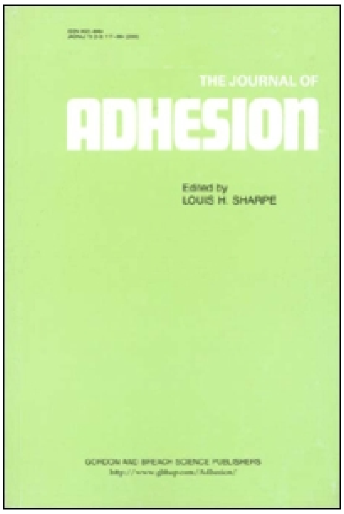

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Vapor-Phase Silanation of Plasma-Polymerized Silica-Like Films by γ-Aminopropyltriethoxysilane

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Silica-like films were deposited onto aluminum substrates by plasma polymerization of hexamethyldisiloxane (HMDSO) in the presence of oxygen using a capacitively coupled Radio-Frequency (RF)-powered plasma reactor. Two types of films, referred to as low hydroxyl and high hydroxyl, were obtained by varying parameters such as the power and the flow rates of oxygen and HMDSO. Two bands that were assigned to hydrogen-bonded silanol groups were observed in reflection–absorption infrared (RAIR) spectra of high-hydroxyl films. The first band was near 3400 cm^{-1} and was very broad; this band was assigned to the OH-stretching mode of silanol groups in which the hydrogen atom was hydrogen bonded to the oxygen atom of an adjacent silanol group. The second band was near 3650 cm^{-1} and was assigned to OH stretching in isolated silanol groups in which the hydrogen atom was hydrogen bonded to the oxygen atom of an Si–O–Si group. Only the band near 3650 cm^{-1} was observed in RAIR spectra of low-hydroxyl films. RAIR spectra of the high-hydroxyl films were characterized by a band near 934 cm^{-1} assigned to the Si–O-stretching mode of silanol groups. This band was not observed in spectra of the low-hydroxyl films. γ-Aminopropyltriethoxysilane (γ-APS) was adsorbed onto the silica-like films from the vapor phase at a substrate temperature of 100°C. Results obtained from X-ray photoelectron spectroscopy (XPS) showed that some of the nitrogen atoms in the adsorbed γ-APS films were protonated, probably by strong hydrogen bonding with silanol groups on the surface of the silica-like films. However, most of the amino groups were not protonated, indicating that adsorption in that case involved condensation of ethoxy groups with surface silanol groups. Thus, a band observed near 1100 cm^{-1}

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in RAIR spectra of γ-APS that adsorbed onto silica-like films was tentatively assigned to a vibrational mode characteristic of Si–O–Si$_{substrate}$ bonds. Lap joints were prepared using a two-part epoxy adhesive and aluminum substrates that were primed with silica-like films. Joints prepared from substrates that were primed with low-hydroxyl films had an average strength of about 23.4 MPa whereas those prepared from substrates primed with high-hydroxyl films had an average strength of about 14.3 MPa. Vapor-phase silanation of the primer films did not have a significant effect on the initial strength of the joints. However, it did have an effect on the locus of failure as determined by XPS. When no silane was used, joints prepared using substrates primed with the low-hydroxyl films failed near the adhesive–primer interface. Joints prepared using substrates primed with the low-hydroxyl films and coated with γ-APS failed cohesively, within the adhesive.

Keywords: Aminopropyltriethoxysilane; Films; Silica-like films; Lap joints; Plasma polymerization; Primers; Vapor-phase silanation; Silanes; Spectroscopy; Reflection-absorption infrared spectroscopy; X-ray photoelectron spectroscopy

INTRODUCTION

Plasma polymerization is a versatile technique for the deposition of films for a wide range of applications. The properties of the deposited films can be controlled by carefully varying the deposition parameters. Plasma-polymerized silica-like films produced from hexamethyldisiloxane (HMDSO) and oxygen have been determined to be suitable primers for the structural adhesive bonding of aluminum. The films adhere tenaciously to aluminum substrates and prevent corrosion at the adhesive–substrate interface [1–3]. In previous studies conducted by our group, it was reported that higher pressures and richer monomer content favored the formation of hydrogen-bonded hydroxyl groups throughout the film, whereas lower pressures and lesser amounts of monomer led to the formation of films with a higher number of isolated hydroxyl groups [4, 5]. The adhesion and durability of joints prepared from substrates coated with the silica-like films were found to be comparable with adhesion and durability of joints prepared using substrates that were given "conventional" pretreatments. However, analysis of the failed surfaces of lap joints showed that joints prepared from the silica-like films and an amine-cured epoxy adhesive invariably failed near the interface of the adhesive and the primer film. Therefore, we considered the use of silane coupling agents to enhance adhesion of amine-cured epoxies to the surface of silica-like films. Derivatization of the silica-like films could provide novel interaction capabilities to the silica-like films by providing ideal reactive attachment sites for adhesive bonding and could, therefore, enhance adhesive-joint-performance.

Silane coupling agents can be used for surface derivatization of silica, because they are useful in immobilizing specific chemical species onto surfaces in organized monolayer assemblies [6]. Aminofunctional silanes have the general formula $H_2N{-}R{-}Si{-}R'_3$ where R typically consists of three methylene groups and R′ is a hydrolysable group such as methoxy. When aminosilanes are used as silanating agents, the nucleophilic nitrogen can enter into hydrogen-bonding interactions with hydrogen-donating groups, such as the silanol (Si−OH) groups present on the silica surface. The adsorbed amine group can then catalyze the condensation of the groups R′ with a surface silanol, resulting in the formation of siloxane bonds with the silica surface even in the absence of water [7]. Aminosilanated surfaces are extensively used in diverse applications such as catalyst technology [8], electronic materials [9, 10], and biochemistry [11–13].

Conventionally, the silanation procedure has been carried out in either aqueous solutions or organic solvents. When silanation is carried out in solution, several problems such as irreproducibility of product, uncontrollable surface density, and nonuniformity of the deposit are encountered [6, 14]. Vapor-phase deposition of silanes on different substrates has been reported as an alternative to solution-phase silanation [9, 12–27]. Vapor-phase silanation eliminates the need to use solvents, and problems such as controlled hydrolysis, polycondensation reactions, and solvent removal and recovery can be reduced. In vapor-phase silanation of silica-like materials, direct reaction of the silane with surface hydroxyls results in the formation of siloxane bonds and reproducible monolayers can be formed on surfaces [15].

Haller [9] silanated silicon wafers by refluxing vapors of γ-APS in toluene to produce monolayer coverage of the surface with aminopropylsilyl groups. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies showed that when silanation was performed in the vapor phase, there was good monolayer coverage of closely packed particles with the absence of any particle greater than 10 nm. When the same silanation reaction was performed in the solution phase, undesirable polymeric globules with typical particle size of about 100 nm were formed because of polycondensation reactions of the alkoxysilanes.

Wikstrom *et al.* [12] deployed gas-phase silanation of epoxysilanes and γ-APS in the presence of triethylamine at temperatures between 100°C and 160°C to prepare supports used in high pressure liquid chromatography (HPLC) for protein recovery. The silica was spread in a glass container at the bottom of an alumina reactor and dried for 1 h at 100–160°C under vacuum (the pressure was <2 mm Hg). A syringe was used to inject the aminosilane through an airtight membrane at the top of the reactor and silanation was carried out for 1 h at 160°C. After silanation, the silica was removed from the reactor and the remaining alkoxy groups were hydrolyzed at 90°C for 15 min. The silica was rinsed with acetone and placed back into the reactor and the procedure was repeated until the desired surface coverage of functional groups was achieved. Wikstrom *et al.* concluded that when silanation was performed by the gas-phase technique, chromatographic supports gave a significantly improved performance when compared with the supports that were prepared when the silanation procedure was carried out in organic solvents or in aqueous solutions.

Basuik and Chuiko [13] synthesized acylamide stationary phases for HPLC by successive gas-phase modification of silica gel with γ-APS and benzoyl chloride at temperatures between 150°C and 170°C. They used a simple reactor with an attached stopcock to carry out the silanation procedure. Silica gel was placed on the bottom of the reactor and evacuated for 1 h at 150°C. After cooling the silica to room temperature, the reactor was disconnected from the vacuum system and a tube containing γ-APS was placed in it. After evacuation of the system, the bottom zone of the reactor, which had the reagents, was heated for 1 h at 150–170°C for the silanation reaction to take place. Excess silane was removed by evacuation at the modification temperature. Derivatization of the aminosilane-modified surface by benzoyl chloride was performed similarly at a temperature of 170°C for 0.5 h. Bands related to amide groups were observed at 1655–1670 cm^{-1} and 1550–1570 cm^{-1} in fourier-transform infrared (FTIR) spectra of the derivatized γ-APS, thus confirming that the amino groups had reacted with benzoyl chloride.

Kurth and Bein [16] investigated the reactivity of immobilized functional groups in thin layers of vapor-deposited γ-APS on oxidized, flat aluminum substrates by the quartz-crystal microbalance technique (QCM). They concluded that reproducible formation of thin films was possible by the vapor adsorption of silane coupling agents at room temperature and reported successful immobilization of the enzyme pepsin on monomolecular layers of γ-APS. Kurth and Bein used FTIR to confirm the formation of γ-APS monolayers that have thicknesses of 0.5–0.7 nm on oxidized aluminum. They observed bands resulting from free and associated NH_2 groups at 1609 and 1582 cm^{-1}, respectively. Bands related to CH stretching in CH_3 and CH_2 groups were observed at 2970 and 2926 cm^{-1} whereas bands resulting from deformation modes were observed at 1390 and 1455 cm^{-1}. They attributed bands at 1118 and 1264 cm^{-1} to $-\text{Si}-\text{O}-\text{C}$ and $\text{Si}-\text{O}-\text{Si}$ bonds, respectively.

