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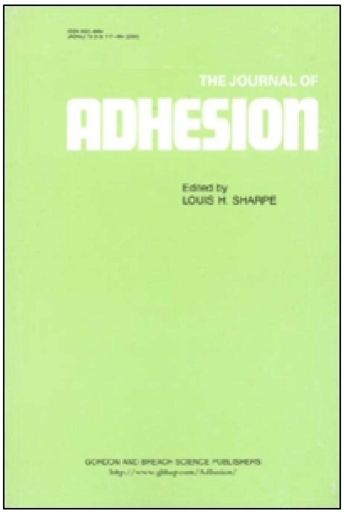

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Metal Alkoxide Primers in Titanium/Epoxy Bonding

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Factors influencing the durability of Ti–6Al–4V/metal alkoxide/epoxy interphases were determined by studying the chemical composition of three metal alkoxides and evaluating the bond durability of Ti–6Al–4V/epoxy bonds primed with these materials. The three alkoxides were sec-butyl aluminum alkoxide, tetra-isopropyl titanate and tetra-*n*-butyl titanate.

Because adhesive bonds made using phosphate fluoride (P/F) pretreated Ti–6Al–4V substrates were not durable, P/F treated Ti–6Al–4V was chosen as the substrate for testing the possible durability enhancement by the titanium and aluminum alkoxide coatings. Sec-butyl aluminum alkoxide significantly enhanced the bond durability of the P/F pretreated bonds, while the titanium alkoxide primers showed no improvement in durability. The locus of failure and infrared studies indicated the enhancement in durability by the aluminum alkoxide was due to the high concentration of hydroxyl groups on the alkoxide surface available to interact with the epoxy adhesive.

KEY WORDS Aluminum alkoxide; titanium alkoxide; primers; durability; Ti–6Al–4V alloy; adhesion.

1 INTRODUCTION

Metal alkoxides have been used in sol/gel chemistry and in the formation of glasses for many years.[1-5] A new application for alkoxides is as primers on metal adherend surfaces to enhance polymer/metal bond durability.[6-9] Investigation of both adhesion and chemical properties of the alkoxide coatings is thus important to understand better the mechanism of adhesion enhancement.

Organic primers are often applied to metal adherends following chemical pretreatment to protect the surfaces prior to adhesive bonding and to enhance bond durability. Pike[6-9] found that "inorganic primers," such as metal alkoxides, improved the durability of aluminum/epoxy bonds. Sec-butyl aluminum alkoxide, applied to both porous and non-porous aluminum oxide surfaces, improved the durability of bonds made with a 177°C-cured epoxy four to ten times over organic

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primers. Enhanced durability was also observed for 121°C-cured epoxy systems.[7]

The reason for this enhanced durability of aluminum/epoxy bonds using an "inorganic" or alkoxide primer in place of the conventional organic primer is not clear. Pike[6–7] postulates that the mechanism for this improvement is the formation of a stable amorphous boehmite, AlO(OH) layer upon hydrolysis of the alkoxide primer. The hydrolysis may occur by adsorbed water on the surface oxide of the adherend, by water in the solvent or by atmospheric moisture. The hydrolysis would yield not only the oxide, but also the alcohol which would evaporate with the application solvent. The resulting primer layer is smooth, and thus mechanical interlocking arguments commonly used for porous and rough surfaces to explain good durability are not tenable. An alternate explanation for the improved durability would be a chemical interaction between the alkoxide primer and the epoxy.[7,9] Another possibility would be that the primer reduces the chances for weak boundary layer formation[9] because the surface is no longer rough or porous where it is believed low molecular weight polymer fragments segregate, changing the crosslink density at the interface.[10] Thus, the phenomenon of alkoxide primers enhancing bond durability has been observed; however, we need to understand the nature of the alkoxide interaction with the metal adherend surface and the adhesive.

Although new to adhesive bonding, metal alkoxides are not new to chemistry. Sol/gel studies involving metal alkoxides have received much attention in the formation of glasses. The solution chemistry of metal alkoxides may provide an understanding of the chemistry of metal alkoxides when used as primers.

Metal alkoxides hydrolyze to form metal hydroxides or metal oxides and alcohol as shown by the following generalized reactions:

$$\mathrm{M(OR)_v + vH_2O \longrightarrow M(OH)_v + vROH} \qquad (1)$$

$$\mathrm{M(OH)_v \longrightarrow MO_{v/2} + (v/2)H_2O} \qquad (2)$$

where M is the metal, R is the alkyl group, and v is the valence of the metal.[2] Usually, the hydrolysis of metal alkoxides is not as straightforward as the above reactions indicate. A hydrolysis and a polymerization reaction occur simultaneously as shown below for a metal with a valence of four, such as titanium,

$$\mathrm{\equiv M{-}OR + HOH \longrightarrow \equiv M{-}OH + ROH} \qquad (3)$$

$$\mathrm{\equiv M{=}OH + RO{-}M\equiv \longrightarrow M{-}O{-}M\equiv + ROH} \qquad (4)$$

