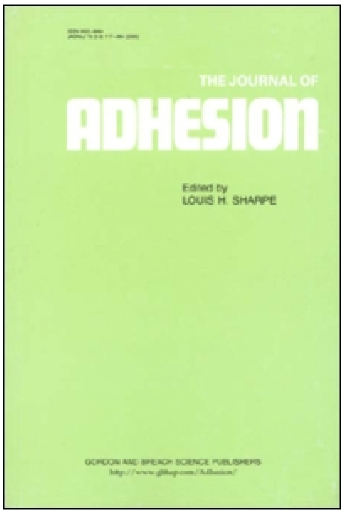

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Effect of Plasma-Polymerized Primers on the Durability of Aluminum/Epoxy Adhesive Bonds

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The durability of aluminum/epoxy adhesive joints prepared from substrates pretreated by plasma etching and then deposition of plasma-polymerized primers was determined using the wedge crack testing method. Plasma etching and polymerization were conducted using both direct current (DC) and microwave (2.45 GHz) driven plasma systems. Plasma-polymerized primers were deposited using trimethysilane (TMS) and hexamethyldisiloxane (HMDSO) to form siloxane-like and silica-like films, respectively. Plasma etching with argon and argon/hydrogen plasmas was used as a substrate pretreatment. In some cases etching with an oxygen plasma was used as a post-treatment to give a silica-like surface to siloxane-like films deposited from TMS. Adhesive joints were prepared using two different epoxy adhesives, Cytec FM-300 and FM-123-2. Differences in initial adhesion were observed for primer films with chemical differences. Siloxane-like primer films were not wetted by the adhesive and resulted in poor wedge test results. Silica-like primer films were not wetted by the adhesive and resulted in poor wedge test results. Silica-like primer films deposited onto aluminum substrates resulted in wedge specimens with good adhesion and durability. The initial crack was cohesive within the adhesive. However, crack growth occurred at the interface between the adhesive and silica-like primer. Durability of the wedge specimens was essentially invariant of the type of microwave plasma pretreatment for grit-blasted aluminum substrates that were coated with silica-like primers before bonding with FM-123-2.

Keywords: Plasma polymerization; plasma etching; durability testing; wedge crack testing; structural bonding; aluminum/adhesive bonding

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INTRODUCTION

In order to obtain strong, durable adhesive bonds to metal substrates, it is necessary to prevent corrosion at the adhesive/metal interface by, for example, applying a protective coating to the surface of the metal. Aluminum has a readily-formed surface oxide that plays an important role in the durability of adhesive joints made with aluminum adherends. Durable adhesive joints must withstand exposure to humid environments. The hydration of aluminum oxide is a common failure mechanism in adhesive joints made with aluminum adherends. In humid environments the oxide layer will corrode to form the aluminum hydroxide known as pseudo-boehmite by the hydration reaction [1]:

$$Al_2O_3 + H_2O \rightarrow 2AlOOH$$

Aluminum hyroxide formed by this process is mechanically weak and leads to failure at the hydroxide/aluminum interface. Etching and electrochemical methods provide for the reduction and chemical modification of the oxide layer to aid in adhesive joint durability. Current techniques used to prepare the surface of aluminum for durable adhesive bonding include the P2 etch, FPL (chromic-sulfuric acid) etching, and PAA (phosphoric acid anodization).

The P2 etch, developed as a chromate-free alternative to the FPL etch, uses water, sulfuric acid, and ferric sulfate. This etchant readily corrodes the aluminum, providing an acceptable surface for the PAA process before adhesive bonding. In comparison with FPL etching before PAA processing, P2 etching seems to yield similar durability results for aluminum bonding [2].

Chromic-sulfuric acid etching is commonly applied to aluminum surfaces to reduce the thickness of the oxide layer. A typical etching method is the Forest Products Laboratory etch, generally referred to as the FPL etch [3]. FPL etching removes the bulk of the native aluminum oxide on aluminum surfaces while forming a new oxide layer that is strong and structurally controlled [2]. This does not improve the overall long term durability due to the instability of the oxide when exposed to humid environments.

Phosphoric acid anodization (PAA) is especially effective at improving the durability of adhesive bonds to aluminum. Surface preparation of aluminum with the PAA process requires prior removal of the native oxide layer and that is typically accomplished by FPL etching, a similar chromic-sulfuric acid etching, or P2 etching. The PAA process forms an oxide layer that has a cellular hexagonal tube morphology and is thicker relative to the low profile FPL-oxide. It is commonly accepted that this morphology leads to good penetration and mechanical interlocking by the adhesive or primer to the PAA-oxide [4]. A monolayer of phosphate is formed on the surface of the oxide layer and it has been found that when exposed to humidity the dissolution of this phosphate layer is slow and rate limiting to corrosion of the oxide [5]. Since the PAA-oxide is less susceptible to dissolution than the FPL-oxide by humid environments, long term environmental durability of adhesive joints can be achieved.

However, the chemicals used for FPL etching and PAA processing provide serious problems since they are reactive, hazardous, and must be disposed of after time. Environmental awareness has prompted efforts to develop cleaner processing methods with less impact on health and environment. The P2 etch process was developed as an alternative to the FPL etch with health and environment in mind. The Clean Air Act of 1990 has impacted industry with federal regulations regarding processes involving hexavalent chromium [6]. Surface cleaning and coating processes that incorporate the use of hazardous liquids must be replaced using newer and cleaner technologies. Clearly a reduction or elimination of liquid chemical processing of aluminum would benefit industry and environment.

