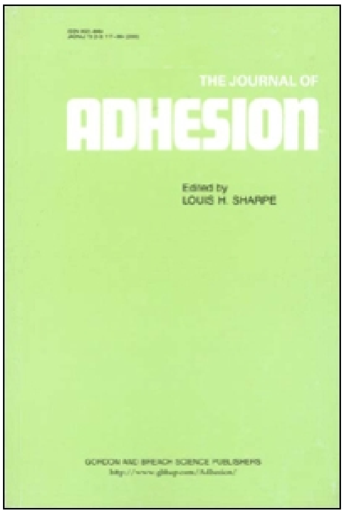

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Surface and Interfacial Studies of Plasma-Modified Composite Surfaces

Joannie W. Chin[a,b]; James P. Wightman[a]
[a] Department of Chemistry, Center for Adhesive and Sealant Science, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA [b] National Institute of Standards and Technology, Gaithasburg, MD, USA

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Surface and Interfacial Studies of Plasma-Modified Composite Surfaces*

JOANNIE W. CHIN** and JAMES P. WIGHTMAN†

Department of Chemistry, Center for Adhesive and Sealant Science,
Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

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Model epoxy and bismaleimide compounds in thin film form were used to simulate epoxy and bismaleimide composite surfaces, in order to study compositional changes and interfacial reactions induced by oxygen plasma treatment. X-ray photoelectron spectroscopy (XPS) and infrared reflection-absorption spectroscopy (IR-RAS) were used to probe chemical changes which occurred. XPS and IR-RAS were found to be complementary techniques in determining the nature of functional groups incorporated into surfaces by plasma treatment. IR-RAS analysis of the model surfaces following exposure to a liquid epoxy resin revealed that while adsorption of the liquid epoxy occurred on both plasma-treated and nonplasma-treated surfaces, the oxygen plasma-treated surface alone was capable of initiating ring-opening reactions in the epoxy. However, this effect was not observed unless immediate contact was made between the plasma-treated surface and the liquid epoxy resin, illustrating the short-lived reactivity of the functional groups on the plasma-treated surface.

KEY WORDS: infrared spectroscopy; x-ray photoelectron spectroscopy; epoxy; bismaleimide; plasma treatment; surface analysis; interfacial reactions.

INTRODUCTION

When fiber-reinforced composites are adhesively bonded to form structural components, some type of surface preparation is usually necessary to optimize adhesive performance. Composite surfaces are known to be contaminated by various types of mold-release agents and processing aids, all of which inhibit wetting and spreading of an adhesive[1–3]. Surface pretreatments such as solvent wiping, grit blasting and peel ply have been used to remove or prevent contamination and prepare the surface for adhesive application, with widely varying degrees of success[4–7].

Oxygen plasma has been shown to be highly effective in removing contamination from and introducing polar functionality into composite surfaces[8–11]. These effects have been observed to improve the hot/wet resistance of adhesively-bonded composite joints relative to other pretreatment techniques. The mechanism by which

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† Corresponding author.

** Present address: National Institute of Standards and Technology Gaithasburg, MD 20899, USA.

hot/wet durability in composite-to-composite bonds is enhanced by plasma treatment has not been extensively studied. This is in part due to the difficulties encountered in analyzing composite surfaces. Surface heterogeneity, topography, complex (and often undisclosed) resin chemistries and the presence of underlying fibers combine to make detailed analysis at the molecular level troublesome, with the result that many aspects of the composite/adhesive interphase remain unknown. Studies by Jacques Schultz and coworkers have contributed significantly to our knowledge of interfacial and surface phenomena and provide a foundation for current research in the field of adhesion[12-15].

The objective of this research was to study the changes in oxygen plasma-treated composite surfaces by using model polymer systems with known structures and stoichiometries to approximate closely the resin-rich composite surface. A tetrafunctional epoxy and diaminodiphenylsulfone (DDS) system was chosen to represent an epoxy composite matrix resin, and a commercial two-component bismaleimide simulated a bismaleimide composite. Infrared reflection absorption spectroscopy (IR-RAS) and x-ray photoelectron spectroscopy (XPS) analysis of thin films made from these materials enabled molecular information on the plasma-treated surfaces to be obtained, and provided insight into the mechanism of interaction between the plasma-treated surfaces and an adhesive material.

EXPERIMENTAL

Materials

To prepare model composite surfaces, thin films were spin-coated from commercially available resins. To simulate a high-performance epoxy composite, Araldite® MY 720 epoxy resin and HT 976 curing agent from Ciba Geigy (Hawthorne, New York) were utilized. The structures of MY 720 (N,N,N'N'-tetraglycidyl-4,4'-methylenebisbenzeneamine, also known as tetraglycidylmethylene-dianiline) and HT976 (4,4'-diaminodiphenylsulfone) are shown in Figure 1. This particular epoxy and curing agent combination was one of the earliest high performance epoxy matrix resins developed, possessing good long-term high temperature performance as well as high mechanical strength and chemical resistance[16].

A bismaleimide composite surface was represented by Matrimid® 5292, also from Giba Geigy. Matrimid® 5292, a two-component BMI resin system, is a commonly used starting formulation for many commercial BMI composites and adhesives, with the ability to retain superior mechanical properties at elevated temperature and elevated humidity[17]. Matrimid® 5292 part A is a 4,4'-bismaleimidophenylmethane resin and Matrimid® 5292 part B is o,o'-diallyl bisphenol A; chemical structures are shown in Figure 2.