Very recently, Satu Ek *et al.* [15] examined the modification of porous silica by aminosilanes under an inert atmosphere by a gas-phase technique called atomic-layer deposition or atomic-layer epitaxy (ALE) [28]. They reported that the surface density of aminosilanes on silica was directly dependent on the number of isolated silanol groups but was independent of the total number of silanol groups of silica. Ek, *et al.,* Satu *et al.* performed diffuse reflectance FTIR spectroscopy (DRIFTS) to study the reaction of aminosilanes with silica that had been heat-treated at 200–800°C. They observed the disappearance of the strong O−H band of free silanols at 3748–3740 cm^{-1} but observed no changes in the intensity of the broad bands resulting from hydrogen-bonded silanols in the region of 3550–3500 cm^{-1}, indicating that no reaction of the aminosilane molecules with the vicinal OH groups had taken place. They concluded that all isolated silanol groups reacted with the aminosilanes until the surface was saturated.

Schick and Sun [23] used XPS and FTIR to investigate the immobilization reaction of benzenesulfonyl chloride (BSC) on porous silica surfaces that had been derivatized by γ-aminopropyltrimethoxysilane (γ-APS) in the vapor phase. They observed bands at 3298, 3367, and 3176 cm^{-1} in the FTIR spectra after silica was modified with the aminosilane and attributed them to amino groups. Upon subsequent reaction with BSC, the bands associated with the NH_2 stretching modes collapsed to a single broad band at 3282 cm^{-1}, indicating the formation of an amide. The appearance of a peak resulting from N(1 s) electrons in the XPS survey spectrum of the aminosilane-modified silica confirmed the presence of silane adsorption. Components were observed at 398.8 and 401.0 eV in high-resolution N(1s) spectra, indicating formation of free and protonated primary amine groups. Upon reaction of the modified silica with BSC, an additional component at 399.9 eV appeared, suggesting the formation of an amide.

In this article, we discuss the use of γ-APS for the vapor-phase silanation of plasma-polymerized, silica-like films. Two different types of plasma-polymerized silica-like films were deposited onto aluminum substrates in a RF-powered plasma reactor using hexamethyldisiloxane (HMDSO) as the "monomer" and oxygen as a coreactant. High-hydroxyl and low-hydroxyl films were obtained by varying the relative flow rates of HMDSO and O_2. The silica-like films were silanated by γ-APS in the vapor phase at a substrate temperature of 100°C. XPS and RAIR were used to characterize the silica-like films before and after derivatization with γ-APS. Lap joints were prepared using a two-part epoxy adhesive and aluminum substrates coated with silica-like films or silica-like films that were derivatized with γ-APS. The initial strength and the locus of failure of the joints were determined so that the effect of vapor-phase derivatization of the silica-like films with γ-APS could be evaluated. In a subsequent article, we will discuss the effect of vapor-phase silanation on the durability of lap joints that were prepared using a two-part epoxy adhesive and aluminum substrates that were coated with silica-like films or silica-like films that were derivatized with γ-APS.

EXPERIMENTAL

HMDSO and γ-APS were obtained from Sigma-Aldrich (Milwaukee, WI, USA) and used without further purification. Oxygen, which was used as a carrier gas in the plasma-polymerization process, was obtained from Matheson Gas Products (Secaucus, NJ, USA). Araldite AV-3131, a one-component epoxy adhesive containing the curing agent dicyandiamide (DDA) was obtained from Ciba-Geigy (Basel, Switzerland). A two-component adhesive consisting of epoxy resin (Epon® 828) and a polyamide–amine curing agent (EPI-cure® 3140) was obtained from Shell Chemicals (Houston, TX, USA). Aluminum sheets (2024-T3 alloy) with a thickness of 1.6 mm were obtained from Alcoa (Pittsburgh, PA, USA). Distilled water was obtained from Pharmco Products Inc. (Brookfield, CT, USA) and toluene was obtained from Fisher Chemicals (Fairlawn, NJ, USA).

Aluminum substrates (101.6 mm × 25.4 mm × 1.6 mm) were cleaned with acetone and then etched for 10 min in an O_2 plasma using a capacitively coupled, RF-powered (13.6 MHz) reactor. The upper electrode was powered and was located 3.0 cm above the lower electrode, which was grounded to the case of the reactor. Substrates were placed on an aluminum sheet that was fitted with a cartridge heater for temperature control and placed on the lower electrode. During plasma etching, the pressure was 0.1 Torr, power was 150 W, and flow rate was 40 sccm (see Table 1).

TABLE 1 Reaction Parameters Used for Oxygen-Plasma Etching and for Plasma Polymerization of Silica-Like Films on Aluminum and Ferrotype Plate Substrates

Reaction parameter	Oxygen-plasma etching	High-hydroxyl silica-like films	Low-hydroxyl silica-like films
Time (min)	10	5–7	35–45
RF power (watt)	150	150	150
Total mass flow rate (Sccm)	40	100	40
Percent oxygen flow rate	100	95	98
Percent monomer flow rate	0	5	2
Reactor pressure (Torr)	0.150	0.50	0.150

After plasma etching, plasma-polymerized silica-like films were deposited onto the aluminum substrates using HMDSO as the monomer and oxygen as a coreactant. Films containing relatively low concentrations of hydroxyl groups were deposited using a pressure of 0.15 Torr, power of 150 W, oxygen flow rate of 39.2 sccm, HMDSO flow rate of 0.8 sccm, and time of 35 min. Films with relatively high hydroxyl content were deposited for 7 min using a pressure of 0.50 Torr, power of 150 W, oxygen flow rate of 95.0 sccm, and HMDSO flow rate of 5.0 sccm (see Table 1). Substrates were again placed on the aluminum sheet on the lower electrode.

In some cases, films were simultaneously deposited on ferrotype substrates placed next to the aluminum substrates so that ellipsometry, infrared spectroscopy, and X-ray photoelectron spectroscopy of the films on ferroplate could be carried out. Ferrotype is steel sheet plated with chromium; it is available commercially through outlets for photographic supplies. The surface of ferroplate is smooth and highly reflective, making it a nearly ideal substrate for ellipsometry and reflection–absorption infrared (RAIR) spectroscopy. Ferrotype substrates were prepared by rinsing in acetone and then being passed through the flame of a Bunsen burner several times.

After film deposition, the reactor chamber was pumped down to the base pressure of 0.035 Torr and a current was applied to the cartridge heater to increase the temperature of the aluminum plate that supported the sample substrates. The current was controlled using a rheostat that was connected to the cartridge heater through a flange equipped with electrical feedthroughs. A J-type thermocouple was used to measure the temperature of the plate. After about 90 min, the valve of the cylinder containing γ-APS was slowly opened and the reactor was backfilled with the vapors of the silane. The valve between the vacuum chamber and the pump was closed and the pressure was allowed to increase until it reached 0.1 Torr; the chamber was held at that pressure for 45 min for the silanation reaction to take place. After 45 min, the reactor chamber was brought up to atmospheric pressure and the silanated substrates were removed.

The reaction of an epoxy resin with the silanated silica-like films was also investigated. In these experiments, an aluminum substrate was coated with a low-hydroxyl silica-like film and the film was silanated with γ-APS in the vapor phase (see previous). After analysis of the silanated silica-like film by XPS, the substrate was immersed in a beaker containing Epon 828 epoxy resin and the beaker was placed into a vacuum oven at 100°C under a nitrogen atmosphere. After one h, the beaker was removed from the vacuum oven and allowed to cool to room temperature. The aluminum substrate was removed from the beaker, thoroughly rinsed with toluene to remove any unreacted epoxy, and then examined again using XPS.