Plasma processing of surfaces has many advantages over conventional cleaning and coating methods [7]. Chemical reactions in discharge plasmas are carried out in the gas phase, usually under a degree of vacuum, resulting in well controlled containment of the process and by-products. Multiple plasma processes, such as cleaning, etching and coating of surfaces, can be performed sequentially without exposing the surface to atmospheric contaminants. Reactive species in plasmas, such as ions and free radicals, generally have a very short lifetime and easily become neutral and inert.

Recent work in plasma polymerization has produced coatings that protect againts corrosion of metals and promote adhesion of adhesives [8]. Preliminary adhesion and corrosion protection studies have been made using oxygen-plasma-etched plasma-polymerized trimethylsilane

(TMS) films and plasma-polymerized hexamethyldisiloxane (HMDSO) that produce inorganic, silica-like thin films (< 100 nm). In other work that we have done, aluminum panels coated with plasma-polymerized silica-like films from HMDSO performed similarly to conversion coated control specimens evaluated for preventing corrosion around a scribed mark through the coating [9]. These thin silica-like films find interesting applications aside from conventional coatings since they are amorphous, have low or no solubility, good thermal stability, form uniform films with high crosslink density, adhere well to substrates, and are readily adhered to by most standard adhesives. As an alternative to electrochemical processes, etching aluminum with a plasma and then coating the aluminum with a plasma-polymerized film produces little or no waste.

Durability testing of adhesive bonds using plasma-polymerized primer films is essential in evaluating the feasibility of using plasma techniques over conventional surface preparations. Although initial adhesion studies have been made, evaluating the durability of adhesive joints that use these films as adhesion primers has just begun.

Some recent durability tests of lap joints made from aluminum substrates with plasma-polymerized HMDSO primer films have been conducted [8]. Specimens were loaded in tension at ~20% of their ultimate tensile strength for the duration of testing. The joints were then exposed to a cyclically varying corrosive environment until failure occurred. Each cycle was 24 hours long and consisted of 15 minutes in a 5% aqueous solution of sodium chloride, 1 hour and 45 minutes drying at room temperature, and 22 hours in a humidity chamber at 90% relative humidity and 50°C (samples were left in the humidity chamber during weekends). Excellent durability results were obtained for these tests. Lap joints made from substrates etched in an argon plasma and coated with a silica-like primer usually fail due to corrosion of the substrate. They do not fail due to destruction of the bonds. By comparison, poor pretreatments lead to adhesive failure after only a few cycles.

The durability of adhesive joints prepared from substrates coated with plasma-polymerized primer films depends heavily on the physical and chemical characteristics of the metal-film interface, the film, and the film-adhesive interface. These characteristics depend strongly on processing variables used in plasma etching and plasma polymerization.

The goal of this work was to determine the durability of adhesive joints that were prepared using substrates primed with plasma-polymerized thin films. Comparison of conventional chemical pretreatment with plasma pretreatment and deposition of primer films for the durability of adhesive joints was carried out using the wedge crack test. Plasma-treated surfaces and films were characterized using surface analytical techniques. Substrate pretreatment parameters as well as film deposition parameters were varied within the experiment to illustrate routes for optimizing durability.

EXPERIMENTAL

1. DC Plasma Deposition

Eight aluminum alloy (2024-T3) panels (3-1/2" × 6" × 1/8") (8.9 cm × 15.2 cm × 0.32 cm) were grit blasted using a silicon carbide medium and blown clean of debris with dry nitrogen gas. The substrates were then either cleaned with acetone, acid etched, or given no additional pretreatment before being placed in a DC plasma reactor for additional processing (see Fig. 1 for a schematic drawing of the DC reactor). Table I shows processing variables used in plasma etching of the substrates and in deposition of plasma-polymerized primers in the DC reactor.

The etching gas flow rates for argon and hydrogen were 2.2 SCCM (standard cubic centimeters per second) and 6 SCCM, respectively. All Ar/H_2 etching was carried out at 65 mtorr for 10 minutes at a power level of 28 Watts and a pulse width of 40 ms at 700 volts. Deposition was carried out with a 2.45 SCCM flow rate of TMS. The deposition was carried out for 5 minutes at 65 mtorr, with 24 Watts power, and a pulse width of 20 ms at 1200 volts. Selected samples were post-treated with an oxygen plasma to produce a more silica-like surface. The oxygen post-treatment was carried out for five minutes using 7.7 SCCM flow at 65 mtorr with a power of 26 Watts and a pulse width of 35 ms at 750 volts.

Wedge test specimens were made by bonding pairs of panels together using FM-300 adhesive and then cutting out three 6" × 1" (15.2 cm × 2.5 cm) bonded specimens. The wedge test specimens were tested as described below.

