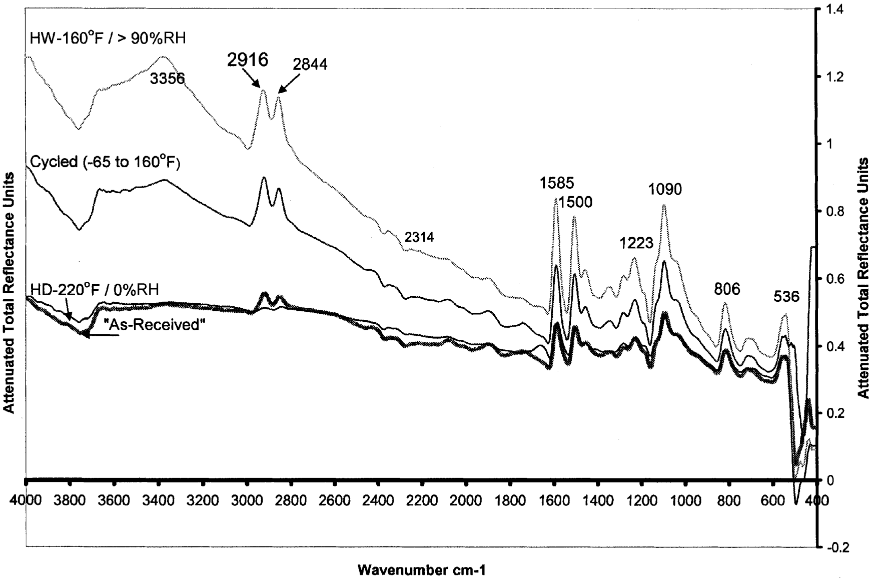


FIGURE 9 ATR-FTIR spectra of AF-191 at various environmental exposures.

suggest various kinds of N–H, C–H and C=O bending due to the medium-to-weak absorption bands. It is evident from these spectra that humidity plays a greater role in inducing O–H stretching for hot/wet conditions, which is not visible in "as-received" and hot/dry exposures.

The spectrum given in Figure 9 for AF191 appears very similar to the spectrum for the modified epoxy of FM®73 in Figure 10. The greatest and most important change in FM®73's ATR data is the rise of the C=O stretch at 1720 cm^{-1} and the broadness of the peak at 3400 cm^{-1}, suggesting that high humidity exposures could possibly initiate chain scission and introduce absorption bands that are consistent with C=O), C–O, and O–H. This observation could also indicate that FM®73's structural arrangement allows carbonyl groups to be detected by this technique. It also very evident that O–H stretch does not appear in 0% RH.

FM®5, being a polymer blend, demonstrates very interesting behavior as seen in ATR-FTIR spectra (Figure 11). The "as-received" samples show very weak absorption peaks in the 2300 cm^{-1} alkyne region (C≡C), but this peak is seen to rotate to the negative absorption