Thin Film Preparation

Commercial Ferrotype plates were used as substrates for the composite films and were obtained from Apollo Metals (Bethlehem, PA). These plates consist of a 0.5 mm

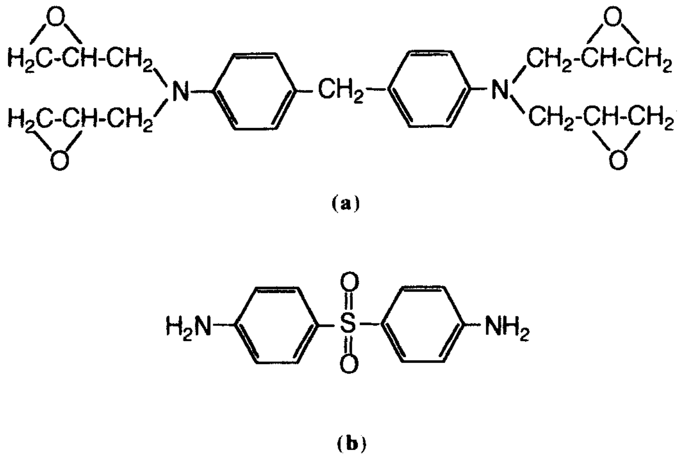

FIGURE 1 Chemical structures of (a) Araldite® MY 720, N,N,N'N'-tetraglycidyl-4,4'-methylenebisbenzeneamine, and (b) HT 976, 4,4'-diaminodiphenylsulfone.

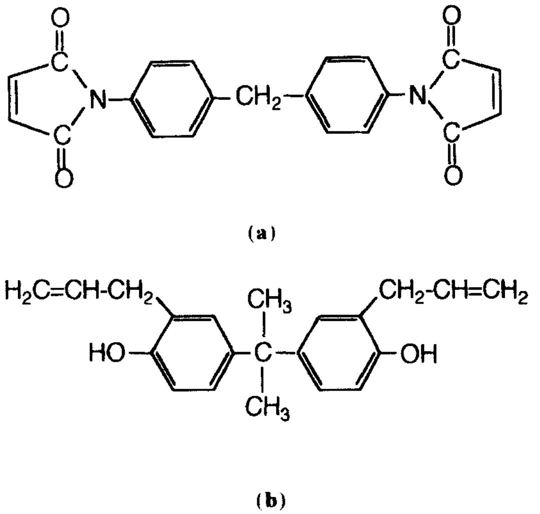

FIGURE 2 Chemical structures of (a) Matrimid® 5292 part A, 4,4'-bismaleimido-phenylmethane resin, and (b) Matrimid® 5292 Part B, o,o'-diallyl bisphenol A.

steel base plated with nickel and approximately 80 nm of chromium oxide on the outermost surface. The high reflectivity and high refractive index of the chromium oxide are ideal for reflection-absorption infrared spectroscopy. Prior to spin-coating, 3.8 cm x 3.8 cm (1.5 in. x 1.5 in). Ferrotype plates were cleaned in a 50-watt oxygen plasma for 15 minutes, scrubbed vigorously with deionized water and a Kimwipe® tissue, rinsed in deionized water and dried under a stream of nitrogen gas.

To generate dilute solutions of MY 720/HT976, 100 parts by weight (pbw) of MY 720 were combined with 44 pbw of HT 976 and mixed throughly by hand. This mixture was then diluted to a concentration of 1.3% w/w in a solvent mixture consisting of a 2 pbw acetone to 1 pbw methyl ethyl ketone (MEK). Spin-coating was carried out on a custom-built lab spin-coater. Coatings were cured by heating in a forced-air Blue M oven, using a cure cycle consisting of a 30-minute heat-up from room temperature to 200°C and a 90-minute hold at 200°C. When curing was complete, samples were allowed to cool to room temperature before removal from the oven. Ellipsometric measurements of the film thickness ranged from 40–45 nm.

Matrimid® 5292 solutions were produced by combining 100 pbw of Part A and 85 pbw Part B thoroughly by hand and diluting with 2-methoxyethyl ether (diglyme) to a concentration of 6.8% w/w. Coatings were cured by heating in a forced-air Blue M oven, using a cure cycle consisting of a 30-minute heat-up from room temperature to 200°C and a 60-minute hold at 200°C, followed by a 20-minute heat-up from 200°C–250°C and a 60-minute holt at 250°C. Following the cure step, samples were allowed to cool to room temperature before removal from the oven. Film thickness was measured by ellipsometry to be 25–27 nm.

Surface Analysis of Plasma-Treated Films

6.4 mm (1/4 in.) diameter discs were punched from the coated Ferrotype samples and exposed to a 50-watt oxygen plasma in a March Instruments Plasmod® Unit for 30 seconds, taking care to avoid excessive erosion of the thin films.