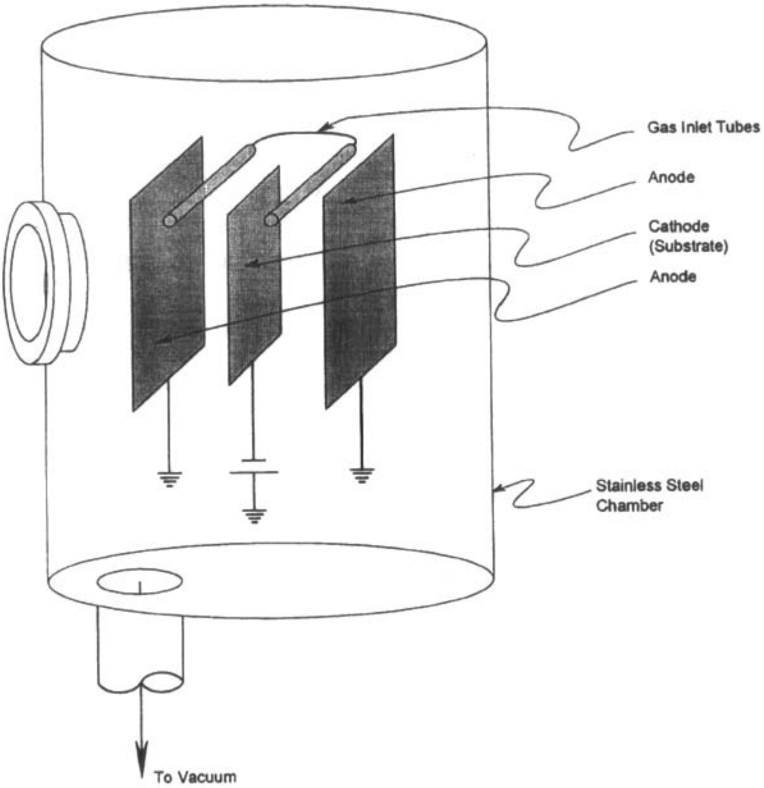

FIGURE 1 DC plasma reactor diagram.

TABLE I Etching and Deposition Parameters used in DC Reactor

Chemical Cleaning	*Plasma Pre-Treatment*	*Monomer*	*Plasma Post-Treatment*
None	Ar/H_2	TMS	None
Acetone	Ar/H_2	TMS	None
FPL Etch	Ar/H_2	TMS	None
None	Ar/H_2	TMS	Oxygen

2. *Microwave Plasma Etching and Film Deposition*

Thirty aluminum alloy (2024-T3) panels (1" × 6" × 1/8") (2.5 cm × 15.2 cm × 0.32 cm) were grit blasted using a silicon carbide medium and blown clean of debris using dry nitrogen gas. Pairs of panels were then placed in a microwave-powered plasma reactor. The reactor (see

Fig. 2 for a diagram of the microwave reactor) used a pulsed microwave power source, 2.45 GHz, to drive a plasma confined to a stainless steel vessel. Several access ports shown on the vessel were modified to enable the necessary etching, carrier, and deposition gases to be introduced into the reactor. Other ports provided rotary motion for the sample stage, vacuum, and a quartz window feed-through for microwave power. Table II shows the processing variables used for plasma etching of aluminum substrates and for deposition of plasma-polymerized primers.

Plasma etching was carried out at a pressure of 500 mtorr in atmospheres of argon (20 SCCM), Ar/H_2(10 SCCM each), and Ar/H_2 (20 SCCM Ar, 5 SCCM H_2). Deposition of plasma-polymerized films was then carried out at 500 mtorr using a mixture of argon, oxygen, and HMDSO at flow rates of 5, 45, and 0.2 SCCM, respectively. Each etch

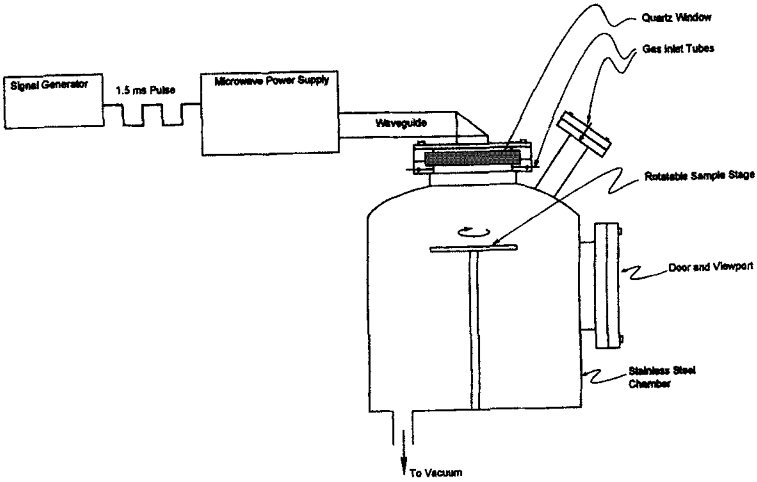

FIGURE 2 Microwave plasma reactor diagram.

TABLE II Etching and Deposition Parameters used in Microwave Reactor

Plasma Pre-Treatment	*Monomer*
Ar	HMDSO
Ar/H_2 50%	HMDSO
Ar/H_2 20%	HMDSO

and deposition was carried out for 10 minutes at 200 Watts pulsed power, using a pulse width of 1.5 ms. Fifteen wedge test specimens were made by bonding each pair of panels together using FM-123-2 adhesive. The wedge test specimens were tested as described below.

3. *Bonding and Wedge Testing*

Substrates coated with plasma-polymerized primers were bonded for wedge crack testing in accordance with ASTM test method D-3762. Cytec FM-300 adhesive (Cytec Ind., W. Paterson, NJ, USA) was used for the samples prepared in the DC reactor, and Cytec FM-123-2 adhesive was used for the samples prepared in the microwave reactor. FM-300 adhesive was cured for one hour at a temperature of 350°F and under a pressure of 40 psi. The heating and cooling rate was 5°F/min (2.8°C/min). FM-123-2 adhesive was cured for one hour at a temperature of 250°F (121°C) and under a pressure of 40 psi (0.28 MPa). The heating and cooling rate was also 5°F/min (2.8°C/min). Wedge testing was conducted in a controlled temperature and humidity chamber at 60°C and 95% relative humidity. Initial crack lengths after driving the wedges were measured and the joints were then placed in the humid environment. Crack lengths were measured periodically thereafter as a function of exposure time. Testing was concluded after the specimens failed or after approximately 7 days. The specimens were then removed from the humid environment and pulled apart so that the failure surfaces could be examined.

Failure analysis was performed by using XPS (X-ray photoelectron spectroscopy) and SEM (scanning electron microscopy) on the failure surfaces. Areas of specific interest were carefully sectioned from the panels and examined.