A Perkin-Elmer Model 5300 X-ray Photoelectron Spectrometer (Perkin-Elmer, Eden Prairie, MN, USA) was used to characterize the surface composition of the silica-like primer films. MgKα radiation (1253.6 eV) was used to excite the spectra; the X-ray source was operated at 15 KV and 300 W. Most XPS spectra were acquired using a take-off angle of 45 deg but a take-off angle of 15 deg was sometimes used to increase the surface sensitivity of the XPS investigations. Survey spectra were taken between binding energies of 0 and 1100 eV

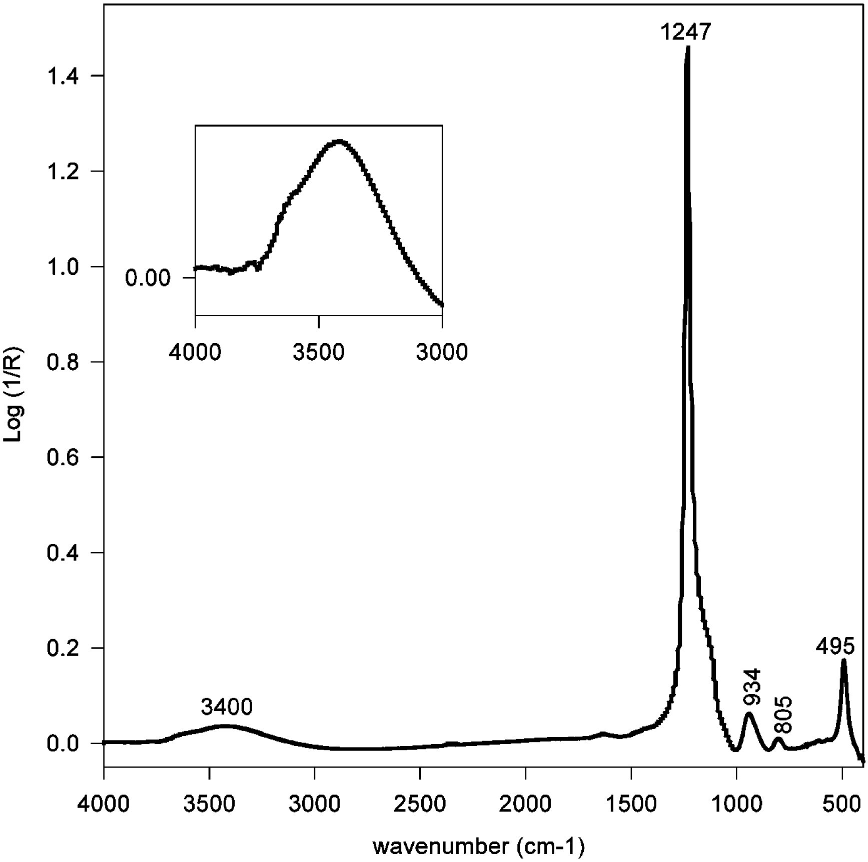

FIGURE 1 The RAIR spectrum of a high-hydroxyl silica-like primer film that was deposited onto a ferroplate substrate during 5 min in the RF reactor. Oxygen was used as a coreactant.

using a pass energy of 89.45 eV. High-resolution XPS spectra were obtained using a pass energy of 35.75 eV. All spectra were corrected for charging by referencing the C(1s) peak to a value of 284.6 eV.

Reflection–absorption infrared (RAIR) spectra were obtained from plasma-polymerized silica-like films deposited onto polished aluminum substrates using a Nicolet Magna 760 Fourier-Transform Infrared Spectrometer (Nicolet Instrument Corp., Madison, WI, USA). Spectra were acquired using a Nicolet FTS-85 accessory, which provided one reflection from the sample at an angle of approximately 82 deg from the perpendicular to the sample surface. The spectra were

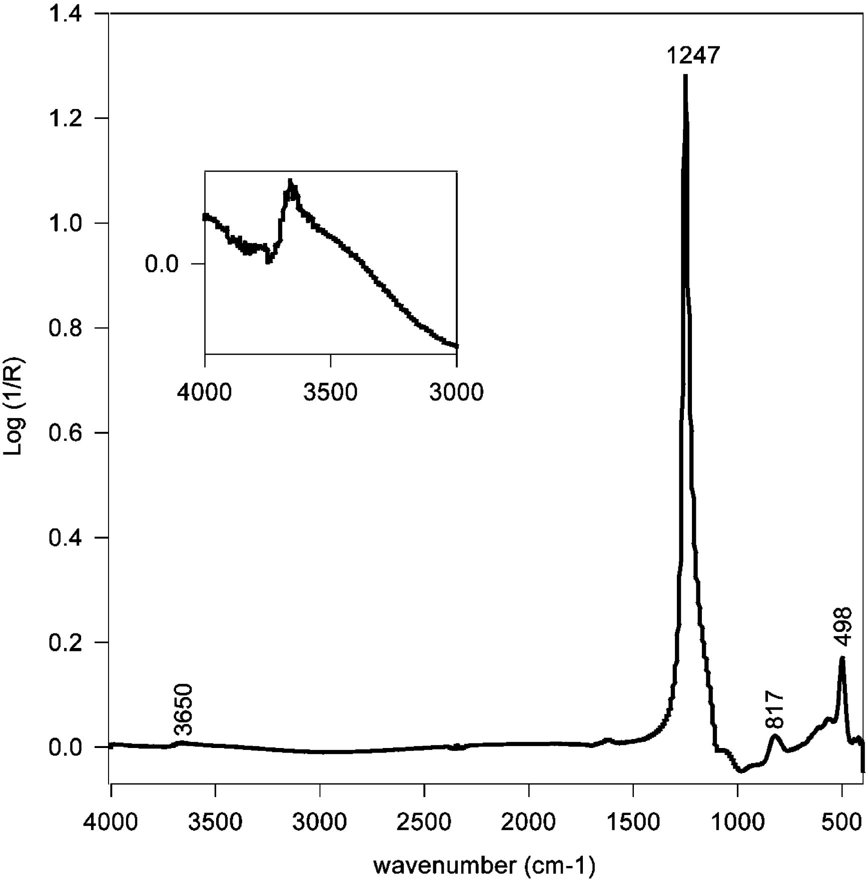

FIGURE 2 The RAIR spectrum of a low-hydroxyl silica-like primer film that was deposited onto a ferroplate substrate during 45 min in the RF reactor. Oxygen was used as a coreactant.

collected by averaging 512 scans at a resolution of 4 cm^{-1}. Spectra of polished but uncoated aluminum substrates were subtracted from spectra of coated substrates to obtain the spectra of the films.

Plasma-polymerized silica-like films were deposited on polished aluminum substrates and analyzed using a variable-angle, spectroscopic ellipsometer supplied by J. A. Woollam Co., Inc. (Lincoln, NE, USA). Data were collected through angles of incidence of 60 to 75 deg in increments of 5 deg and wavelengths of 300–1000 nm in increments

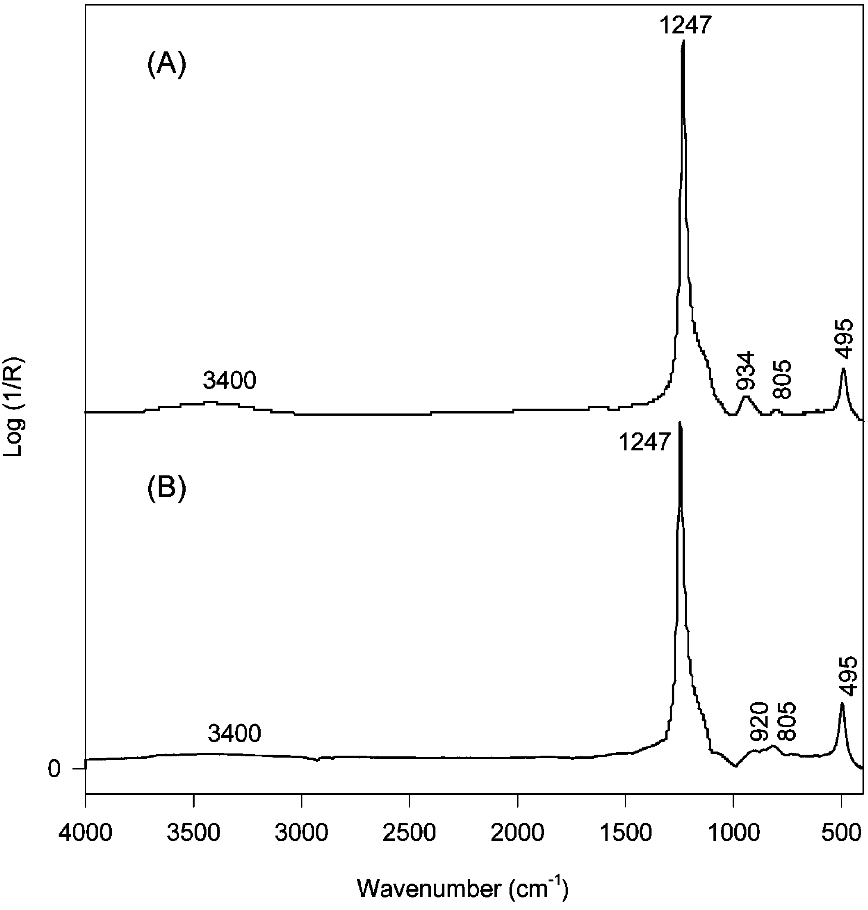

FIGURE 3 The RAIR spectra of a high-hydroxyl silica-like film that was deposited on a polished aluminum substrate during 5 min in the RF reactor: (a) before and (b) after vapor-phase silanation with γ-APS for 45 min at a substrate temperature of 100°C.

of 10 nm. A Cauchy model was used to determine the thickness and refractive index of the films.