XPS analysis was performed on a Perkin-Elmer PHI 5400 spectrometer with a MgK_α achromatic X-ray source (1253.6 eV), operating at 15 keV and 400 watts with an emission current of 30 mA. The spectrometer was calibrated to the $4f_{7/2}$ photopeak of gold and $2_{p3/2}$ photopeak of copper. Pressure inside the analysis chamber was maintained below 6.6×10^{-5}Pa(5×10^{-7}torr) during the course of analysis. Dimensions of the analyzed areas on the samples were typically 1 mm × 3 mm. No neutralization with the electron gun was necessary since only minimal charging effects were present.

For each sample analyzed, a survey scan encompassing the region of 0–1100 eV was first taken. Multiplex scanning of all significant peaks seen in the survey was then carried out. Binding energies for all observed photopeaks were referenced to the value for C-C/C-H hydrocarbon species at 284.6 ev. Atomic concentration calculations and curve fitting were carried out on an Apollo 3500 computer, using PHI software version 4.0.

Infrared reflection-absorption analysis was used to examine the molecular changes in the plasma-treated model composite resins. Although not generally considered to be a surface-sensitive analytical technique. IR-RAS is highly suitable for the analysis of thin films on high refractive index substrates[18–20]. The strategy which is used involves making the films thin enough so that the surface and near-surface regions constitute a significant percentage of the entire coating thickness. In this way, signals which arise from the near surface layers can be separated from the signals originating in the bulk.

IR-RAS experiments were performed on a Nicolet 510 Fourier transfrom infrared spectrometer equipped with a triglycine sulfate (TGS) detector. Reflectance measurements were taken with a Seagull® variable angle reflection accessory from Harrick Scientific Corporation, set at an incidence angle of 75°. A zinc selenide polarizer from Spectra-Tech was placed in the optical path of the IR beam to produce parallel (p)-polarized radiation. The spectrometer bench was purged with dry nitrogen for 30–45 minutes between samples. 800 scans were collected and averaged at a resolution of 4 cm^{-1}. A clean, bare Ferrotype plate served as a background. Difference spectra were obtained by subtracting the spectra of non-treated surfaces from the spectra of the plasma-treated surfaces, utilizing Nicolet software for interactive subtraction.

IR-RAS EPOXY Adsorption Studies

Immediately following treatment with a 30-second/50-watt oxygen plasma, polymer-coated Ferrotype plates were immersed in a bath of neat EPON® 830 (no crosslinking agent added). The polymer-coated plates were then heated in the EPON® 830 bath at 180° C for one hour in a convection oven. Following this thermal treatment, excess EPON® 830 was drained from the sample surfaces and the samples then subjected to repeated rinses with methylene chloride solvent in shaker jar. Six 1-minute rinses were performed, utilizing fresh methylene chloride for each rinse. Following the methylene chloride rinses, sample surfaces were rinsed in a stream of acetone for approximately 30 seconds, then dried under a stream of nitrogen. Non-plasma-treated samples were also treated according to this procedure and served as control specimens.

IR-RAS analysis was carried out as described above on the non-treated and plasma-treated surfaces and the plasma-treated surfaces exposed to EPON® 830. Neat EPON® 830 was also analyzed by IR-RAS in order to identify those peaks which were unique to it and which would not be observed in the spectra of MY 720/DDS or Matrimid® 5292.

RESULTS AND DISCUSSION

Surface Analysis of Model Epoxy

XPS and IR-RAS were used to study the changes which occur in the surface of oxygen plasma-treated MY 720/HT 976 thin films. Table I shows the theoretical

TABLE I
Theoretical and XPS atomic compositions of unmodified and oxygen plasma-treated MY 720/HT 976 epoxy films

	Surface Composition (atomic %)		
	Theoretical	Unmodified	Oxygen Plasma
Carbon	77	76	53
Oxygen	13	16	35
Nitrogen	8	7	8
Sulfur	2	1	4

atomic concentration of a formulation composed of 100 pbw of MY 720 and 44 pbw HT 976, compared with the measured XPS atomic concentrations of a cured, unmodified MY 720/HT 976 film and a cured film treated in oxygen plasma. Good agreement is observed between the theoretical and actual atomic concentrations for the unmodified surface. The excess oxygen which is found on the unmodified film surfaces may originate from residual solvent used to spin-coat the films or from surface oxidation which occurred during the cure cycle. Following oxygen plasma exposure, the atomic concentrations of oxygen and sulfur are seen to increase.

Curve-fitting of the carbon 1s photopeaks was carried out and is depicted in Figure 3. In the unmodified surface of Figure 3(a), peaks at 284.6, 286.0, 287.5 and 289.0 eV can be fitted to the main peak envelope. These peaks are usually assigned to C—C/C—H hydrocarbon species, C—O/C—N, C=O and O—C=O functionality, respectively[21]. The presence of C—O moieties can be accounted for in the epoxide rings from the MY 720 and C—N linkages in both the MY 720 and HT 976.

A few anomalies are present in the XPS curve fit analysis of the cured MY 720/HT 976 films. XPS analysis of poly(ether sulfone) by Beamson and Briggs showed that the carbons directly adjacent to the sulfone group exhibit a binding energy shift of approximately + 0.6eV relative to hydrocarbon species at 284.6 eV; however, no peaks could be fitted to the MY 720/HT 976 C1s photopeak at this binding energy[22]. In addition, no C=O or O—C=O groups are present in either the epoxy resin or the crosslinker, yet peaks corresponding to these functional groups are observed in the curve-fitted spectrum. On the other hand, no carbonyl stretches were observed in the IR-RAS spectrum of the cured MY 720/HT 976 films. It is possible that surface oxidation may have occurred during the high temperature cure cycle, resulting in the formation of various oxidized carbon species, detectable by XPS but not by IR-RAS.