4. *Film Characterization*

Reflection-absorption infrared spectroscopy (RAIR) was performed on polished substrates that were coated with the plasma polymer films at the same time as the wedge test specimens. Baseline spectra were obtained for the bare substrates and then subtracted from the spectra of the coated substrates. RAIR was done on a Perkin-Elmer Model 1800 FTIR with a reflection accessory (Harrick Scientific Corp.) set to an angle of incidence of 78°. Bands due to water vapor were eliminated by purging the system with dried air.

The thickness of the films was determined using an ellipsometer (Rudolph Research Model 436) to examine the polished substrates before and after deposition of the films. A program written by McCrakin [10] was used to calculate the thickness from the parameters Δ and Ψ.

XPS analysis of films was performed using a Perkin-Elmer Model 5300 X-ray photoelectron spectrometer with magnesium K_α radiation at 300 Watts. Typically 89.45 eV and 35.75 eV pass energies were used for survey and high resolution spectra, respectively. The effects of sample charging were eliminated by correcting the observed spectra to yield a C(1s) binding energy for saturated hydrocarbons equal to 284.6 eV.

RESULTS AND DISCUSSION

Film Characterization

1. DC Plasma Polymerized Films

Ellipsometry measurements indicated a film thickness of about 75 nm for the TMS films and for the oxygen plasma post-treated TMS films. Therefore, the post-treatment had little effect on the measured film thickness.

RAIR spectra of TMS plasma-polymerized films with no post-treatment and with an oxygen plasma post-treatment were obtained (see Fig. 3). Both spectra showed characteristic peaks at 1050 and 850 cm^{-1} due to Si—O—Si stretching and Si—H_2 wagging, respectively. Si—H stretching gave rise to a band in the region of 2125 cm^{-1} for both films.

The oxygen plasma post-treated TMS film showed an additional peak at about 1225 cm^{-1}, due to the longitudinal optical phonon mode of SiO_2 bonds. The observation of this band indicated that the surface of the oxygen plasma post-treated film was oxidized and more silica-like than the TMS film without the oxygen post-treatment.

XPS survey spectra of the TMS film and the oxygen plasma treated TMS film are shown in Figures 4 and 5. Atomic concentrations calculated from high resolution XPS spectra of both films are shown in Table III.

The carbon concentration in the TMS film with the oxygen plasma post-treatment was significantly lower than that of the TMS film with

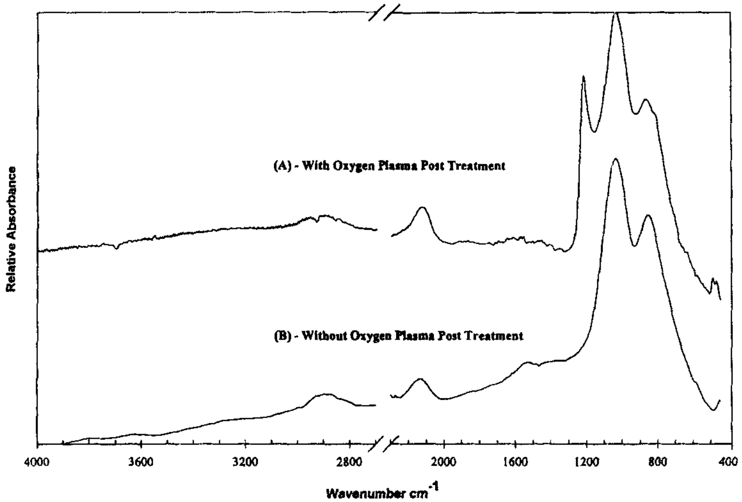

FIGURE 3 RAIR Spectra of DC-Plasma-Polymerized TMS Films Deposited onto Aluminium with (A)-Oxygen Plasma Post Treatment and (B)-without Post Treatment.

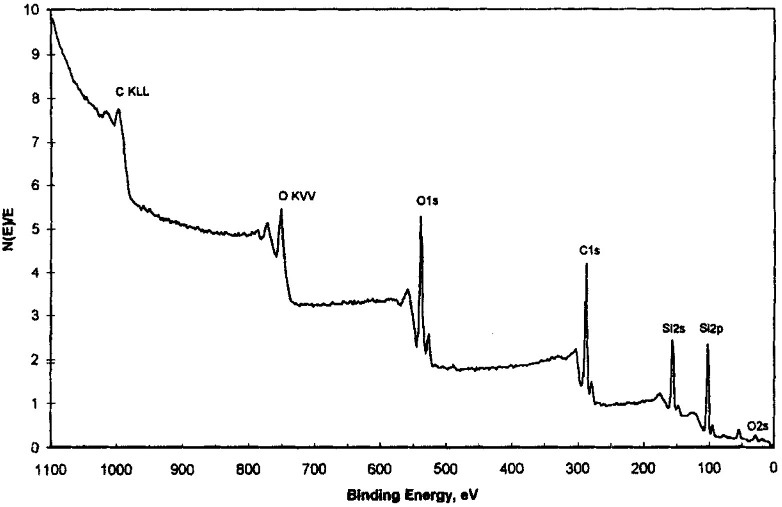

FIGURE 4 XPS survey spectrum of DC-plasma-polymerized TMS on aluminum.

no post-treatment. This signified that the oxygen plasma had a severe oxidizing effect on the organic constituent in the film. Additionally, a very small amount of nitrogen was detected, perhaps due to