Aluminum substrates (101.6 mm × 25.4 mm and 1.6 mm) were used to make lap joints in accordance with the American Society for Testing Materials (ASTM) standard D1002. Two adhesives were used for construction of the lap joints. The first was a commercial, one-part, dicyandiamide-cured epoxy whereas the second was a two-part adhesive formulated using a ratio of 100:150 by weight of Epon 828 epoxy resin and Epicure 3147 polyamide–amine curing agent. Lap joints made with the one-part and two-part epoxies were cured overnight at room temperature and then post-cured in an oven at 175°C for 30 min and 100°C for 1 h, respectively. In some cases, the aluminum

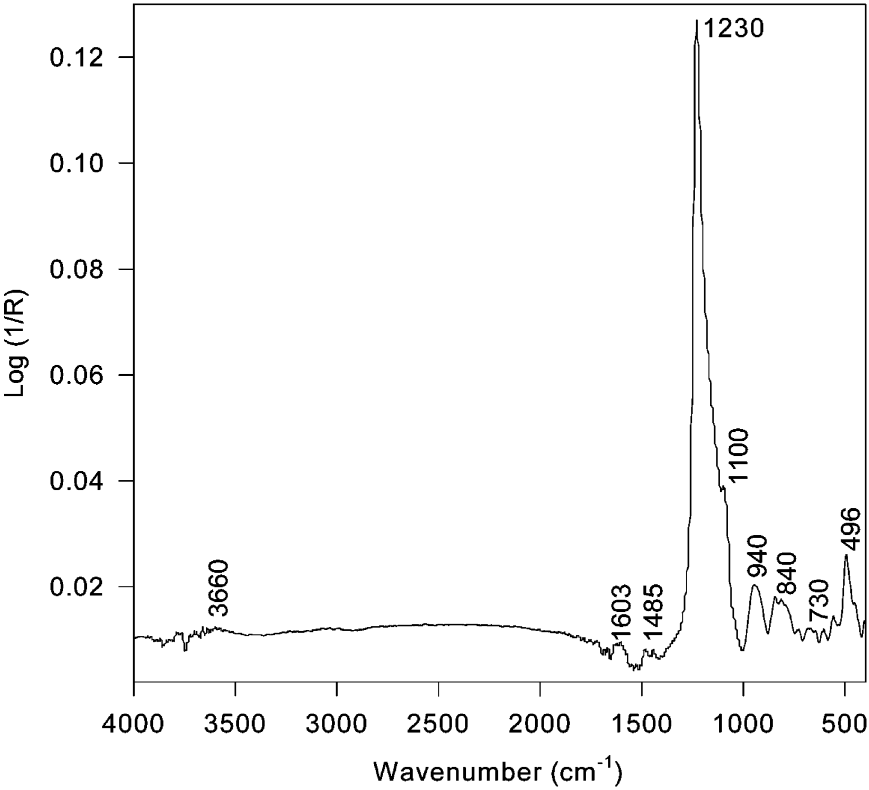

FIGURE 4 The RAIR spectrum of a low-hydroxyl silica-like film that was deposited on a polished aluminum substrate during 3 min in the RF reactor and then silanated by γ-APS in the vapor phase for 90 min at a substrate temperature of 100°C.

substrates were coated with thin films of plasma-polymerized silica-like films before bonding. In other cases, the substrates were coated with silica-like films and then coated with γ-APS adsorbed from the vapor phase as described above. The lap joints were pulled to failure on an Instron operating with a speed of 5.08 mm/min to determine their initial strength. The failure surfaces of selected lap joints were analyzed by XPS.

RESULTS AND DISCUSSION

The thickness and refractive indices of the silica-like films deposited onto ferrotype substrates were determined by ellipsometry. Low-hydroxyl films deposited during 45 min had an average thickness of about 75 nm whereas high-hydroxyl films deposited during 7 min had an average thickness of approximately 100 nm. The refractive index for the low-hydroxyl silica-like films was 1.47 at 300 nm and 1.42 at 600 nm. For the high-hydroxyl films, the refractive indices were 1.47 and 1.43 at 300 nm and 600 nm, respectively. These values are very similar to that for thermally grown silicon dioxide, which has been reported as 1.46 at 632.8 nm [29].

The RAIR spectrum of a high-hydroxyl silica-like film that was deposited onto a ferroplate substrate during 5 min using the parameters shown in Table 1 is shown in Figure 1. Two bands related to stretching modes of silanol groups were observed. One of these bands was broad but was centered at about 3400 cm^{-1} and was attributed to O–H stretching of adjacent silanol groups where the hydrogen atom of one was hydrogen bonded to the oxygen atom of the other. The second band was near 3650 cm^{-1} and was assigned to OH stretching in isolated silanol groups in which the hydrogen atom was hydrogen bonded to the oxygen atom of an Si–O–Si group. The strong band at 1247 cm^{-1} was assigned to the longitudinal optical (LO) asymmetric stretching mode of Si–O–Si linkages. The band at 934 cm^{-1} was attributed to the Si–O stretching in silanol groups whereas the bands near 805 and 495 cm^{-1} were attributed to LO rocking and bending vibrations of the Si–O–Si groups, respectively [1, 30].

The RAIR spectrum of a low-hydroxyl film that was deposited onto a ferroplate substrate during 45 min using the reaction parameters shown in Table 1 is shown in Figure 2. These films were characterized by weak bands near 3650 and 3400 cm^{-1} that were attributed to O–H-stretching modes of adjacent and isolated silanol groups, respectively. A very strong band near 1247 cm^{-1} was related to the LO-asymmetrical-stretching mode of Si–O–Si groups. Bands resulting from Si–O–Si rocking and bending vibrations were observed at 800 and 494 cm^{-1}, respectively [1, 30].

RAIR spectra of a high-hydroxyl silica-like film before and after silanation with γ-APS for 45 min at 100°C are shown Figure 3. Bands related to the OH-stretching modes of hydrogen-bonded silanol groups at 3400 and 3650 cm^{-1} and Si–O stretching in silanols at 934 cm^{-1} were reduced in intensity after reaction of γ-APS with the silica-like film. This reduction in intensity of bands resulting from the silanol groups could result from reaction of ethoxy groups on γ-APS molecules with surface silanol groups. However, it could also result from condensation of surface silanol groups when the silica-like films were heated to 100°C during the silanation reaction. Taylor and Boerio [1] investigated the effect of annealing plasma-polymerized silica-like films

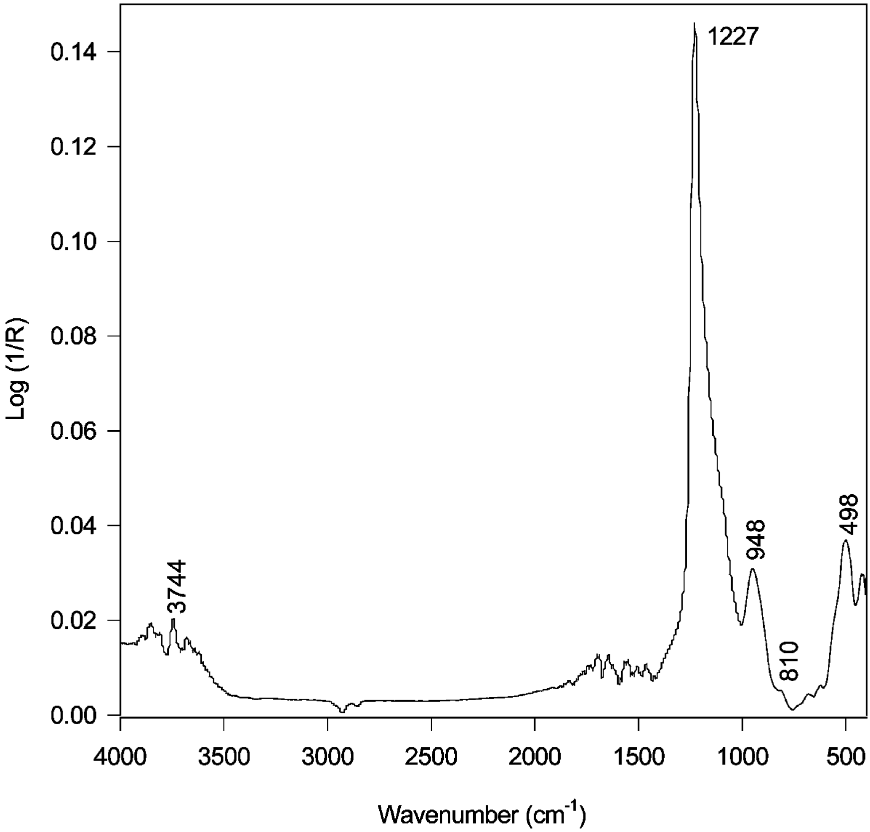

FIGURE 5 The RAIR spectrum of a low-hydroxyl silica-like film that was deposited on a polished aluminum substrate during 3 min in the RF reactor and then heated at a temperature of 100°C for 150 min.

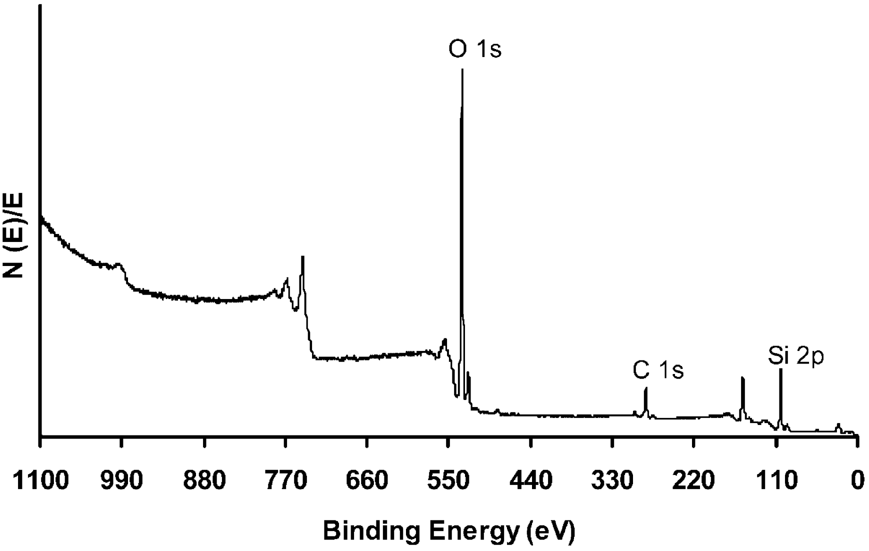

FIGURE 6 The XPS-survey spectrum of a low-hydroxyl silica-like primer film that was deposited onto a polished aluminum substrate during 45 min in the RF reactor. The electron take-off angle was 15 deg.