Figure 3(b) shows the curve-fitted carbon 1s photopeak for the oxygen plasma-treated surface. Peaks at 286.0, 287.5 and 289.0 eV have increased in intensity, indicative of an increase in the surface concentration of hydroxyl, carbonyl and carboxylate/ester species as a result of plasma treatment. A new peak is also observed at 291.0 eV. It is not clear whether this is a peak corresponding to a new oxygen-containing functional group, such as carbonate, or a $\pi \rightarrow \pi^*$ shake-up satellite.

Changes are also observed in the nitrogen 1s photopeak shown in Figure 4. In the unmodified surface, a single nitrogen peak is observed at approximately 399.7 eV, corresponding to amine nitrogens in both the epoxy resin and crosslinker[22]. Following plasma exposure, a peak is observed at 401.8 eV in addition to the original one at 399.7 eV. The peak at 401.8 eV could be due to some type of oxidized nitrogen species[23]. A nitrogen 1s binding energy of 401.8 eV has been reported for $N_2H_6SO_4$[23], and nitrogen in the tertiary amine salt-$N(CH_3)_3^+$ has been observed to exhibit a binding energy of 401.74 eV[22].

No significant changes were observed in the shape or location of the oxygen 1s photopeak. Following oxygen plasma treatment, the sulfur 2p photopeak was observed to shift from its original position at 167.7 eV to 168.6 eV. This shift to higher binding energy is indicative of the transformation of the original sulfone sulfur to a more oxidized form of sulfur, such as sulfate[23].

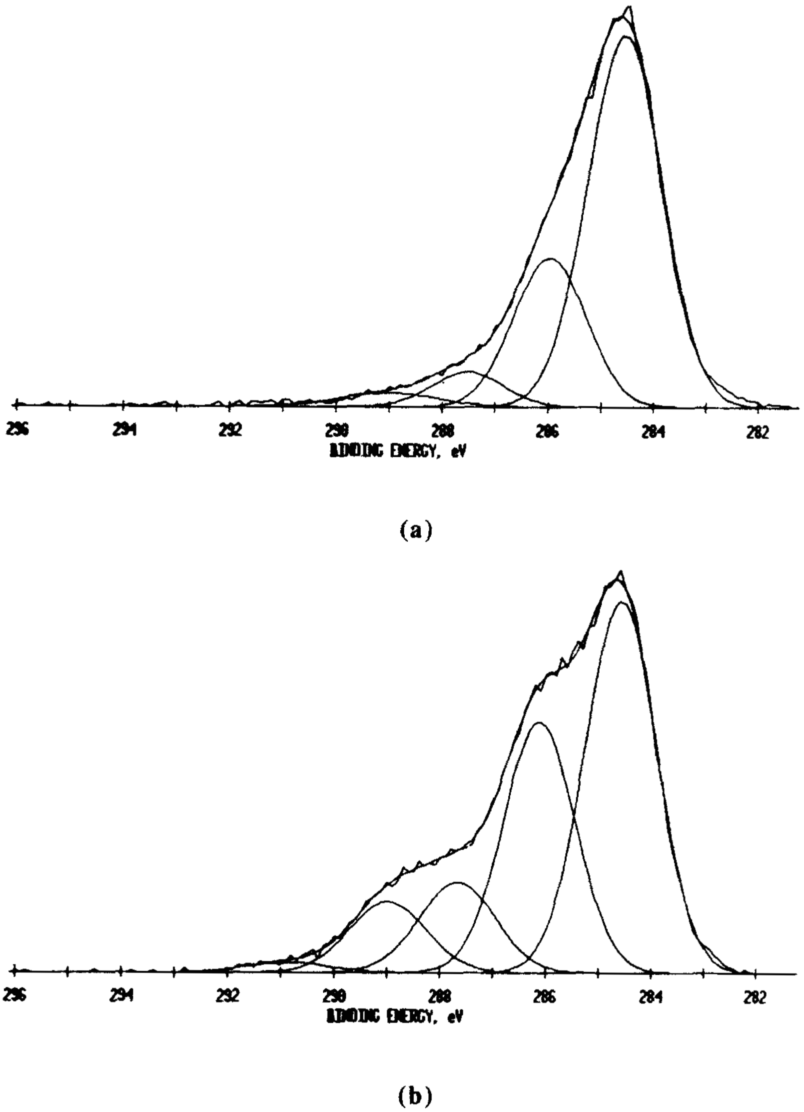

FIGURE 3 Curve-fitted XPS carbon 1s photopeaks for (a) unmodified, and (b) oxygen plasma-treated MY 720/HT 976 epoxy films.