Here, both reactions occur between the OR and OH groups with the polymerization reaction forming bridging oxygens. Note that if complete hydrolysis occurred, polymerization would be impossible, thus no bridging oxygens would be present. A number of parameters affect the rates of hydrolysis and polymerization including the type of alkoxide, the availability of water and hence the alkoxide/water ratio, the dilution of the system, the type of solvent, and the reaction temperature.[2–4]

Aluminum alkoxides hydrolyze vigorously to form initially monohydroxides which later convert to trihydroxides as shown below.[2,4]

$$\mathrm{Al(OR)_3 + 2H_2O \longrightarrow AlOOH + ROH} \qquad (5)$$

$$\mathrm{AlOOH + H_2O \longrightarrow Al(OH)_3} \qquad (6)$$

The hydrolysis product of sec-butyl aluminum alkoxide depends upon the reaction temperature and medium. Non-liquid hydrolysis by atmospheric moisture produces an amorphous monohydroxide, while hot water hydrolysis creates a crystalline monohydroxide or boehmite. A trihydroxide, or bayerite, forms when the alkoxide is hydrolyzed in cold water.[2,5] When the amorphous boehmite is heated to 300°C, amorphous γ-alumina can form.[11]

Titanium alkoxide hydrolysis is very complex.[3] The hydrolysis and polymerization reactions are similar to equations [3] and [4]. Titanium differs from aluminum in that it does not have multiple forms of hydroxides.[2] The oxide content of the final reaction product or oxide polymer depends upon the amount of water initially present. The variability of oxide content in the polymerized alkoxide is described by the following equation:[3]

$$n\mathrm{Ti(OR)_4} + (4n + x - y)\mathrm{H_2O} \longrightarrow \mathrm{Ti}_n\mathrm{O}_{[2n-(x+y)/2]}(\mathrm{OH})_x(\mathrm{OR})_y + (4n - y)\mathrm{R(OH)} \qquad (7)$$

where n is the number of polymerized titanium ions, x is the number of OH groups and y is the number of OR groups in the molecule.

II EXPERIMENTAL

A Materials

Ti–6Al–4V was the metal alloy used in this study. Test specimens were fabricated from lap shear coupons supplied by personnel at the NASA-Langley Research Center, 2.54 × 12.7 × 0.13 cm; wedge coupons were supplied by RMI Titanium, 2.54 × 15.24 × 0.38 cm.

Ferrotype plates (Thompson Photo Products) provided a reflective substrate for reflectance infrared spectroscopy. The steel plates, 1 mm thick, had been coated first with nickel and then with an 80 nm chromium overlayer by Thompson Photo Products.

A 175°C-curing, rubber-modified, structural epoxy unsupported film adhesive, FM-300U (American Cyanamid) was used for all adhesive bonding. Part of the formulation of this adhesive is a brominated diglycidylether of bis-phenol A with an amino-type crosslinking agent.

Tetra-iso-propyl titanate (TIPT), tetra-n-butyl titanate, (TNBT) and sec-butyl aluminum alkoxide (E-8385) were obtained from Stauffer Chemical Company. All three alkoxides are lightly colored viscous liquids which hydrolyze vigorously with water and were therefore stored in a dessiccator.

All other chemicals, unless otherwise indicated, were obtained from Fisher Scientific Company.

B Sample preparation

1 *Pretreatments of Ti–6Al–4V* The Ti–6Al–4V adherends were pretreated by a phosphate/fluoride acidic etch (P/F). Details of the pretreatment procedures have been previously described.[12]

2 *Adhesive bonding* Wedge and stress-durability test samples were prepared as previously described in Ref. 12.

3 *Ferrotype plates* Ferrotype plates were cut as disks (2.54 cm in diameter) for substrates in the XPS analysis of films or as 2.54 cm square plates for substrates in FTIR analysis. The plates were cleaned with acetone, soap and water and dried prior to plasma cleaning. An oxygen plasma was generated in a Plasmod TM dry asher using 50 to 70 watts of radio frequency power. The Plasmod was run for 20 min prior to use. The cleaned samples were then placed in the Plasmod for 20 min. Upon removal, the samples were rinsed with deionized water and dried with prepurified nitrogen immediately before use.

4 *Metal alkoxides* Weight/weight percent alkoxide solutions were prepared in a glove bag under a dry nitrogen atmosphere to prevent atmospheric hydrolysis of the alkoxides. Typically, 1 wt% solutions were prepared in dry toluene. The toluene was dried by stirring it over calcium hydride overnight and distilling it into a dry flask containing activated 4 Å molecular sieves.

The alkoxide solutions were applied to the ferrotype plates by either spin coating or brush coating. The ferrotype plates were attached to the spin coater plate with double stick tape. The plates were flooded with solution and then spun at approximately 1500 to 1600 rpm for 5 to 10 sec in laboratory atmosphere. Solutions were brush coated in one or five coats on the ferrotype or Ti–6Al–4V adherends in a glove bag purged with dry N_2, allowing each coat to dry visibly before the next was applied. The alkoxide coatings were then cured at either room temperature under vacuum or at 300°C for 2 to 24 h. Transfer of the samples from glove bag to vacuum or oven was made in normal laboratory atmosphere.