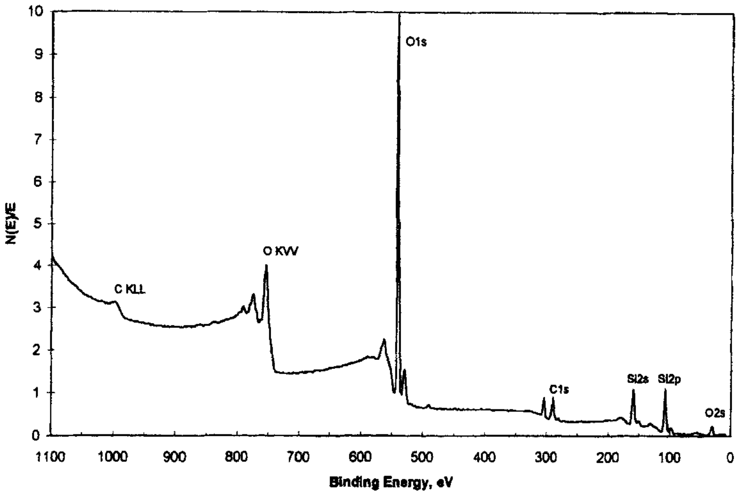

FIGURE 5 XPS survey spectrum of DC-plasma-polymerized TMS on aluminum with oxygen plasma post treatment.

TABLE III Chemical Composition of DC Plasma-Polymerized TMS Films

Element/ Concentration	*Plasma-Polymerized TMS*	*Plasma-Polymerized TMS with Oxygen Plasma Post-Treatment*
Carbon	56.9%	17.3%
Oxygen	17.7%	58.7%
Silicon	24.9%	23.0%
Nitrogen	0.6%	1.1%

chemisorption of atmospheric nitrogen by the oxygen plasma etched surface of the TMS film.

Figure 6 shows the high resolution Si(2p) spectra for the TMS films and the TMS film with oxygen plasma post-treatment. The oxygen post-treated TMS films showed an approximate 2 eV shift upwards for the Si(2p) binding energy. This shift of the Si(2p) binding energy to a higher value was attributed to oxidation, forming a more inorganic silica-like film. This supported the evidence shown in the RAIR spectra of a more oxidized silica-like film after oxygen post-treatment.

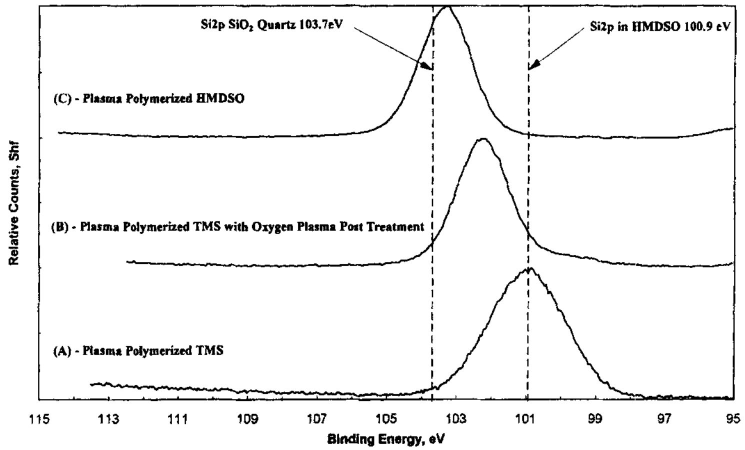

FIGURE 6 XPS high resolution Si(2p) spectra of plasma-polymerized films on aluminum; (A)-plasma-polymerized TMS, (B)-plasma-polymerized TMS with oxygen plasma post treatment, and (C)-plasma-polymerized HMDSO.

2. *Microwave Plasma Polymerized Films*

Ellipsometry measurements indicated a film thickness of about 100 nm for the plasma-polymerized HMDSO films.

The RAIR spectrum of an HMDSO film deposited in the microwave reactor, under the conditions previously described, is shown in Figure 7. The intense peak at 1224 cm^{-1} was due to the longitudinal phonon mode of SiO_2-like structure and indicated that the film was very silica-like. Compared with the plasma-polymerized TMS films, a noticeable shift in the longitudinal phonon mode to higher wavenumbers indicated a more inorganic coordination of the SiO_2-like structure. Absence of the $Si—CH_3$ stretching band near 1250 cm^{-1} indicated that the film had negligible organic characteristic.

The XPS survey spectrum of a film produced in the microwave plasma reactor is shown in Figure 8. From high resolution spectra, atomic concentrations were calculated and are shown in Table IV.

The low concentration of carbon indicated a very silica-like film with low organic content. The high resolution Si(2p) peak, shown in Figure 6C, occurred around 103.3 eV, indicating a very silica-like oxidation state of the silicon.

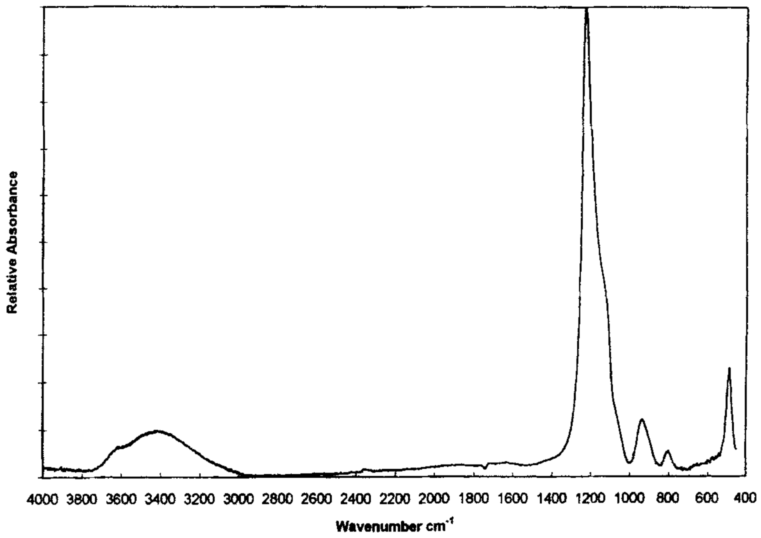

FIGURE 7 RAIR spectrum of plasma-polymerized silica-like film deposited on aluminum from HMDSO using a microwave driven plasma.