Infrared analysis of the plasma-modified epoxy surface served to complement the molecular information obtained from curve-fitting the XPS photopeaks. Figure 5 shows the IR-RAS difference spectrum obtained by subtracting the spectrum of the unmodified surface from the spectrum of the oxygen plasma-treated surface. Peaks are observed in the difference spectrum at 1770, 1438 and 1205 cm^{-1}. The peak at 1770 cm^{-1} can be assigned to C=O stretching in ester or carboxylic acid species[24]. This assignment is consistent with the increase in the XPS peak at 289.0 eV. The

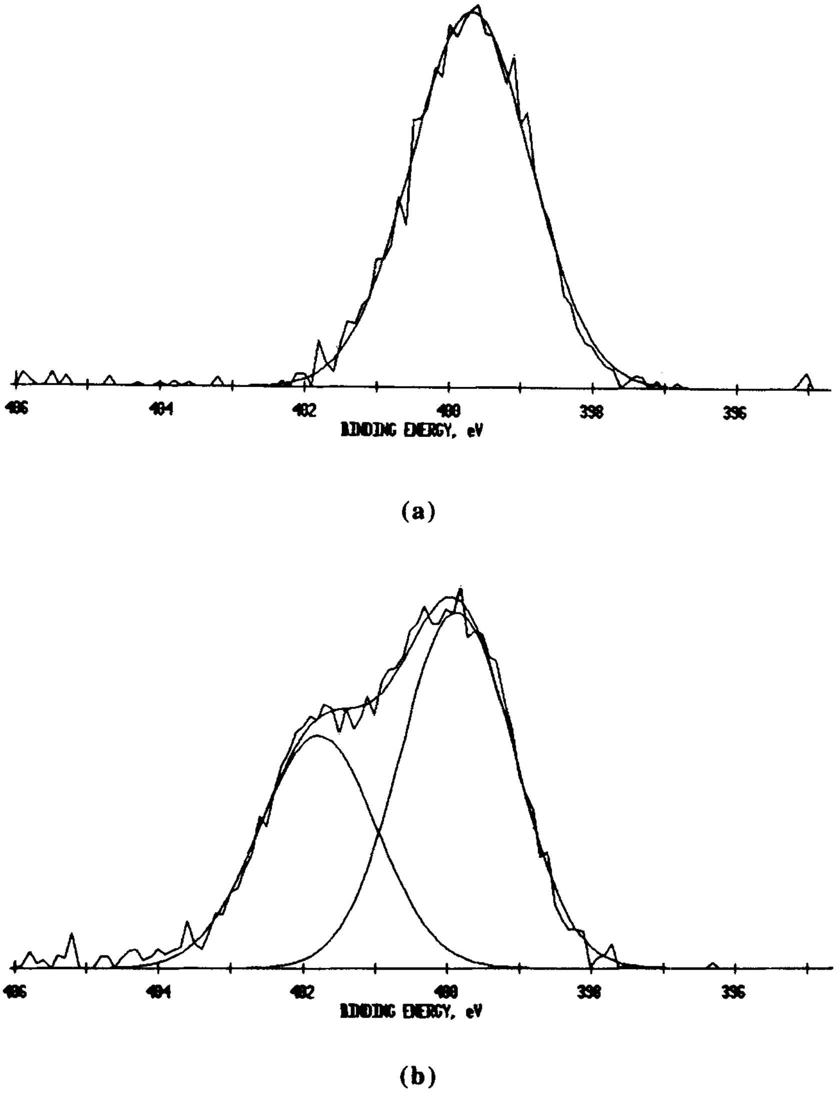

FIGURE 4 Curve-fitted XPS nitrogen 1s photopeak for (a) unmodified, and (b) oxygen plasma-treated MY 720/HT 976 epoxy films.

peak at 1205 cm^{-1} is identified as a C—O stretch[25], which corresponds with the increased intensity of the XPS photopeak at 286.0 eV. The peak at 1438 cm^{-1} can be tentatively assigned to either a ketonic methyl or methylene C-H bend or an O-H bend[24]. In general, it can be seen that the XPS and IR-RAS results are in agreement with each other in terms of the surface functional groups identified following oxygen plasma exposure.

Other researchers have reported similar results for oxygen plasma-modified surfaces. Dunn and McClure studied oxygen sputter-etched poly(ethylene terephthalate)

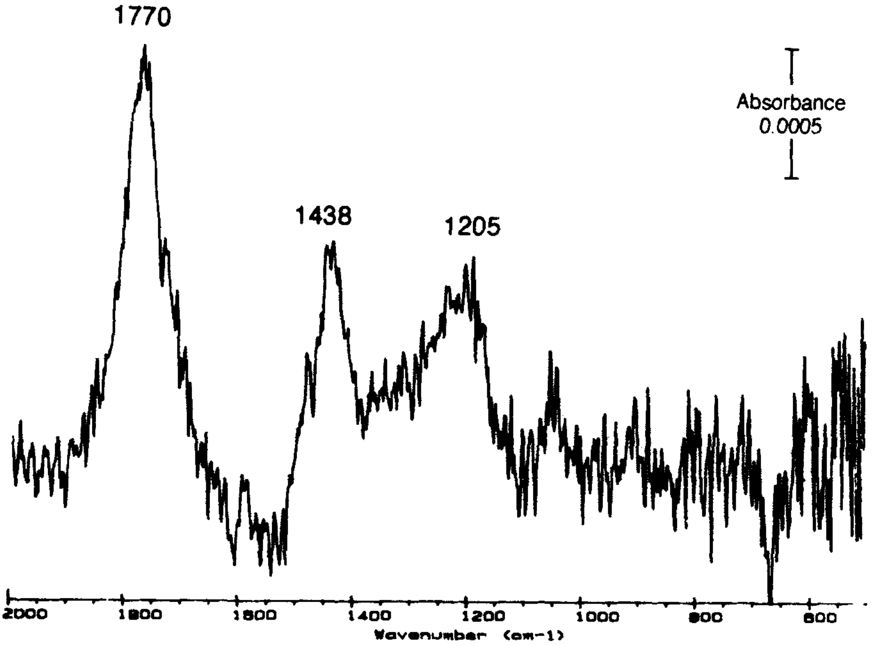

FIGURE 5 IR-RAS difference spectrum of oxygen plasma-modified MY 720/HT 976 epoxy.