C XPS

The chemical composition of the alkoxide surfaces was determined by XPS. Spectra were obtained using a PHI 5300 ESCA system with a magnesium X-ray anode at a power of 250 W. The samples were brush or spin coated on 2.54 cm diameter disks.

D FTIR

Grazing angle reflectance Fourier transform infrared spectrometry was used to study thin alkoxide films on reflective ferrotype plates. A grazing angle reflectance attachment,[15] was used in either a Nicolet 5DX or a 5DXB spectrometer. The sample chamber was purged with nitrogen for 30 to 60 min before a spectrum from 4600 to 400 cm^{-1} was obtained.

Two detectors, a deuterated triglycine sulfate or DTGS detector and a high sensitivity liquid nitrogen cooled mercury cadmium telluride or MCT detector, were used. Peak positions were determined using cursor-selected data points on the computer.

III RESULTS AND DISCUSSION

A Adhesive bonding

Bonds made with P/F-pretreated Ti–6Al–4V showed poor durability to hot, wet conditions compared to bonds made with chromic acid anodization (CAA), sodium hydroxide anodization (SHA), and TURCO-pretreated Ti–6Al–4V[12]. Poor durability of P/F-pretreated Ti–6Al–4V adherends has often been observed.[13,14] Because of its poor durability, the P/F-pretreated substrate was chosen to test metal alkoxide primers for the enhancement of durability.

Two alkoxides, tetra n-butyl titanate (TNBT) and sec-butyl aluminum alkoxide (E-8385) were coated on P/F-pretreated Ti–6Al–4V wedge test samples which were then bonded and immersed in 95°C water. Three alkoxides, TNBT, tetra isopropyl titanate (TIPT) and E-8385 were coated on P/F-pretreated Ti–6Al–4V wedge test samples bonded and exposed to 80°C, 95% r.h. For stress-durability testing, E-8385 was coated on both P/F- and CAA-pretreated Ti–6Al–4V lap shear coupons prior to bonding and exposure to 80°C 95% r.h.

1 *Wedge test* Pike[6–8] showed that, with aluminum substrates, sec-butyl aluminum alkoxide bond performance varied with coating thickness, thus the effect of coating thickness was studied by applying one and five coats of the alkoxide solutions to the Ti–6Al–4V adherend surface prior to bonding. Figure 1 compares the durability of the bonds made with one and five coats of E-8385 and TNBT after immersion in 95°C water. Five coats of the primer showed better durability than one coat for both alkoxides, consistent with results reported by Pike[8] for aluminum adherends coated with E-8385 and bonded with epoxy. The initial slopes of the curves in Figure 1 show that the E-8385 coating improved the durability of the P/F pretreatment over the TNBT coating. The rate of crack growth, da/dt, as a function of time, t, was obtained by fitting a curve to the data in Figure 1 and taking the derivative of the equation of this curve. The rate of crack growth *versus* time showed an increase followed by an initial decrease as seen in Figure 2 for sec-butyl aluminum alkoxide coated P/F samples. Because of the constant displacement of the wedge test, the load decreases with increasing crack length, thus a decrease in the rate would be expected. The environmental effects then became dominant causing an increase in the rate of crack propagation after 12 h, in contrast to the uncoated P/F samples[12] where the rate increased in

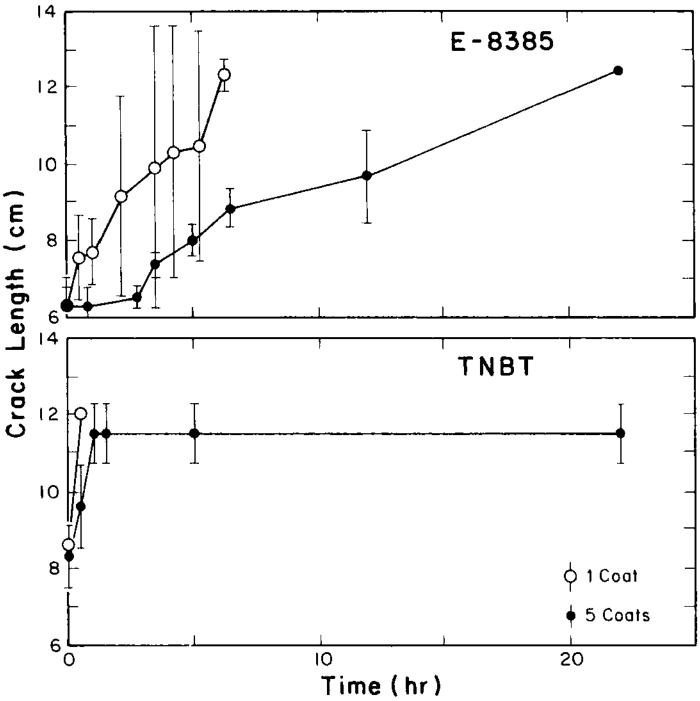

FIGURE 1 Crack extension *vs.* time for P/F-pretreated wedge samples coated with one and five coats of E-8385, (top) or TNBT (bottom) bonded with FM-300U and immersed in 95°C water.