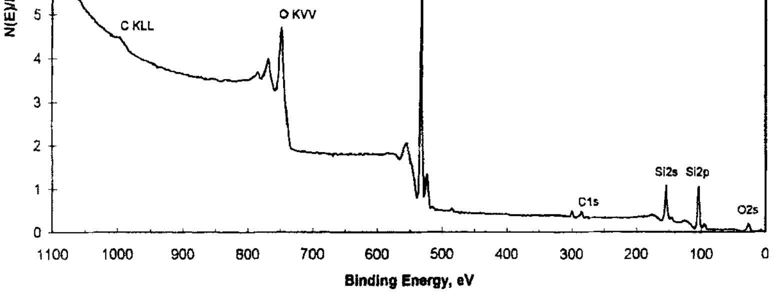

FIGURE 8 XPS survey spectrum of microwave-plasma-polymerized HMDSO.

TABLE IV Chemical Composition of Microwave-Plasma-Polymerized HMDSO Films

Element/Concentration	*Plasma-Polymerized HMDSO*
Carbon	4.6%
Oxygen	68.6%
Silicon	26.7%

Wedge Testing

1. *DC Plasma-Polymerized Primer Films*

Results from the wedge testing of adhesive joints prepared with DC-plasma-polymerized primers bonded with FM-300 are shown in Figure 9, where crack extension is shown as a function of time for the various plasma-polymerized primer coatings. These samples were categorized according to surface pre-treatments prior to plasma etching and deposition. Samples with conventional FPL and PAA surface pre-treatments were also tested to provide a comparison. These additional samples were Grit-Blasted, PAA, and FPL etched substrates bonded with FM-300 adhesive.

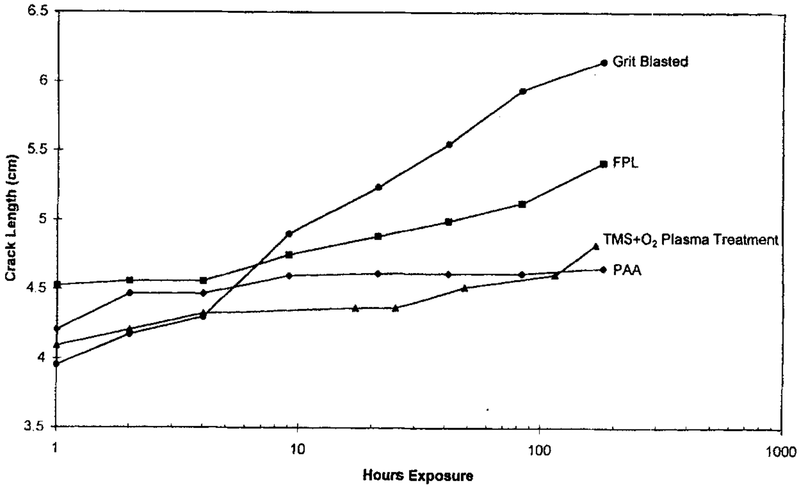

FIGURE 9 Crack growth during exposure to 95% R.H. at 60°C for aluminum wedge test specimens prepared with plasma-polymerized TMS primer films and bounded with FM-300 adhesive.

Wedge crack test specimens made with substrates coated with TMS films that had no plasma post-treatment did not perform as well as the samples that had no oxygen plasma post-treatment. Wedge test specimens made with substrates coated with plasma-polymerized TMS films that had no oxygen plasma post-treatment de-laminated easily when the wedge was initially driven into the joints. The TMS films had low surface energies due to organic constituents, and poor wettability by the adhesive was observed.

As discussed later, XPS results showed that the plasma-polymerized TMS films remained on the metal substrates after interfacial failure between the FM-300 adhesive and the primer film. The adhesive failure surfaces showed no evidence of the TMS film. Since the speciments failed without exposure to the humid environment, no hydration/corrosion products were found or expected on the failure surfaces of the aluminum substrates. Plasma-polymerized TMS films may potentially prevent hydration/corrosion but the FM-300 adhesive did not adhere well to the films. Due to poor initial adhesion, the durability of these joints was not considered and their wedge test results were not included.

The oxygen plasma post-treated TMS films promoted cohesive failure within the adhesive through the initial crack extension. The FM-300 adhesive seemed to wet these primer films very well and thus good adhesion occurred. Very small changes in crack length during the test, as seen in Figure 9, resulted in a small adhesive failure area. XPS analysis of the failure surfaces (see below) indicated that this failure occurred near the interface between the adhesive and plasma-polymerized primer film. Additionally, no corrosion products were detected at the metal/film interface.

2. *Microwave-Plasma-Polymerized Primer Films*

Wedge test results of adhesive joints prepared from substrates coated with microwave-plasma-polymerized films are shown in Figure 10. Also included in Figure 10 are results for wedge test specimens made with FPL- and PAA-treated substrates. The plasma-polymerized HMDSO primer film coated specimens exhibited good durability behavior and performed much better than the FPL-etched specimens. An initial crack length of about 4 cm was produced cohesively for all plasma processed specimens. Crack growth then proceeded in a cohesive/adhesive fashion. Investigation of adhesive failure surfaces using