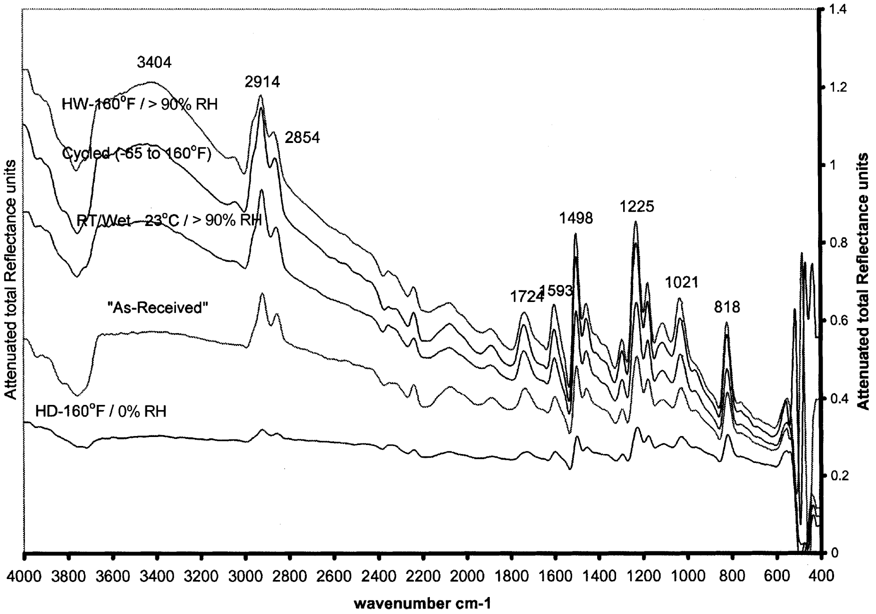


FIGURE 10 ATR-FTIR spectra of FM®73 at various environmental exposures.

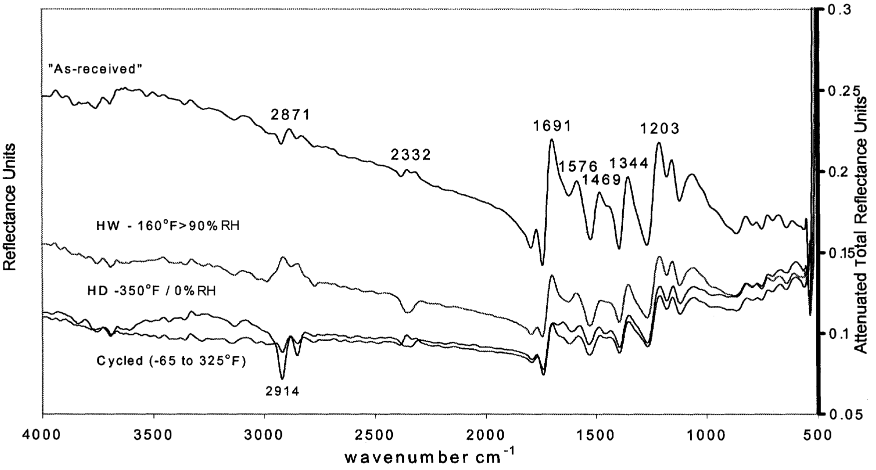


FIGURE 11 ATR-FTIR spectra of FM®5 at various environmental exposures.

direction, while cycled exposures are moderately the same. The same phenomenon is also observed around the 2800–2900 cm^{-1} (C–H or N–H stretch) region but now seen in the hot/dry and cycled exposures. This is rather interesting, and multiple examinations show that the data in Figure 11 are consistent. This might explain why hot/dry conditions result in some reduction in the fracture toughness for Ti/FM®5/Ti joints.

XPS

Preliminary XPS spectra were obtained for as-received and thermally cycled AF-191 adhesives. As seen from Figures 12 and 13, the calculated surface composition suggested 86% carbon, 12–13% oxygen, 1.6–3.1% silicon, and 0.5% sodium present in the neat adhesives. This composition changed to 84% carbon, 13% oxygen, 3.1% Si, and 0.4% Na after thermal cycling. It should be noted that carbon and oxygen did not change much due to environmental exposure, ruling out any significant oxidation effects. As with some other XPS experiments, it is not clear why nitrogen did not show up in the spectra and why Si and Na were present. The presence of small quantities of Na and Si may be the result of handling; however, their presence did not change much between the as-received sample and the aged adhesive. It would be of great interest if a number of similar specimens could be examined by this technique but due to limitations of time, cost, availability