by IR-RAS, and observed new bands at 1740 and 1200 cm^{-1}, which provided evidence for the presence of esters, aldehydes and/or carboxylic acids[26]. Webster and Wightman carried out IR-RAS analysis on oxygen plasma-treated poly(phenylene sulfide) and also found subtraction peaks corresponding to C=O and C—O vibrational modes[27]. Work published by Chin and Wightman on oxygen plasma-treated LaRC-TPI, a thermoplastic polyimide, documented the presence of IR-RAS peaks at 1770, 1390 and 1205 cm^{-1}. These peaks were assigned to carboxylic acid or ester C=O and C—O stretching[28].

Surface Analysis of Model Bismaleimide

XPS and IR-RAS were again used to study the changes which occur in the surface chemistry of oxygen plasma-treated Matrimid® 5292 thin films. Table II shows the theoretical atomic concentration of a formulation composed of 100 pbw of Part A and 85 pbw Part B, compared with the measured XPS atomic concentrations of a cured, unmodified Matrimid® 5292 film and a cured film treated in oxygen plasma. Good agreement is observed between the theoretical and actual atomic concentrations for the unmodified surface. The small amount of excess oxygen which is found on the unmodified film surfaces may originate from residual solvent or surface oxidation during cure. As seen with the MY 720 films, oxygen atomic concentration increases significantly following plasma exposure.

TABLE II
Theoretical and XPS atomic compositions of unmodified and oxygen plasma-treated Matrimid® 5292 BMI films

	Surface Composition (atomic %)		
	Theoretical	Unmodified	Oxygen Plasma
Carbon	84	83	63
Oxygen	12	14	32
Nitrogen	4	3	5

Curve-fitting of the carbon 1s photopeaks was carried out and is depicted in Figure 6. In the unmodified surface of Figure 6(a), peaks at 284.6, 285.8 and 288.2 eV can be fitted to the main peak envelope. These peaks are identified as C—C/C—H hydrocarbon species, C—O/C—N and imide C=O functionality, respectively[29].

Figure 6(b) shows the curve-fitted carbon 1s photopeaks for the oxygen plasma-treated surface. The original peaks at 285.8 and 288.2 eV are seen to be increased in intensity following plasma exposure. New peaks are observed at 286.9, 289.7 and 292.7 eV. The species corresponding to the peaks at 286.9 and 289.7 eV may be identified as C—O and O—C=O, respectively. The peak at 292.7 eV is most likely a shake-up satellite. No significant changes were observed in the shape or location of the oxygen 1s or nitrogen 1s photopeaks.

As in the case of the model epoxy films, infrared analysis of the plasma-modified BMI surface also served to complement the molecular information obtained from curve-ftting the XPS photopeaks. Figure 7 shows the IR-RAS difference spectrum for the oxygen plasma-treated bismaleimide surface. Peaks are observed in the difference spectrum at 1745, 1400 and 1206 cm^{-1}. The peak at 1745 cm^{-1} can be assigned to C=O stretching in ester or carboxylic acid species[24]. This assignment is consistent with the appearance of the XPS peak at 289.7 eV. after plasma treatment. The peak at 1205 cm^{-1} is identified as a C—O stretch[25], which corresponds with the increased intensity of the XPS photopeak at 285.8 eV. The peak at 1400 cm^{-1} can be tentatively assigned to either a ketonic methyl or methylene C—H bend or an O—H bend[24]. It is again seen that the XPS and IR-RAS results are in agreement with each other in terms of the surface functional groups identified following oxygen plasma exposure.

EPON® 830 Adsorption Studies

MY 720/HT 976 Surface

To determine potential interactions of the plasma-treated surface with adhesives, the oxygen plasma-treated MY 720/HT 976 and Matrimid® 5292 surfaces were immersed in liquid EPON® 830 after a 30-second, 50-watt oxygen plasma treatment. It was hypothesized that following solvent rinsing of the immersed surfaces to remove physisorbed EPON® 830, a residual thin layer of more tightly bound or chemisorbed material would remain and should be detected by IR-RAS analysis. A