<1.5 h. Thus, the presence of the sec-butyl aluminum alkoxide delayed the environmental effects and thus enhanced bond durability.

The locus of failure for these samples was investigated using XPS. The locus of failure in the unprimed P/F bonds occurred at the epoxy/titanium oxide interface.[12] The failure surfaces of the TNBT coated P/F bonds also showed

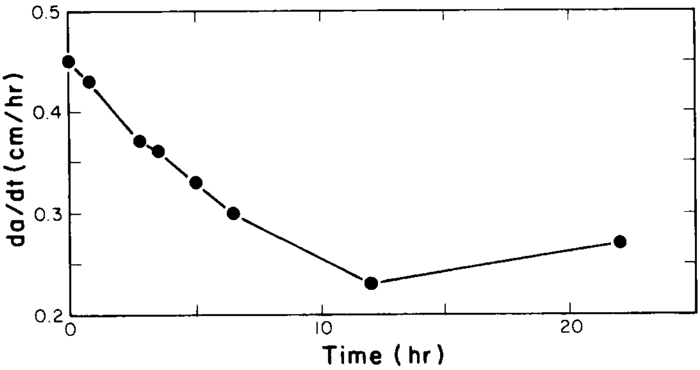

FIGURE 2 Rate of crack growth (*da*/*dt*) *vs.* time for P/F-pretreated wedge samples coated with five coats of E-8385, bonded with FM-300U and immersed in 95°C water.

titanium oxide on the metal failure side (MFS), with no evidence of epoxy, while the adhesive failure side (AFS) showed bromine, nitrogen and high binding energy oxygen, indicative of epoxy, but no titanium. Thus, failure appeared to be interfacial between the titanium alkoxide coating and the epoxy.

For the sec-butyl aluminum alkoxide primed samples, the locus of failure changed. Titanium was present on the MFS, but at a lower concentration than on the MFS of unprimed P/F samples. The striking difference was the presence of aluminum from the primer and nitrogen, presumably from the epoxy, although no bromine was detected. The AFS also showed the presence of aluminum and nitrogen, as well as bromine, with no indication of titanium. The failure occurred, therefore, in the aluminum oxide primer layer. An intriguing feature on the MFS is the presence of nitrogen, which could indicate a preferential adsorption of the nitrogen-containing components in the epoxy on the aluminum alkoxide/oxide surface.

The performance of the three alkoxide primers was tested in 80°C, 95% r.h. The effect of "cure temperature" was studied with the titanate primers by curing the primer layer prior to bonding at 25° and 300°C. The 25°C-cured, TNBT-coated P/F wedge samples failed upon wedge insertion and the 300°C-cured, TNBT-coated P/F wedge samples showed crack propagation to failure within 2.5 hours. The TIPT-coated P/F wedge samples also showed rapid crack propagation with the 25°C cured film samples failing at a slightly higher rate than the 300°C cured film samples. Figure 3 shows the crack length *versus* time for the titanate-primed samples and unprimed-P/F samples used as a control. The initial rates (slopes in Figure 4), for the first 24 h of crack propagation, showed that the slowest crack propagation was with the P/F control samples. The TIPT-primed samples showed a slower rate of crack propagation than the TNBT-primed

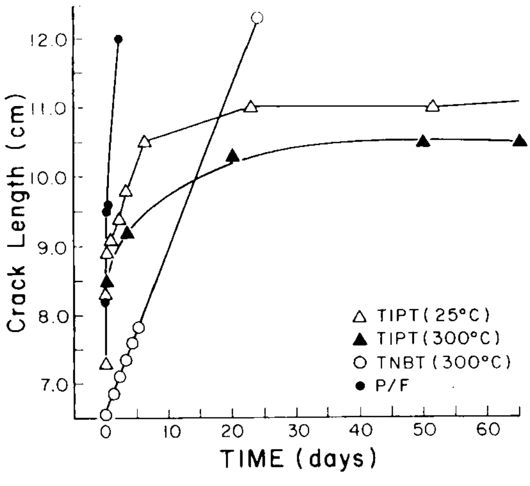

FIGURE 3 Crack extension *vs.* time for P/F-pretreated wedge samples coated with five coats of TNBT and TIPT, bonded with FM-300U and exposed to 80°C, 95% r.h.

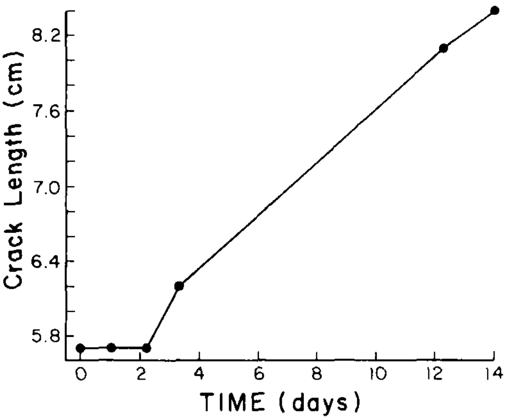

FIGURE 4 Crack extension *vs.* time for P/F pretreated wedge samples coated with five coats of E-8385 bonded with FM-300 and exposed to 80°C, 95% r.h.

sample, but both TIPT and TNBT showed no enhancement in bond durability of P/F-pretreated bonds exposed to 80°C, 95% r.h.