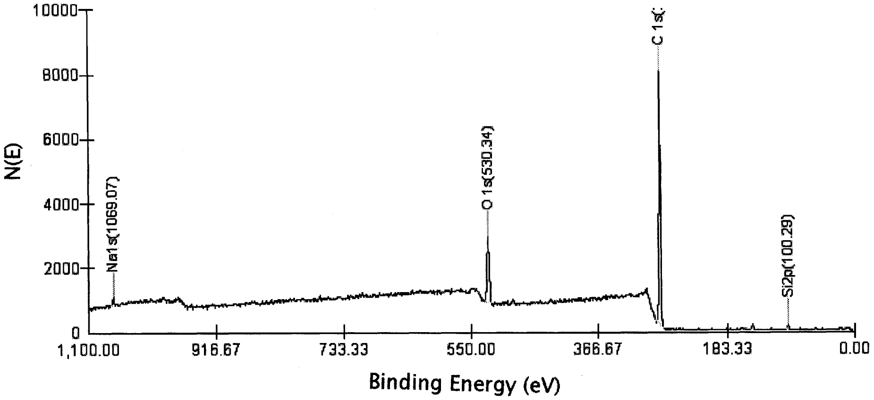


FIGURE 12 XPS spectrum of "as-received" AF-191: C, 86%; O, 12%; Si, 1.6%; Na, 0.6%.

of aged samples, and the limitations of availability of the XPS spectrometer, only a few spectra were taken. Significant information could be obtained by comparing the spectrum from a sample after hot/dry exposures with that of an as-received sample; however, we could not continue with those experiments due to the lack of aged samples.

As-received and thermally cycled FM®73 adhesives were examined using XPS. As seen from Figures 14 and 15, calculated surface composition suggested 86% carbon, 12% oxygen, 1.4% silicon, and 0.4%

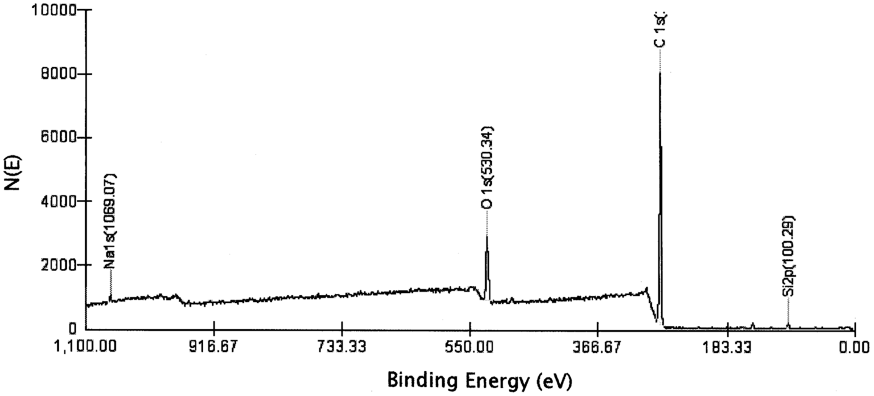


FIGURE 13 XPS spectrum of "thermally cycled" AF-191: C, 84%; O, 13%; Si, 3.1%; Na, 0.4%.

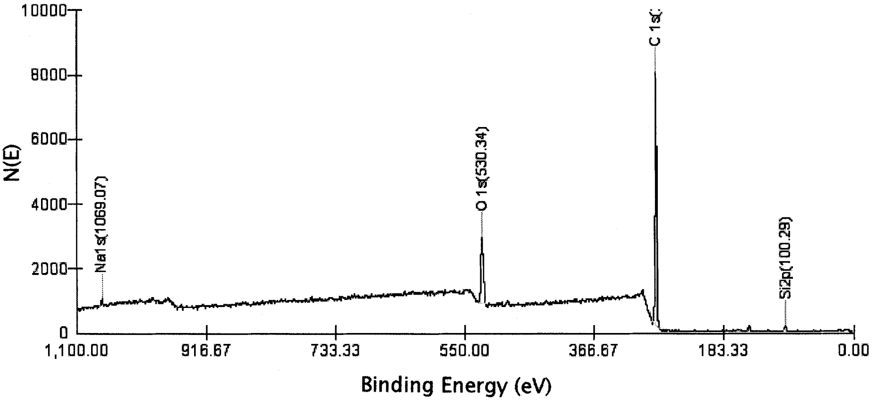


FIGURE 14 XPS spectrum of "as-received" FM®73: C, 86%; O, 12%; Si, 1.4%; Na, 0.4%.

sodium in the as-received state, and 83% carbon, 14% oxygen, 3.3% silicon, 0.2% sodium in the thermally cycled spectra. It is interesting to note that the oxygen and carbon content remained fairly stable during the thermal cycling, indicating the absence of significant thermal oxidation.