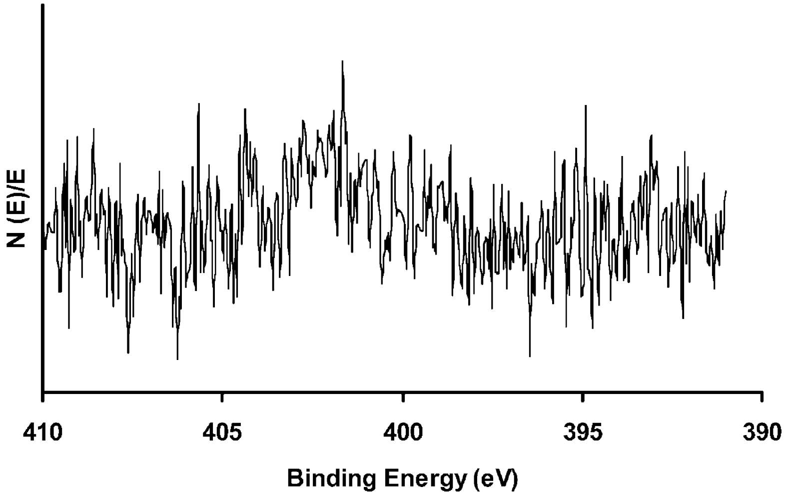

FIGURE 7 The high-resolution N(1 s) XPS spectrum of a low-hydroxyl silica-like primer film that was deposited onto a polished aluminum substrate during 45 min in the RF reactor. The electron take-off angle was 15 deg.

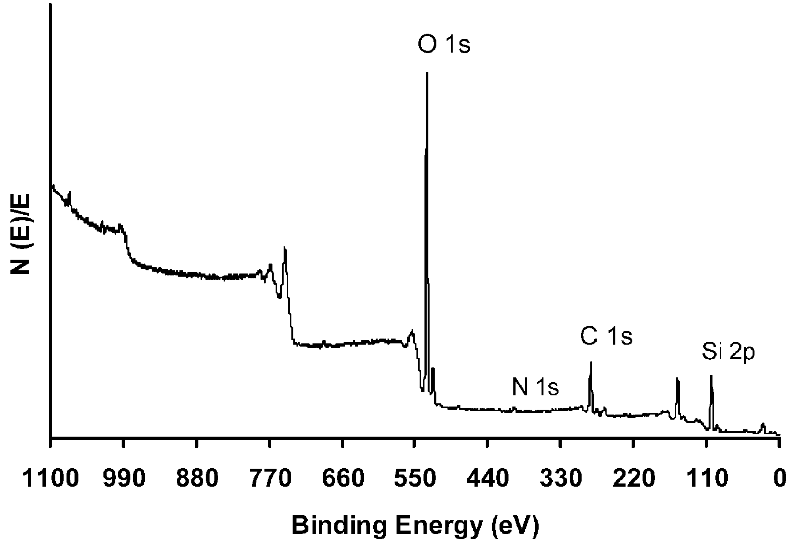

FIGURE 8 The XPS-survey spectrum of a low-hydroxyl silica-like primer film that was deposited onto a polished aluminum substrate during 45 min in the RF reactor and then silanated by γ-APS in the vapor phase for 45 min at a substrate temperature of 100°C. The electron take-off angle was 15 deg.

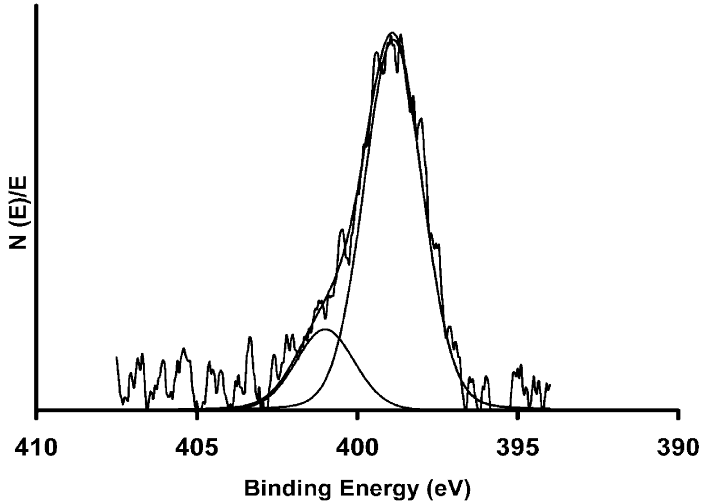

FIGURE 9 The high-resolution N(1s) XPS spectrum of a low-hydroxyl silica-like primer film that was deposited onto a polished aluminum substrate during 45 min in the RF reactor and then silanated by γ-APS in the vapor phase for 45 min at a substrate temperature of 100°C. The electron take-off angle was 15 deg.

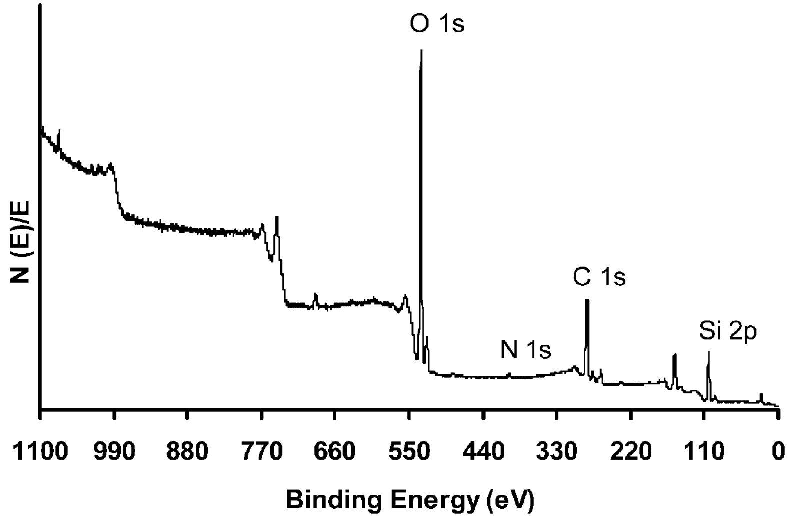

FIGURE 10 The XPS-survey spectrum of a low-hydroxyl silica-like primer film that was deposited onto a polished aluminum substrate during 45 min in the RF reactor, silanated by γ-APS in the vapor phase for 45 min at a substrate temperature of 100°C, and rinsed thoroughly with toluene. The electron take-off angle was 15 deg.

deposited on polished aluminum substrates by RAIR and observed a decrease in the peak intensities related to the silanol groups on annealing the films at 180°C for 30 min. They concluded that the decrease in the concentration of the silanol groups in the silica-like films was due to the thermally activated condensation of adjacent silanol groups to form Si—O—Si linkages and release water. Another interesting aspect of the spectra shown in Figure 3 was that no peaks pertaining to γ-APS were observed despite XPS results (see following discussion) showing that the silane was adsorbed. The likely reason for the failure to observe bands resulting from the silane after adsorption of γ-APS was that the thickness of the adsorbed silane layer (10–30 Å) was very small in comparison with the thickness of the silica-like film (700–1000 Å) and that the weak absorption bands of the silane were buried under the relatively strong absorption bands of the silica-like films.

To investigate the reaction between γ-APS and silica-like films by RAIR, a silica-like film with a thickness of approximately 60 Å was deposited onto a polished aluminum substrate and silanated by γ-APS for 90 min at 100°C. As expected, the RAIR spectrum of the silanated silica-like film showed a strong band at 1230 cm^{-1} and a weaker

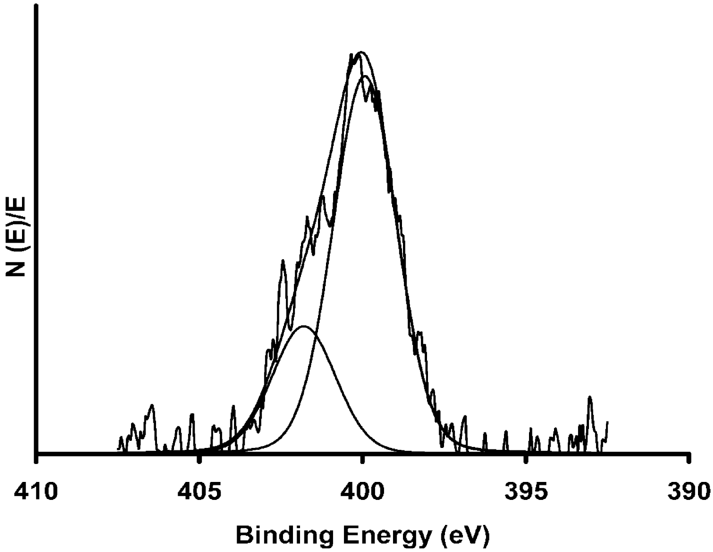

FIGURE 11 The high-resolution N(1s) XPS spectrum of a low-hydroxyl silica-like primer film that was deposited onto a polished aluminum substrate during 45 min in the RF reactor, silanated by γ-APS in the vapor phase for 45 min at a substrate temperature of 100°C, and rinsed thoroughly with toluene. The electron take-off angle was 15 deg.