In contrast to the titanate primers, the aluminum alkoxide primed samples showed a profound enhancement in durability over the P/F control when bonded and tested *via* the wedge test. No crack propagation was observed for two days and even after 14 days the crack still had not propagated to failure, as shown in Figure 4, in contrast to the unprimed P/F samples where the crack usually propagated to failure within 24 hours. Thus, by the wedge test, the aluminum alkoxide primers significantly enhanced the durability of the P/F pretreated samples, whereas the titanium alkoxide primers did not. It should be noted, however, that the aluminum alkoxide primed P/F samples were still less durable than the CAA-treated, unprimed samples.[12]

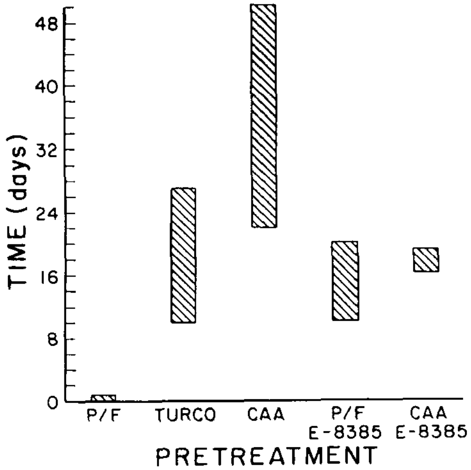

FIGURE 5 Time-to-failure windows for stress-durability test at 80°C, 95% r.h.

2 *Stress durability test* The stress-durability test was a second method used to study the durability enhancement of the aluminum alkoxide primers. The stress durability test results for unprimed P/F and E-8385 primed P/F samples qualitatively agree with the wedge test results with the E-8385 primed P/F bonds lasting 10 to 20 times longer than the unprimed P/F bonds as shown in Figure 5. When the CAA surface was primed with E-8385, the durability was similar to the E-8385 primed P/F bonds as also shown in Figure 5 with a much narrower distribution of time to failure. These results indicated that the aluminum alkoxide coating is not affected by the surface pretreatment of the adherend. It should also be again noted that the CAA-primed bonds were less durable than the unprimed CAA bonds, indicating that the increased surface area of the pores in the CAA surface[12] provided a better interface with the epoxy than the flat, non-porous aluminum alkoxide coating surface.

B Physical and chemical properties of alkoxides

1 *XPS* Since the adhesive bonding results showed that the aluminum alkoxide enhanced durability of the P/F treated Ti–6Al–4V/epoxy bonds while the two titanium alkoxide primers did not, it was of interest to determine the differences between the alkoxides.

The chemical composition of three alkoxide films, TNBT, TIPT, and E-8385 was studied by XPS and the results are listed in Table I. The cure temperature affected the surface composition of films brush-coated from dry toluene onto ferrotype plates. As indicated by the C/Ti ratios, significantly less carbon was detected on the 300°C-cured film than on the 25°C-cured film. While the decrease in carbon could be due to less contamination, it is more likely due to a more complete reaction of the alkoxide to oxide and alcohol with subsequent release of alcohol at the elevated temperature. The chromium was from the ferrotype plates, and thus indicated that the film of metal alkoxide was either thinner than approximately 5 nm or discontinuous. From SEM photomicrographs and angle-dependent XPS studies, it was concluded that the alkoxide films were discontinuous.[26] The silicon contamination primarily resulted from the application brush since only trace levels of silicon were detected on the spun-coat films. The binding energy of the titanium in the titanate films was indicative of a non-stoichiometric titanium oxide.

2 *FTIR*

(*a*) *TIPT*. A 1 wt% solution of TIPT in toluene was brush coated onto ferrotype plates in five coats. The film was then cured at 25°C under vacuum or at 300°C in air, before collecting the reflectance spectra shown in Figures 6 and 7. Table II lists the peak positions and the peak assignments.

The 25°C cure showed a broad —OH absorbance with the C—H stretch region, 2959–2857 cm^{-1},[16] clearly resolved. Correspondingly, the —CH— deformation vibration region at 1445 cm^{-1},[20] the *gem*-dimethyl absorbance at 1377 cm^{-1},[1,21] and the (C—O)Ti stretch at 1053 cm^{-1}[1,21,23] were clearly present. In contrast, the