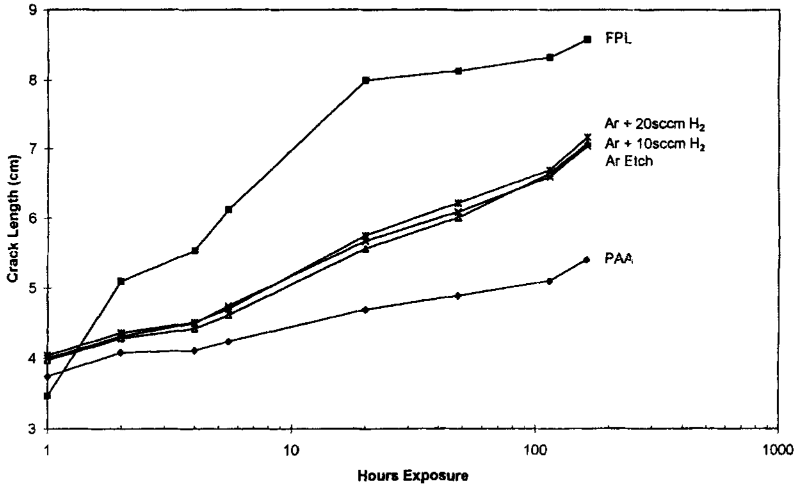

FIGURE 10 Crack growth during exposure to 95% R.H. at 60°C for aluminum wedge test specimens prepared with silica-like plasma-polymerized HMDSO primer films and bonded with FM-123-2 adhesive.

XPS, as discussed in the next section in more detail, indicated that failure occurred predominantly between the adhesive and the silica-like primer film.

No significant differences in durability resulted from various plasma pre-treatments of the aluminum substrates. Specimens that were pre-treated with argon performed in an identical fashion to the argon/hydrogen plasma pre-treatments. Effects of the plasma pre-treatments could not be observed in wedge testing as long as failure occurred predominantly between the adhesive and the primer film. Other work that we have done showed clearly the need for plasma etching of aluminum substrates before deposition of plasma-polymerized primers [11].

Failure Analysis

1. *DC-Plasma-Polymerized Primer Films with Oxygen Plasma Post-Treatment*

No aluminum hydration/corrosion products were visually observed on any of the fracture surfaces. In contrast to the films that did not have oxygen plasma post-treatment, these films showed good wettability by the adhesive across their surface. For the initial crack length, the observed failure mode was predominantly cohesive, occurring within the FM-300 adhesive. The failure that occurred during the duration of humidity exposure was mostly interfacial between the adhesive and primer film. A possible explanation for this observation is the thermodynamic instability of silica/epoxide bonds in the presence of water [12].

XPS analysis of this interfacial failure area showed that the primer film remained mostly intact on the substrate. This was shown by the presence of the strong Si(2p) peak at 102 eV in the XPS survey spectrum of the substrate failure surface (see Fig. 11A). A small amount of adhesive remained on the primer film after failure as indicated by the C(1s) peak at 284.6 eV and N(1s) peak at 401 eV.

The XPS survey spectrum of the adhesive failure surface (Fig. 11B) indicated a mostly organic character. A weak Si(2p) peak was observed, indicating that a small amount of the primer film was removed by the adhesive. Oxygen plasma etching may have cohesively weakened the TMS film, allowing the adhesive to remove a small quantity of the

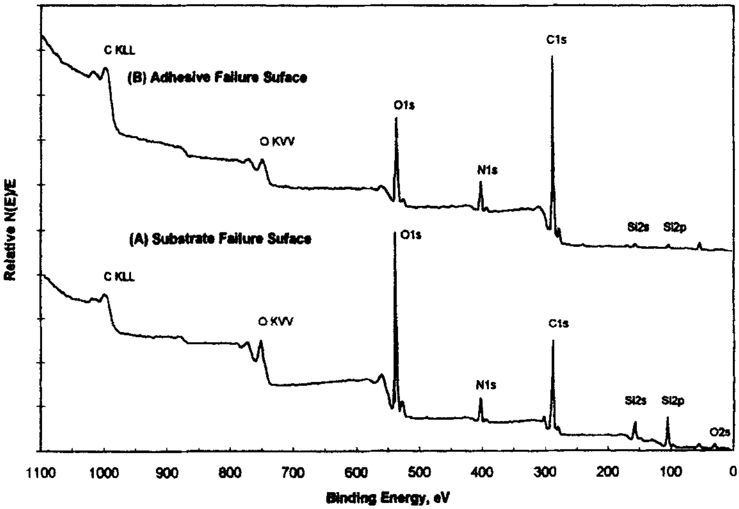

FIGURE 11 XPS survey of (A)-substrate and (B)-adhesive failure surfaces of aluminum wedge test specimens prepared with oxygen post treated TMS primer films and bonded with FM-300 adhesive.

film during fracture. This would account for the detection of silicon on the adhesive failure surface.

2. *Microwave-Plasma-Polymerized Primer Films*

Wedge test specimens prepared from substrates pretreated with plasma-polymerized HMDSO films in the microwave reactor performed well. The initial crack was cohesive within the FM-123-2 adhesive. Failure during humidity exposure was interfacial between the adhesive and the adherends. Some of the specimens had a few small spots on the metallic failure surface where hydration/corrosion products (dark gray regions) seemed to have formed. Corrosion products were not observed at the crack tips.

Three regions were analyzed using XPS: the metallic substrate surface near the crack tip that failed interfacially, the mating adhesive film surface, and the darker (corroded) regions on the substrates. The silica-like film remained on the metallic substrate surface near the crack tip, as indicated by the presence of the Si(2p) peak at 103.5 eV in the XPS survey spectrum (see Fig. 12A). A small amount of adhesive also remained on the surface of the primer film, as indicated by the C(1s) peak at 284.6 eV and N(1s) peak at 401 eV.