band at 498 cm^{-1} that were due to longitudinal optical (LO) modes of Si–O–Si linkages in the silica-like films (see Figure 4). A medium-intensity band was observed at 940 cm^{-1}; this band was possibly related to Si–O stretching of silanol groups. However, the intensity of this band was greater than expected, considering the weakness of the bands associated with the OH-stretching modes of the silanol groups. As a result, the band at 940 cm^{-1} was more reasonably assigned to a vibrational mode of the oxide on the aluminum substrate. Medium-intensity bands were observed at 813 and 840 cm^{-1} and were attributed to the adsorbed γ-APS. A shoulder was observed at 1100 cm^{-1} that was also attributed to the aminosilane. Other investigators have attributed bands near 1100 cm^{-1} to vibrational modes associated with covalent bonds between silanes and inorganic substrates. For example, Underhill *et al.* attributed a band near 1050 cm^{-1} to $\mathrm{Si{-}O{-}Al_{substrate}}$ bonds between γ-glycidoxypropyltrimethoxysilane and the oxidized surface of aluminum [31]. White and Tripp investigated the adsorption of (3-aminopropyl)-dimethylethoxysilane from the gas phase onto silica surfaces and assigned a band near 1080 cm^{-1} to a vibrational mode of $\mathrm{Si{-}O{-}Si_{substrate}}$ groups [32].

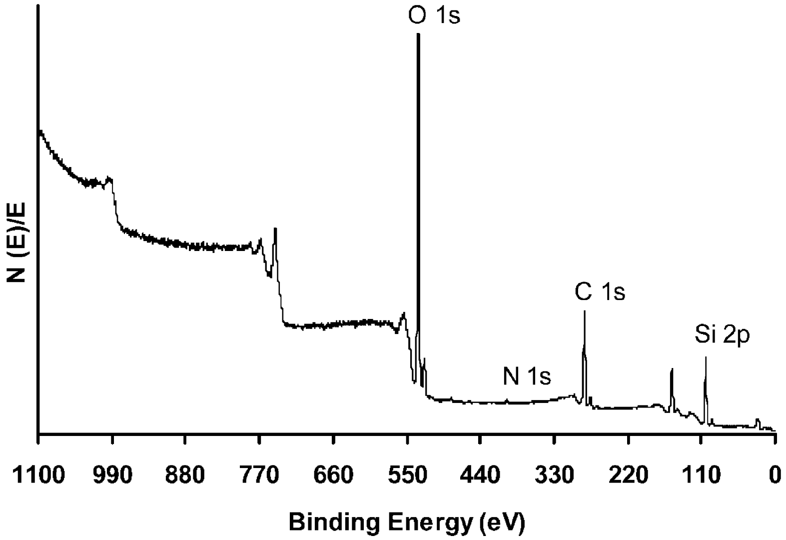

FIGURE 12 XPS-survey spectrum at a 15-deg take-off angle of a 45-min, low-hydroxyl silica-like film deposited on an aluminum substrate. The film was silanated by γ-APS for 45 min at 100°C and rinsed thoroughly with toluene prior to XPS examination.

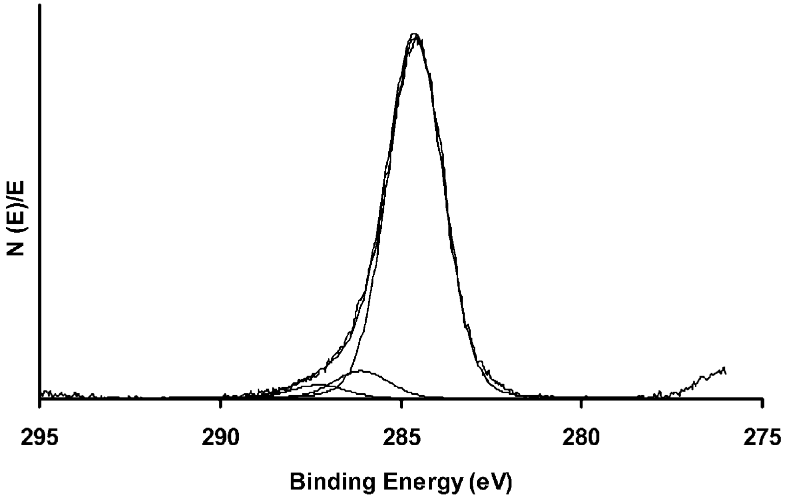

FIGURE 13 High-resolution C(1s) curve fit at a 15-deg take-off angle of a 45-min, low-hydroxyl silica-like film deposited on an aluminum substrate. The film was silanated by γ-APS for 45 min at 100°C and rinsed thoroughly with toluene prior to XPS examination.

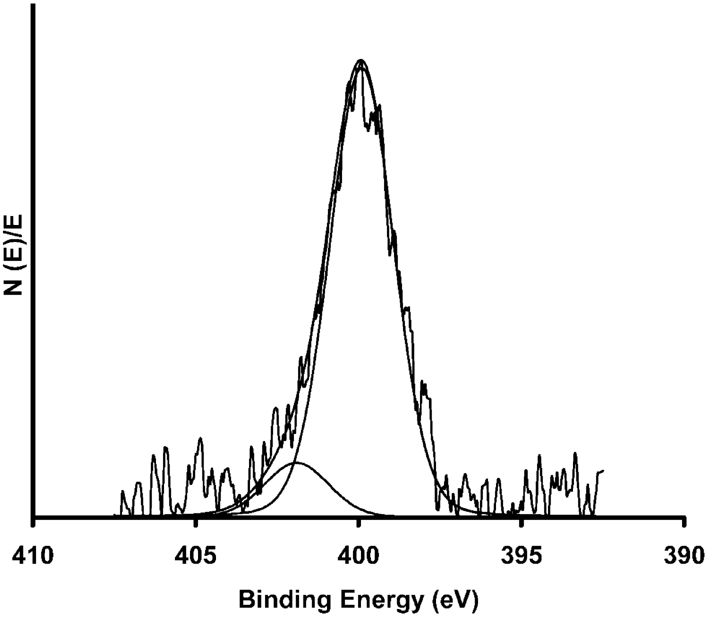

FIGURE 14 High-resolution N(1s) curve fit at a 15-deg take-off angle of a 45-min, low-hydroxyl silica-like film deposited on an aluminum substrate. The film was silanated by γ-APS for 45 min at 100°C and rinsed thoroughly with toluene prior to XPS examination.

A similar assignment of the band near 1100 cm^{-1} to a mode of Si–O–Si$_{\text{substrate}}$ groups was, therefore, tentatively made here. However, additional work will be needed to confirm that assignment because the band near 1100 cm^{-1} could also be related to siloxane groups.

The possibility still existed that the bands near 813, 840, and 1100 cm^{-1} were related to the silica-like films. Therefore, another silica-like film with a thickness of approximately 60 Å was deposited onto a polished aluminum substrate and heated at 100°C for 90 min to simulate the process of adsorbing γ-APS from the vapor phase. The RAIR spectrum of this film was characterized by a strong band near 1227 cm^{-1} and by medium-intensity bands near 948 and 498 cm^{-1} that were related to the silica-like films (see Figure 5). However, the bands near 1100, 840, and 813 cm^{-1} were not seen, supporting their assignment to adsorbed γ-APS.

Figure 6 shows the XPS-survey spectrum of a low-hydroxyl silica-like film that was deposited onto a polished aluminum substrate

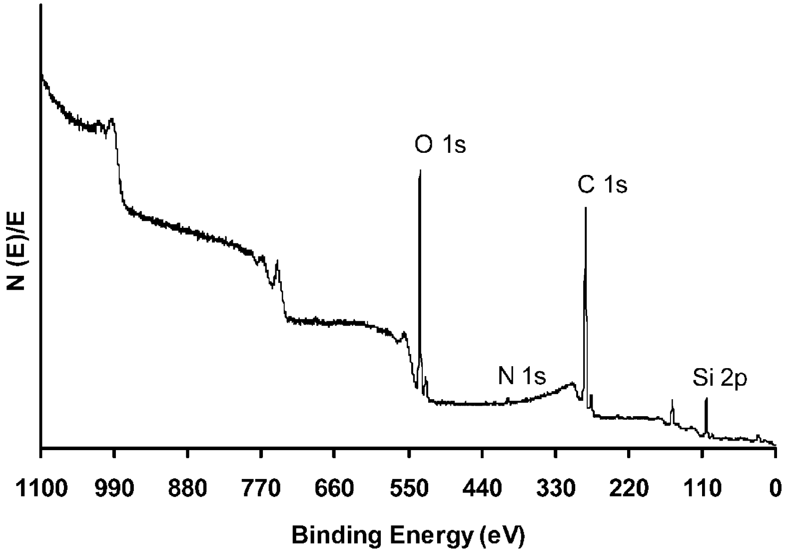

FIGURE 15 XPS-survey spectrum at a 15-deg take-off angle of a 45-min, low-hydroxyl silica-like film deposited on an aluminum substrate and silanated by γ-APS for 45 min. The film was reacted with Epon 828 epoxy resin in a vacuum oven under a nitrogen atmosphere at 100°C for 1 h and then rinsed thoroughly with toluene prior to XPS examination.