TABLE I
XPS analysis of metal alkoxide films on ferrotype plates

Cure temp.	Metal alkoxide	Element	B.E. (ev)	Conc	Ratio to Ti or Al
25°C	TNBT	C	285.0	35.0	2.3
		O	531.2	46.0	3.1
		Ti	459.6	15.0	—
		Cr	—	0	0
		Si	102.0	3.6	0.24
300°C	TNBT	C	285.0	10.0	0.63
		O	530.8	62.0	3.9
		Ti	459.4	16.0	—
		Cr	577.7	2.8	0.18
		Si	102.7	8.6	0.54
25°C	TIPT	C	285.0	31.0	2.1
		O	531.1	47.0	3.1
		Ti	459.5	15.0	—
		Cr	—	0	0
		Si	101.9	6.6	0.44
300°C	TIPT	C	285.0	8.4	0.49
		O	530.9	64.0	3.8
		Ti	459.3	17.0	—
		Cr	577.8	2.0	0.12
		Si	102.6	8.4	0.49
25°C	E-8385	C	285.0	21.0	0.88
		O	532.5	47.0	2.0
		Al	75.0	24.0	—
		Cr	577.8	1.8	0.88
		Si	102.2	6.3	0.26
300°C	E-8385	C	285.0	11.0	0.40
		O	532.0	53.0	1.8
		Al	74.6	29.0	—
		Cr	577.4	2.1	0.07
		Si	102.4	4.2	0.14

C—H stretch region was absent in the 300°C-cure film and only a small (C—O)Ti stretch was observed at 1049 cm^{-1} indicating that the alcohol portion of the alkoxide was removed at the 300°C cure. These results are in agreement with the XPS results showing a notably lower C/Ti ratio at the 300°C cure compared with the 25°C cure. The Ti–O stretch region appeared to broaden greatly after the 300°C cure indicating that a titanium oxide layer was formed.

(*b*) *TNBT*. TNBT films were prepared similarly to the TIPT films and the spectra are shown in Figures 8 and 9 with the peak positions and assignments listed in Table III. The absorption of *n*-butyl groups and the (C—O)Ti stretch contributed to the peaks at 1126, 1098, and 1042 cm^{-1}.

Similar to the TIPT spectra of the 25° and 300°C-cure films, the 1045 cm^{-1} band was due to the (C—O)Ti stretch and was the only remaining peak of the three

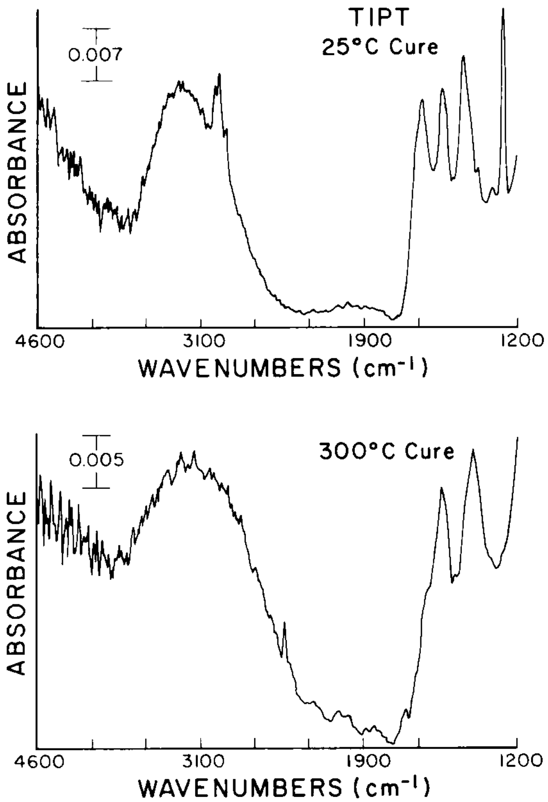

FIGURE 6 Grazing angle FTIR spectra from 4600 to 1200 cm^{-1} of TIPT on ferrotype plates, cured at 25°C and 300°C.

TABLE II
Grazing angle FTIR peak positions and assignments for TIPT films on ferrotype plates

TIPT 25°C (cm^{-1})	TIPT 300°C (cm^{-1})	Peak assignment
3300		—OH str. [16]
	3140	—OH str.
2959		C—H asym. str. CH_3 [16]
2926		C—H asym. str. —CH_2 alkanes
2857		C—H sym. str. —CH_2—
1636		OH water of cryst. [17–19]
	1616	OH water of cryst.
1539	1543	—CH_2 scissors vib. [20]
1445		CH_3 asym. def. vib.
1377	1404	sym C—$(CH_3)_2$ def. vib. [21, 22]
1310		
1261		inplane O—H def. vib. [16]
1098		iso-branching vib. [22]
1053	1049	(C—O)M str. [1, 21–23]
820	837	Ti—O [24]
679	704	Ti—O

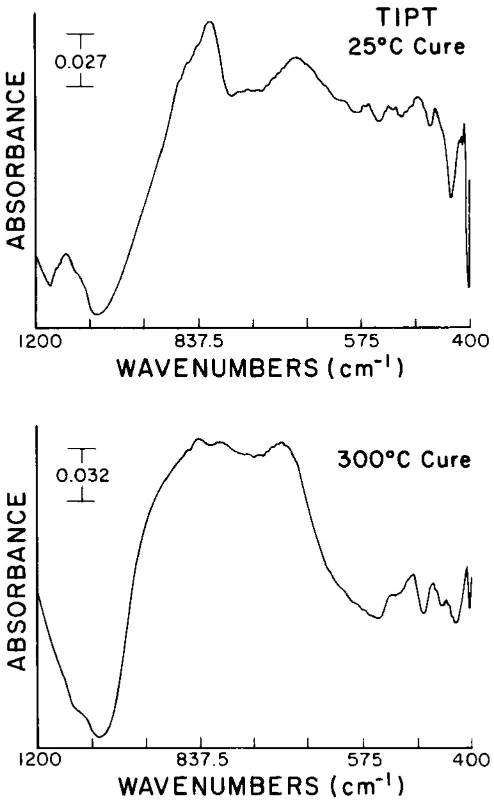

FIGURE 7 Grazing angle FTIR spectra from 1200 to 400 cm^{-1} of TIPT on ferrotype plates, cured at 25°C and 300°C.