In Figures 16 and 17, the surface composition of as-received FM®5 is 57% carbon, 24% flourine, 13% oxygen, 4.6% silicon, and 1.1% potassium. The cycled specimen shows 74% carbon, 13% oxygen, 9.1% flourine, and 4.0% silicon. The presence of such a high flourine content

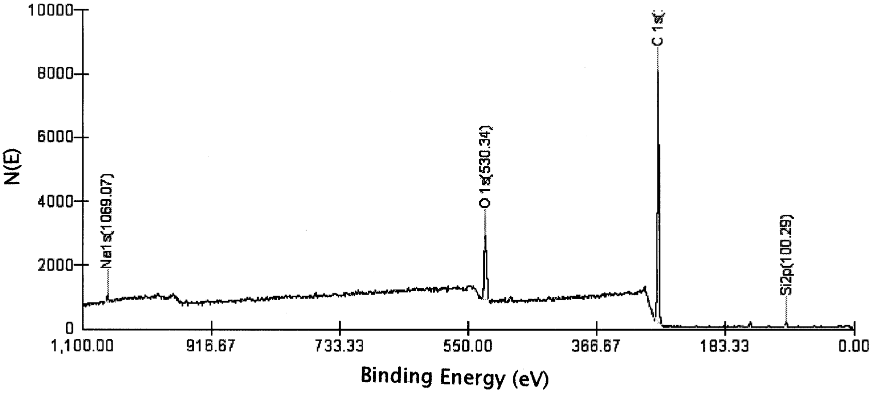


FIGURE 15 XPS spectrum of "thermally cycled" FM®73: C, 83%; O, 14%; Si, 3.3%; Na, 0.2%.

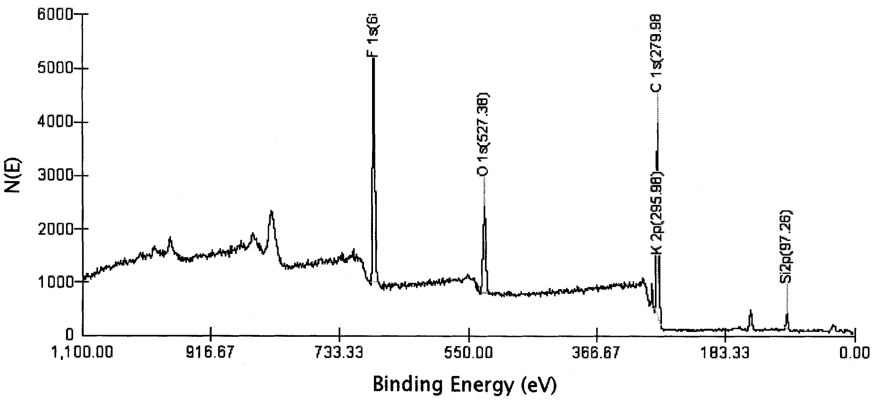


FIGURE 16 XPS spectrum of "as-received" FM®5: C, 57%; F, 24%; O, 13%; Si, 4.6%; K, 1.1%.

in the as received FM®5 indicates that flourine is either an undisclosed component of the adhesive or incorporated into the adhesive from handling, possibly through contact with Teflon. This result rules out the possibility of F entering through surface contamination during the joining process or in the ageing process. Once again, the oxygen content has not changed due to the exposure.