during 45 min; a take-off angle of 15 deg was used to obtain the spectrum. As expected, peaks related to oxygen, carbon, and silicon were observed. No peaks characteristic of nitrogen were observed in the survey spectrum. However, a very weak peak related to nitrogen was observed in the high-resolution N(1s) spectrum (Figure 7). This weak peak was probably related to residual γ-APS adsorbed onto the reactor walls. The XPS-survey spectrum obtained from a low-hydroxyl silica-like film that was silanated for 45 min at a substrate temperature of 100°C is shown in Figure 8; the spectrum shown in Figure 8 was obtained using an electron take-off angle of 15 deg. A small peak related to N(1s) electrons was observed near 400 eV, indicating the likely presence of the silane on the surface of the silica-like film. The high-resolution N(1s) spectrum obtained from the same sample is shown in Figure 9. Two components were observed in the N(1s) high-resolution spectrum, near 398.8 and 401.0 eV, and assigned to free and protonated primary amines, respectively. Schick and Sun [23] reported similar results for silica powders silanated with aminopropyltrimethoxysilane. The presence of the protonated amines on the

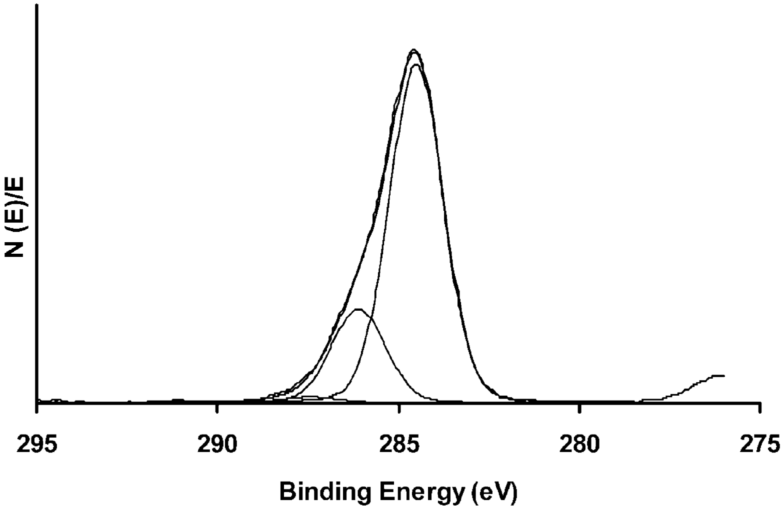

FIGURE 16 High-resolution C(1s) curve fit at a 15-deg take-off angle of a 45-min, low-hydroxyl silica-like film deposited on an aluminum substrate and silanated by γ-APS for 45 min. The film was reacted with Epon 828 epoxy resin in a vacuum oven under a nitrogen atmosphere at 100°C for 1 h and then rinsed thoroughly with toluene prior to XPS examination.

surface indicated that some silane molecules were adsorbed through the amino groups as reported by Horner *et al.* [33]. However, the observation of the much more intense peak near 398.8 eV showed that most γ-APS molecules were adsorbed by condensation of ethoxy groups with silanol groups on the silica-like films or, perhaps, by hydrogen bonding between the amine groups and surface silanols.

The sample used to obtain the spectra shown in Figures 8 and 9 was vigorously rinsed with toluene to determine if any of the γ-APS was physisorbed. However, the survey spectrum and the high-resolution N(1s) spectrum after rinsing were similar to those obtained before rinsing, indicating that the aminosilane was strongly adsorbed onto the silica-like film (see Figures 10 and 11).

The silanated silica-like films are intended to serve as primers for structural bonding of aluminum with epoxy adhesives. Therefore, we investigated the reactivity of the silanated surfaces with a typical epoxy compound. The XPS survey spectrum and the C(1s) and N (1 s) high-resolution XPS spectra obtained from a silica-like film that was silanated in the vapor phase and rinsed with toluene are shown in Figures 12, 13, and 14, respectively. The spectra obtained from the silanated film after it was reacted with the epoxy under nitrogen

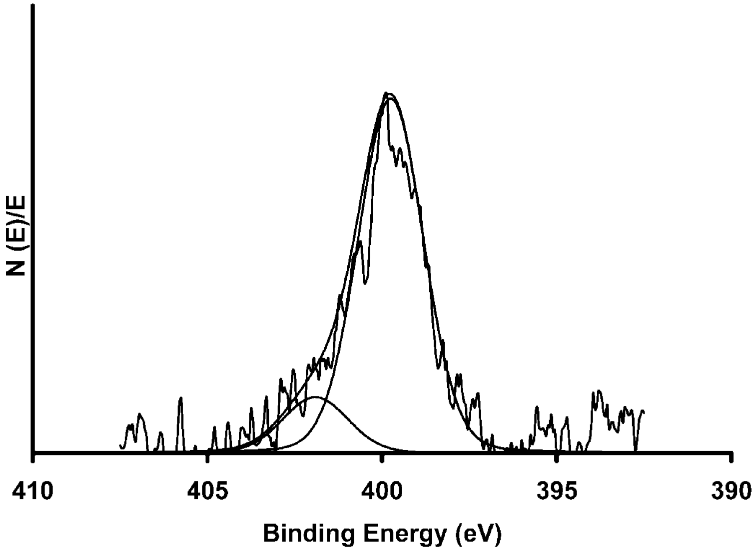

FIGURE 17 High-resolution N(1s) curve fit at a 15-deg take-off angle of a 45-min, low-hydroxyl silica-like film deposited on an aluminum substrate and silanated by γ-APS for 45 min. The film was reacted with Epon 828 epoxy resin in a vacuum oven under a nitrogen atmosphere at 100°C for 1 h and then rinsed thoroughly with toluene prior to XPS examination.

at 100°C and then rinsed thoroughly with toluene are shown in Figures 15, 16, and 17. Comparison of the survey spectra shown in Figures 12 and 15 shows that the C(1s) peak was much greater in intensity after reaction of the silanated silica-like film with the epoxy compound than before. Reference to the C(1s) spectra shown in Figures 13 and 16 shows that reaction of the silanated silica-like films with the epoxy compound resulted in a significant increase in intensity of a component that was shifted upward from the main C(1s) peak by about 1.5 eV. This component was attributed to C–O bonds and was additional evidence that some of the epoxy remained on the surface of the silanated film after vigorous rinsing with toluene.

The average breaking strength of lap joints prepared using the one-part and two-part epoxy adhesives and aluminum substrates that were prepared in various ways are shown in Tables 2 and 3, respectively. The breaking strengths were 23.4 MPa (two-part adhesive) and 19.8 MPa (one-part adhesive) when the substrates were pretreated with a low-hydroxyl silica-like film. The breaking strengths were 14.3 MPa (two-part adhesive) and 16.8 MPa (one-part adhesive)

TABLE 2 Average Breaking Strength and Standard Deviation of Lap Joints Prepared Using the One-Part Epoxy Adhesive and Aluminum Substrates Coated with Low-Hydroxyl and High-Hydroxyl Silica-Like Films

Surface treatment	Average stress (MPa)	Standard deviation (MPa)
Low-hydroxyl silica-like film	19.8	0.2
High-hydroxyl silica-like film	16.8	0.5

when the substrates were pretreated with a high-hydroxyl silica-like film. Joints prepared using the one-part adhesive appeared visually to have failed cohesively in the adhesive. However, joints prepared using the two-part adhesive appeared to fail near the interface between the adhesive and the primer. Therefore, the effect of γ-APS primers on the characteristics of joints prepared using the two-part adhesive and substrates coated with silica-like films was investigated. The results obtained are shown in Table 3. Reference to Table 3 shows that the silane did not have a significant effect on the breaking strength of the joints. However, the silane did have a significant effect on the locus of failure.

XPS-survey spectra obtained from the adhesive and substrate failure surfaces of a lap joint that was prepared using the two-part epoxy adhesive and aluminum substrates that were coated with a low-hydroxyl silica-like film are shown in Figures 18 and 19, respectively. The elemental compositions of these surfaces are summarized in Table 4. The spectrum obtained from the adhesive-failure surface showed evidence for a trace of silicon but was otherwise similar to the survey spectrum of the neat two-part adhesive. Evidence of significant amounts of silicon and nitrogen were observed in XPS spectra of the substrate-failure surface. These results indicated that failure in

TABLE 3 Average Stress and Standard Deviation of Lap Joints Prepared Using the Two-Part Epoxy Adhesive and Aluminum Substrates That Were Given Different Surface Pretreatments

Surface treatment	Average stress (MPa)	Standard deviation (MPa)
Oxygen-plasma etching	22.7	1.0
Low-hydroxyl silica-like film	23.4	1.9
Low-hydroxyl silica-like film plus γ-APS	24.2	2.4
High-hydroxyl silica-like film	14.3	1.8
High-hydroxyl silica-like film plus γ-APS	13.5	2.2

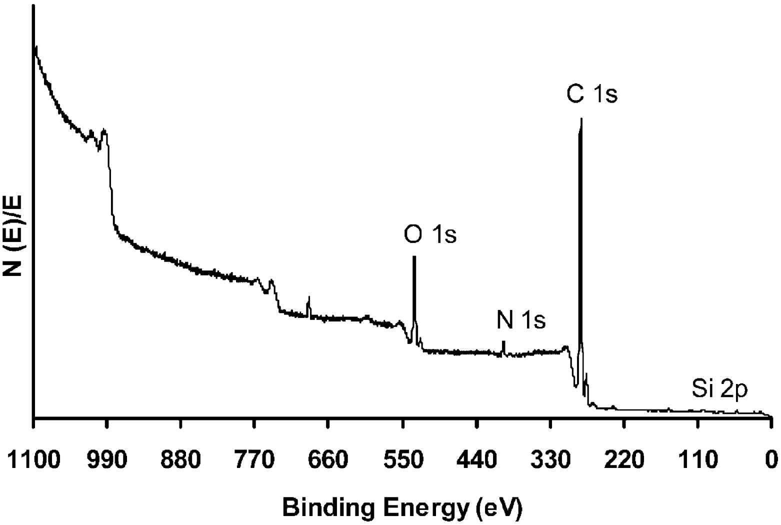

FIGURE 18 XPS-survey spectrum obtained from the adhesive failure surface of a lap joint that was prepared using the two-part epoxy adhesive and aluminum substrates that were coated with a low-hydroxyl silica-like film. The electron take-off angle was 45 deg.