TABLE III
Grazing angle FTIR peak positions and assignments for TNBT films on ferrotype plates

TNBT 25°C (cm^{-1})	TNBT 300°C (cm^{-1})	Peak assignment
3370		—OH str. [16]
2957		C—H asym. str. CH_3 [16]
2924		C—H aym. str. —CH_2 alkanes
2859		C—H sym. str. —CH_2—
1632		—OH water of cryst. [17–19]
1600		—OH water of cryst.
1535	1541	
	1485	—CH_2— scissors vib. [20]
1447	1441	—CH_3 asym. def. vib.
1377	1408	
1307		
1250		inplane O—H def. vib. [16]
1126		induced alkyl absorp. [21, 22]
1098		C—O str. [1, 21, 22]
1042	1045	
816	876	
760		Ti-O [24]
683	710	

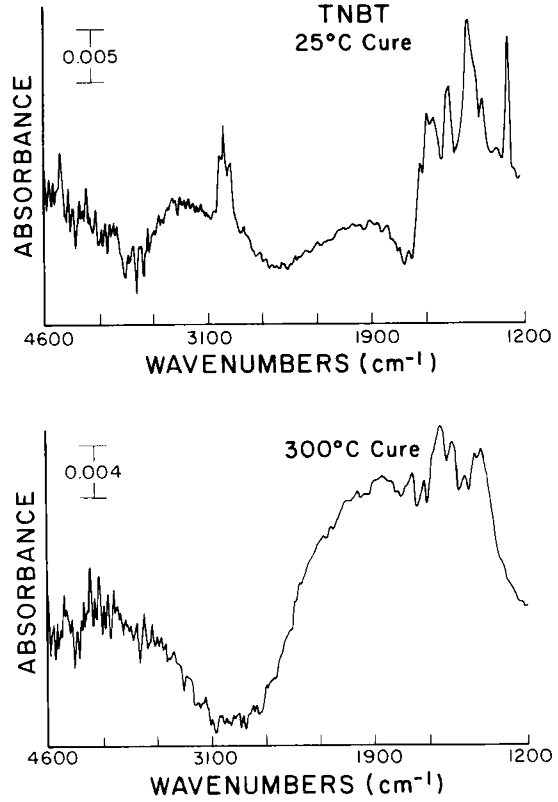

FIGURE 8 Grazing angle FTIR spectra from 4600 to 1200 cm^{-1} of TNBT on ferrotype plates, cured at 25°C and 300°C.

TABLE IV
Grazing angle FTIR peak positions and assignments for E-8385 films on ferrotype plates

E-8385 25°C (cm^{-1})	E-8385 300°C (cm^{-1})	Peak assignment
3395	3223	—OH str. [16]
2963		C—H asym. str. CH_3 [16]
2926		C—H asym. str. —CH_2 alkanes
	1622	—OH water of cryst. [17–19]
1512		
1462	1462	—CH_2 scissoring, alkanes [20] CH_3 asym. def. vib.
1418	1423	
1261		—OH in plane def. vib. [16]
	1147	
1094		
1053		C—O(Al) str. [1, 23]
856	883	Al—O str.
806		

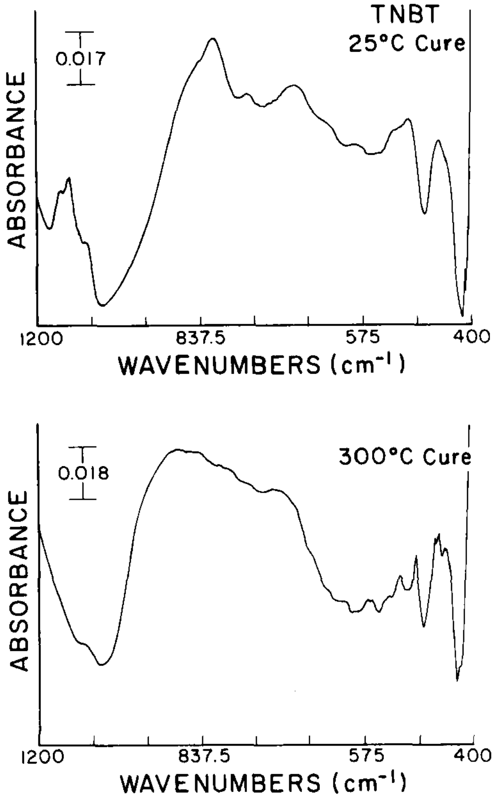

FIGURE 9 Grazing angle FTIR spectra from 1200 to 400 cm^{-1} of TNBT on ferrotype plates, cured at 25°C and 300°C.

after the 300°C cure. The C—H stretch region, 2957 – 2859 cm^{-1}, disappeared after the 300°C cure again agreeing with the XPS data which showed a decrease in the C/Ti ratio after the 300°C cure. The broad Ti–O stretch at 875 cm^{-1} was also present in the TNBT film as in the TIPT film.