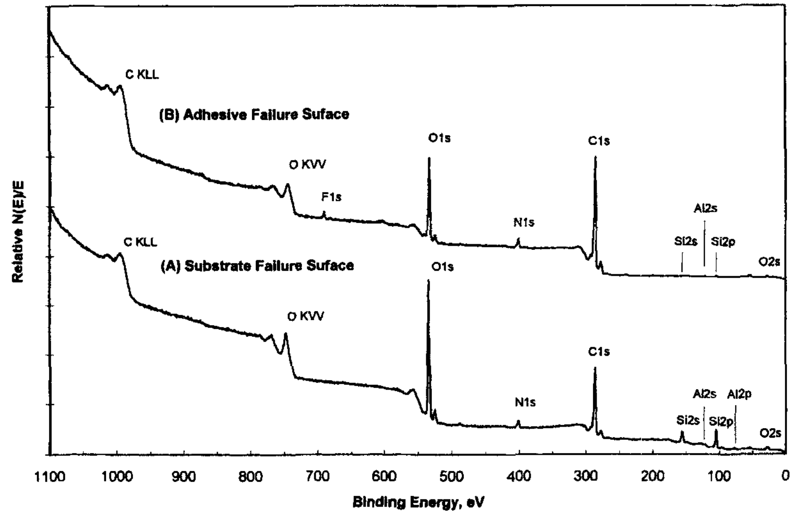

FIGURE 12 XPS survey spectra of (A)-substrate and (B)-adhesive failure surfaces near the crack tip of aluminum wedge test specimens prepared with silica-like plasma-polymerized HMDSO primer films and bonded with FM-123-2 adhesive.

The XPS survey spectrum of the mating adhesive failure surface showed little evidence of silicon (see Fig. 12B). A small amount of aluminum (~1%) was found on the adhesive failure surface near the crack tip. The presence of intact primer film on the substrate failure surface and the absence of the film on the adhesive failure surface indicated that the failure mode was adhesive between the silica-like primer film and the adhesive.

A significant amount of silicon was detected using XPS when analyzing the dark corroded regions on the metallic substrate failure surfaces, indicating that the primer film was at least partially present in these regions (see Fig. 13). Since the primer film was still present on the substrate, this corrosion likely occurred after adhesive failure and did not take an active role in the failure mode.

SEM was used to examine the three areas previously analyzed with XPS: the metallic substrate surface that failed interfacially at the crack tip, the mating adhesive surface, and a hydrated/corroded region on the metallic substrate failure surface. SEM examination of the metallic substrate failure surface showed no evidence of corrosion products and appeared similar to a freshly grit-blasted surface. The mating

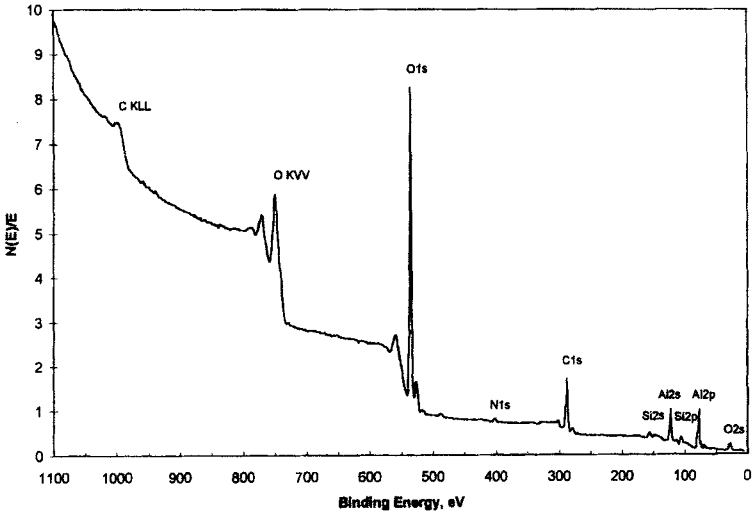

FIGURE 13 XPS survey spectrum of corroded area on failure surface of aluminum wedge test specimen prepared with silica-like plasma-polymerized HMDSO primer films and FM-123-2 adhesive.

adhesive failure surface showed no evidence of corrosion products and had a matching surface morphology of the primer-coated metal substrate. SEM examination of a darker (corroded) region on the metallic failure surface indicated the presence of hydration/corrosion products. The hydration/corrosion products were visually identified as aluminum hydroxide or pseudo-boehmite. It has not yet been determined whether these corrosion products formed with the substrate beneath the primer film or from nucleating and growing on the exposed film after interfacial failure between the adhesive and primer film.

CONCLUSION

Plasma processes provide an alternative method for pre-treatment of aluminum surfaces for adhesive bonding over wet chemical methods. Silica-like films, plasma polymerized from TMS and HMDSO, deposited after plasma etching of aluminum functioned similarly to conventional pre-treatments. These films had good cohesive strength, adhered well to aluminum substrates, were easily wetted by commercial epoxide adhesives, and were outstanding primers for structural adhesive bonding of aluminum. The structure and properties of the films dependend strongly on the processing variables. TMS films deposited using argon as the carrier gas were siloxane-like, were not wetted by typical structural adhesives, and performed poorly as primers. When these siloxane-like films were post-treated with an oxygen plasma, a silica-like surface layer was produced which was wetted by structural adhesives. Films with silica-like chemistry were deposited using HMDSO and oxygen as the carrier gas. These films had good cohesive strength, adhered well to aluminum substrates, were easily wetted by the adhesive, and were outstanding primers for structural adhesive bonding of aluminum. The durability of joints made with silica-like film coated aluminum substrates in wedge testing during exposure to 95% RH at 60°C was good in comparison with joints prepared from substrates that were PA anodized or FPL etched. This study concluded that silica-like films made by plasma polymerization worked well as adhesive primers to form strong bonds that were environmentally durable.

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