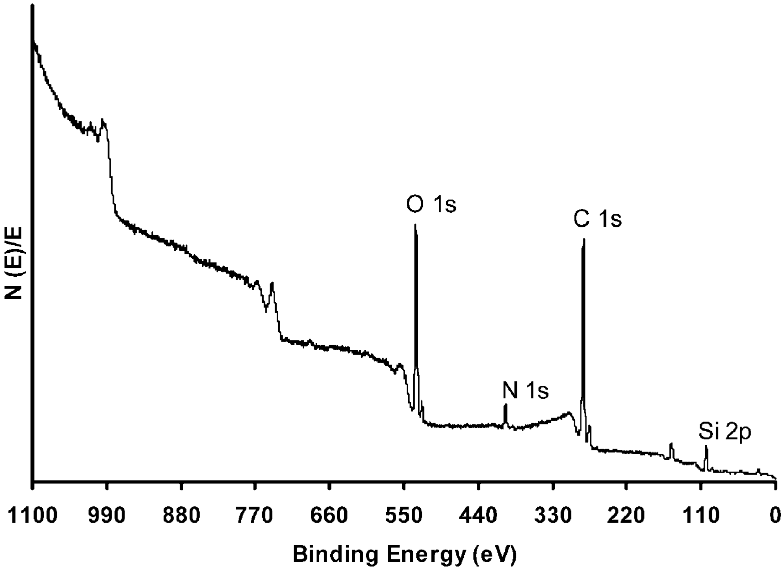

FIGURE 19 XPS-survey spectrum obtained from the substrate failure surface of a lap joint that was prepared using the two-part epoxy adhesive and aluminum substrates that were coated with a low-hydroxyl silica-like film. The electron take-off angle was 45 deg.

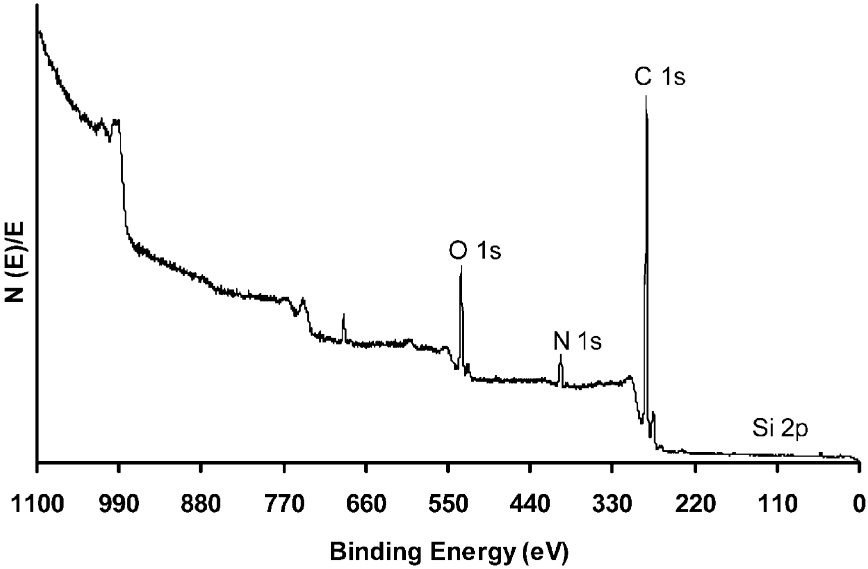

FIGURE 20 XPS-survey spectrum obtained from the adhesive failure surface of a lap joint that was prepared using the two-part epoxy adhesive and aluminum substrates that were coated with a low-hydroxyl silica-like film and then silanated with γ-APS in the vapor phase at a substrate temperature of 100°C. The electron take-off angle was 45 deg.

this case was near the adhesive–primer interface but partly cohesive within the adhesive.

The XPS-survey spectrum obtained from the adhesive-failure surface of a lap joint that was prepared using the two-part epoxy adhesive and aluminum substrates that were coated with a low-hydroxyl silica-like film and then silanated with γ-APS in the vapor phase is shown in Figure 20. The elemental composition of this surface is presented in Table 5. Evidence for traces of silicon was observed in the XPS spectrum of the adhesive-failure surface; however, the spectrum of the adhesive-failure surface was otherwise very similar to the spectrum of the neat adhesive. The spectrum of the substrate-failure surface is shown in Figure 21. The elemental composition of this surface is also presented in Table 5. This spectrum was also similar to that of the neat two-part adhesive although some evidence for silicon was observed. Considering that the spectra of the adhesive and substrate-failure surfaces were so similar to the spectrum of the neat adhesive and that some evidence for silicon was observed on both failure surfaces, it was concluded that failure was mostly cohesive

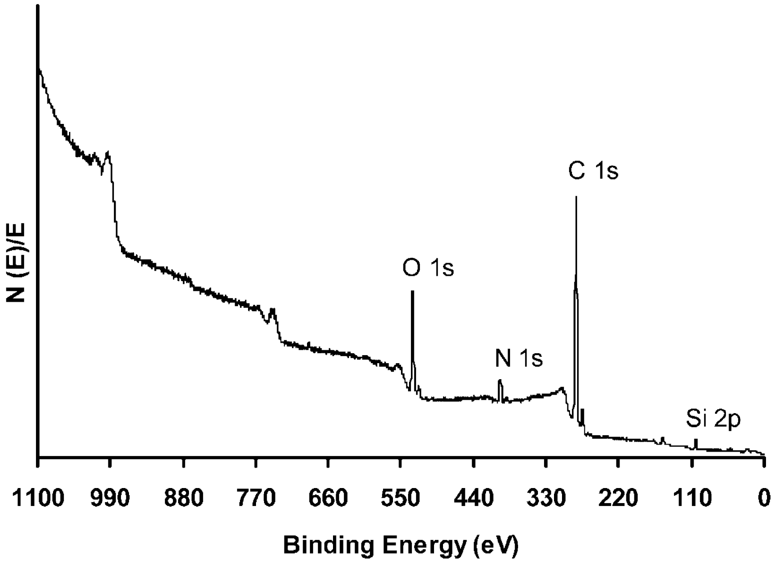

FIGURE 21 XPS-survey spectrum obtained from the substrate failure surface of a lap joint that was prepared using the two-part epoxy adhesive and aluminum substrates that were coated with a low-hydroxyl silica-like film and then silanated with γ-APS in the vapor phase at a substrate temperature of 100°C. The electron take-off angle was 45 deg.

TABLE 4 Atomic Concentration of Elements on Adhesive and Substrate Failure Surfaces of Lap Joints Prepared Using the Two-Part Epoxy Adhesive and Aluminum Substrates That Were Primed with Low-Hydroxyl Silica-Like Films

Failure surface	C (%)	O (%)	N (%)	Si (%)	F (%)	Failure mode
Substrate	61.8	22.4	4.7	10.4	0.7	Interface film/adhesive
Adhesive	82.5	11.5	3.2	1.3	1.6	

TABLE 5 Atomic Concentration of Elements on Adhesive and Substrate Failure Surfaces of Lap Joints Prepared Using the Two-Part Epoxy Adhesive and Aluminum Substrates That Were Primed with Low-Hydroxyl Silica-Like Films and Then Silanated With γ-APS in the Vapor Phase for 45 min

Failure surface	C (%)	O (%)	N (%)	Si (%)	F (%)	Failure mode
Substrate	74.9	13.2	6.1	5.2	0.5	Cohesive within adhesive
Adhesive	81.5	11.0	5.4	0.2	1.8	Interface film/epoxy

within the adhesive but close to the adhesive–primer interface and that use of the silane resulted in a change in the locus of failure.

CONCLUSIONS

Plasma-polymerized silica-like films were deposited onto aluminum substrates using HMDSO as the monomer and oxygen as a coreactant. Reaction parameters such as power and gas-flow rates were used to vary the hydroxyl content of the films. γ-APS was chemisorbed onto the surfaces of plasma-polymerized silica-like films through the amine and the alkoxy groups of the silane and silanol groups present on the silica-like film surface. The adsorbed silane reacted easily with epoxy compounds and, presumably, with epoxy adhesives.

Lap joints were prepared using aluminum substrates that were primed with silica-like films. Those prepared using the one-part adhesive mostly failed cohesively within the adhesive. Those prepared using the two-part adhesive mostly failed near the adhesive–primer interface. Whereas the adsorbed aminosilane did not affect the breaking strength of these joints, the silane did affect the locus of failure and caused it to change from adhesive to mostly cohesive within the adhesive.

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