Microscopy

As illustrated in Figure 1, the bonded composite joints using AF-191 adhesives a showed significantly lower toughness when tested at −54°C, especially after thermal cycling or thermal exposure [10]. Since the investigation discussed above found little evidence of

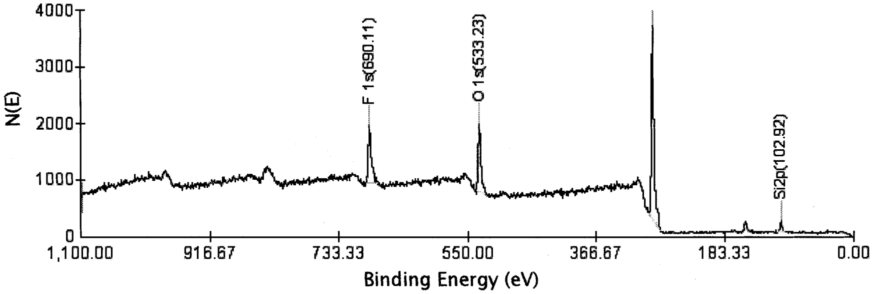


FIGURE 17 XPS spectrum of thermally cycled FM®5: C, 74%; O, 13%; F, 9.1%; Si, 4%.

chemical changes that would explain this large a drop in toughness, we wanted to investigate the possibility that microcracks were introduced into the adhesive during the thermal conditioning.

From the micrographs (not shown) it is not obvious if microcracks do develop in the adhesive or along the adhesive/adherend interface after exposure to various environmental conditions. The Gr-BMI/AF191/Gr-BMI system shows possible fiber degradation in the composite adherend but no cracking along the interface.

SUMMARY AND CONCLUSIONS

Determining possible relationships between mechanical damage and chemical degradation is an important aspect of characterization techniques because such information could fundamentally assist in characterizing and designing future durable adhesive structures for the aircraft industry. This work sets a basis for future investigation on the behavior of AF191, FM®73, and FM®5 adhesives after exposure to typical aircraft environments.

The extent of chemical degradation quantified from chemical and physical characterizations is small, indicating that these adhesives are chemically very stable under the test conditions. The test conditions were similar to those experienced by an aircraft during service, indicating that these adhesives are chemically suitable for aircraft joints. The temperature used for all three adhesives were lower than their glass transition temperatures or degradation temperature. Therefore, it can be concluded that realistic aircraft exposures do not significantly affect the durability of the adhesives themselves, except for acute environmental conditions. Our own earlier work, supported by other work from the literature [19] (where 10–20% reduction in energy release rate values after 6 months exposure at 204°C in ambient air, a temperature higher than used in the present study) indicates the reduction of mechanical properties for joints due to various environmental exposures. Since substantial changes in the chemical or physical characteristics of the adhesives were absent in these experiments, the basic changes responsible for the reduction in mechanical properties must be occurring elsewhere than in the bulk adhesive region, such as at the interface.

The hot/wet exposures are known to reduce tensile and fracture toughness properties of some adhesives joints. It has been shown using the ATR technique that hot/wet exposures intensify O–H, C–H, and N–H absorption bands, signifying the possibility of chain breakage or bond scission. Neither the decomposition temperature nor the glass transition temperature seems to be affected by thermally cycled environments, but hot/wet conditions reduce the T_g in all three adhesives. The hot/dry exposures only affected the T_g of the AF191 adhesive; however, ATR spectra showed some molecular changes in the adhesive. Comparison between ATR and XPS presented worthwhile answers to chemical composition and structure.

In few cases a change in the glass transition temperature was observed, without any other noticeable changes. In these cases, the reduction in mechanical properties may be due to a change in free volume, particularly close to the interface. Additional specific experiments must be conducted to identify the exact physical or chemical changes in the adhesive that are causing the changes in mechanical properties in specific cases. The mismatch in thermal expansion between the adhesive and the metal could be another cause it may affect the interface bonding rather than affecting the chemical or bulk physical structure of the adhesive.

Due to the sequential execution of environmental exposure and physical and chemical characterization, and due to logistical restrictions, the time between actual environmental exposure and chemical testing was approximately 34 months. However, all samples were kept in a protect environment, in an air-conditioned room with humidity control. Thus, the storage conditions were such that the possibility of contamination, hydrothermal degradation, or solid-state polymerization is either eliminated or kept to a minimum. In addition, the lack of noticeable physical and chemical changes in the exposed adhesives rule out any secondary degradation in the adhesives during the period when the joints were in protective storage.

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