(*c*) *E*-8385. E-8385 films were also prepared similarly to the titanate films with the spectra shown in Figures 10 to 11 and the peak positions and assignments listed in Table IV. Characteristic peaks fell at 1094, 1053, and 856 cm^{-1}, also present in the literature[27] and neat spectra[26] and were due to (C—O)Al stretching and Al–O stretching vibrations.[1,23] After 300°C cure, the methyl stretch region at 2961 cm^{-1} disappeared and a broad peak formed at 1144 and 883 cm^{-1} after 300°C cure.

The E-8385 films differed from the titanate films in the area of the OH stretching region. The —OH band was greater for the E-8385 films than in the TIPT film which was significantly greater than the TNBT film, indicating the highest concentration of hydroxyl groups was on the E-8385 surface. The presence of a higher concentration of hydroxyl groups may indicate a more

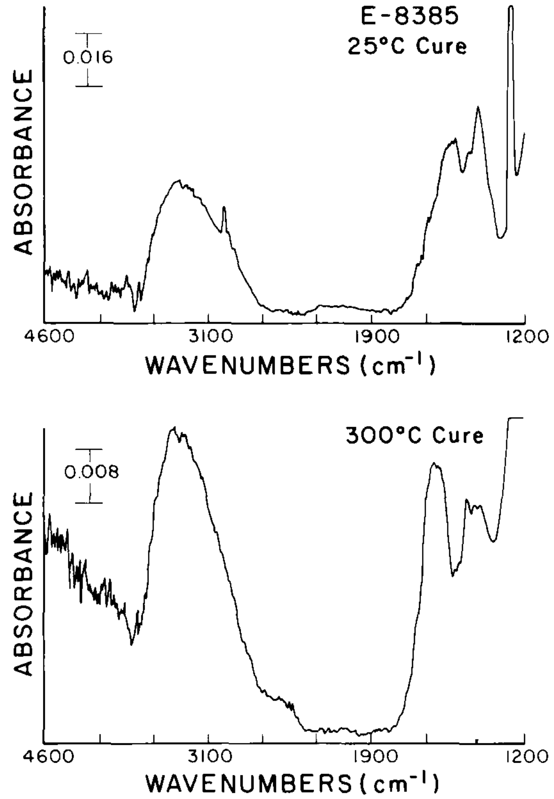

FIGURE 10 Grazing angle FTIR spectra from 4600 to 1200 cm^{-1} of E-8385 on ferrotype plates, cured at 25°C and 300°C.

chemically active surface for forming hydrogen or chemical bonds with the epoxy, thus providing more durable adhesive bonds.

IV SUMMARY

The E-8385 primed P/F bonds were clearly more durable than the TIPT- or the TNBT-primed bonds and possessed the highest concentration of hydroxyl groups. The TIPT samples showed slightly better durability than the TNBT samples and also a higher concentration of —OH groups than on TNBT. As evidenced by the locus of failure results, aluminum alkoxide primer was found on both sides of the failed joint, whereas in the titanium alkoxide primed joints, the failure was interfacial between the primer and the epoxy. This failure locus indicated less or weaker interactions between the titanium alkoxide and the epoxy than between the aluminum alkoxide and epoxy.

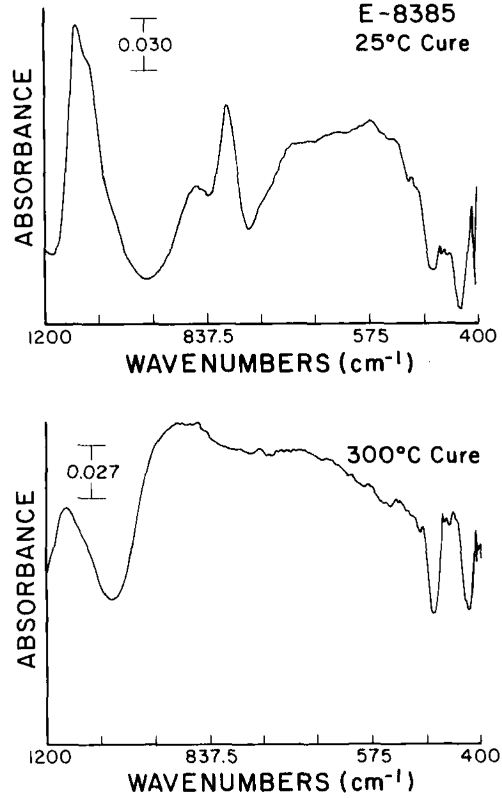

FIGURE 11 Grazing angle FTIR spectra from 1200 to 400 cm^{-1} of E-8385 on ferrotype plates, cured at 25°C and 300°C.

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