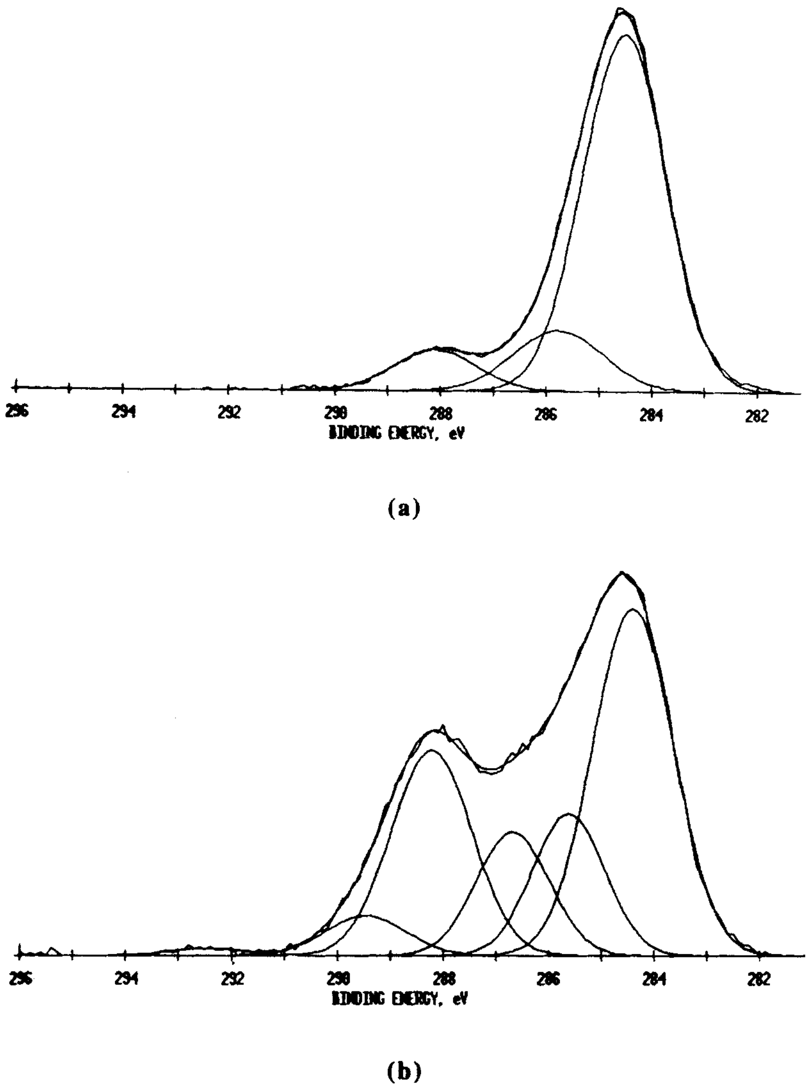

FIGURE 6 Curve-fitted XPS carbon 1s photopeak for (a) unmodified, and (b) oxygen plasma-treated Matrimid® 5292 BMI films.

similar study was carried out by Webster and Wightman, using plasma-treated poly(phenylene sulfide) as a substrate for EPON® 828 adsorption[27].

It was first necessary to carry out the IR-RAS analysis on neat EPON® 830 films so that infrared bands unique to this DGEBA epoxy could be identified and used to determine if adsorption had taken place on the plasma-treated model epoxy surfaces. The IR-RAS spectrum of EPON® 830 is shown in Figure 8. Bands of significance include an aromatic C—C stretch at 1512 cm^{-1}, aryl C—O stretch and C—O—C symmetric deformation at 1254 cm^{-1}, in-plane C—H bend and

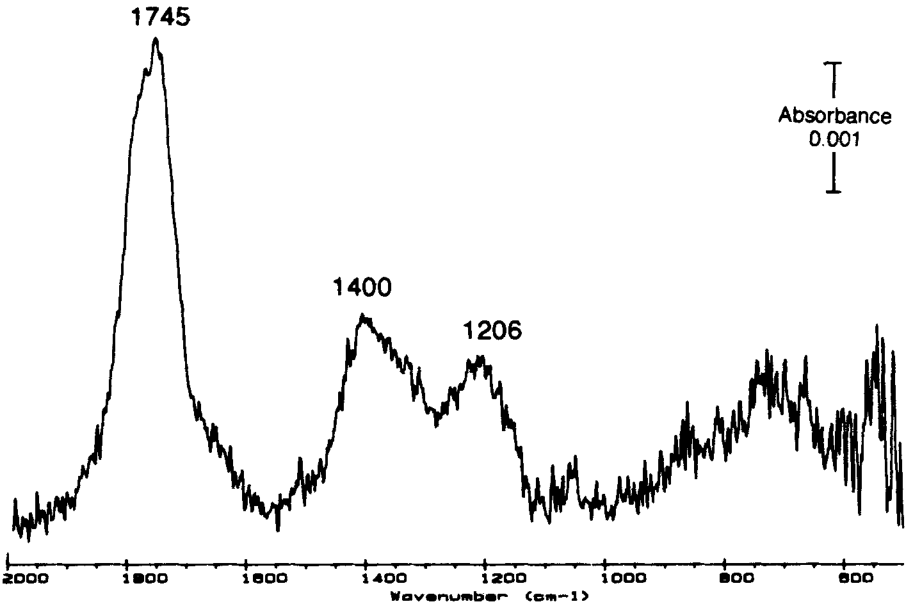

FIGURE 7 IR-RAS difference spectrum of oxygen plasma-modified Matrimid® 5292 BMI.

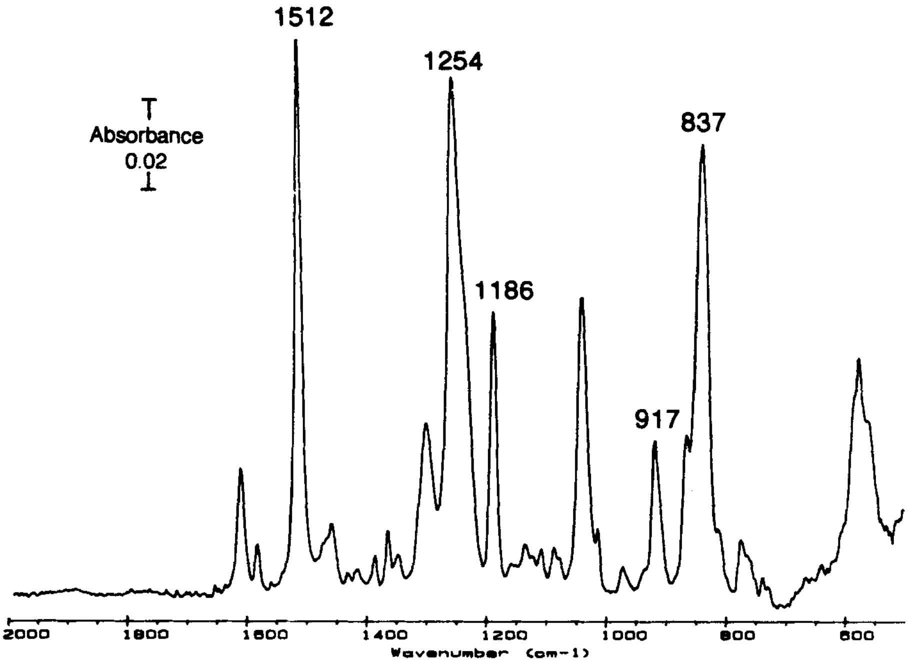

FIGURE 8 IR-RAS spectrum of EPON® 830 resin.

aryl-C—aryl stretch at 1186 cm^{-1}, and an out-of-plane, para-disubstituted benzene bending mode at 837 cm^{-1}. Bands which correspond to the unopened epoxide ring are found at 864 and 917 cm^{-1}. The 837 cm^{-1} peak is also assigned to the epoxide ring by a number of researchers[24,30].

A comparison of the EPON® 830 spectrum and the spectrum of the cured MY 720/HT 976 coating is shown in Figure 9. Peaks at 1254 and 917 cm^{-1}, corresponding to EPON® 830 C—O—C stretching and the epoxide ring vibrations are clearly not observed in the spectrum of the cured epoxy model composite.

Figure 10(a) shows the IR-RAS spectrum of a nonplasma-treated MY 720/HT 976 film following EPON® 830 immersion and solvent rinsing. When compared to the original spectrum of MY 720/HT 976, new peaks are observed at the 1254 and 917 cm^{-1} positions. There are also increases in the intensities of peaks at 1519 and 1186 cm^{-1}, which are present in the EPON® 830 spectrum as well as in the spectrum of unmodified MY 720/HT 976 prior to EPON® 830 immersion.

These changes observed in the MY 720/HT 976 spectrum following immersion in an epoxy bath confirm that adsorption of EPON® 830 has occurred on the surface of the MY 720/HT 976 film. However, the presence of the epoxide ring vibration at 917 cm^{-1} indicates that no reaction has taken place between the MY 720/HT 976 surface and the EPON® 830, because the epoxide rings in EPON® 830 remain intact.

When the procedure is repeated using an oxygen plasma-treated MY 720/HT 976 substrate, the IR-RAS spectrum shown in Figure 10(b) results. This spectrum is virtually identical to the spectrum of the nonplasma-treated surface in Figure 10(a). Once again, the presence of the epoxy ring vibration at 917 cm^{-1} originating from the EPON® 830 indicates that no reaction has occurred in the adsorbed EPON® 830 layer. These preliminary results appear to indicate that the plasma-treated surface is not capable of initiating a reaction with an epoxy resin.

However, the experiment was repeated with one important change made to the procedure. The original method involved obtaining the IR-RAS spectrum of the plasma treated MY 720/HT 976 substrate *prior* to immersion in the EPON® 830 bath. This was an additional step which added 30–45 minutes between the plasma treatment and EPON® 830 exposure. When the plasma-treated MY 720/HT 976 surfaces were *immediately* submerged into the EPON® 830 bath following plasma treatment, the IR-RAS spectrum in Figure 10(c) results. The peak at 1254 cm^{-1} is evident, confirming that adsorption of the EPON® 830 has taken place. However, in this instance, no peak is seen at 917 cm^{-1}, indicating that the epoxide rings have indeed undergone a ring-opening reaction. This result is evidence of interaction between the plasma-treated surface and the liquid epoxy resin. Webster and Wightman also reported epoxy adsorption and polymerization on the surface of oxygen and ammonia plasma-treated poly(phenylene sulfide)[27].

The fact that reaction is observed only when the elapsed time between plasma treatment and epoxy immersion is very short confirms the instability of the plasma-treated surface. The surface is very likely quite reactive immediately following plasma exposure but quickly becomes deactivated upon exposure to the atmosphere.

The types of reactions which are possible between the plasma-treated surface and the epoxide ring in the EPON® 830 resin are numerous. The results of XPS and

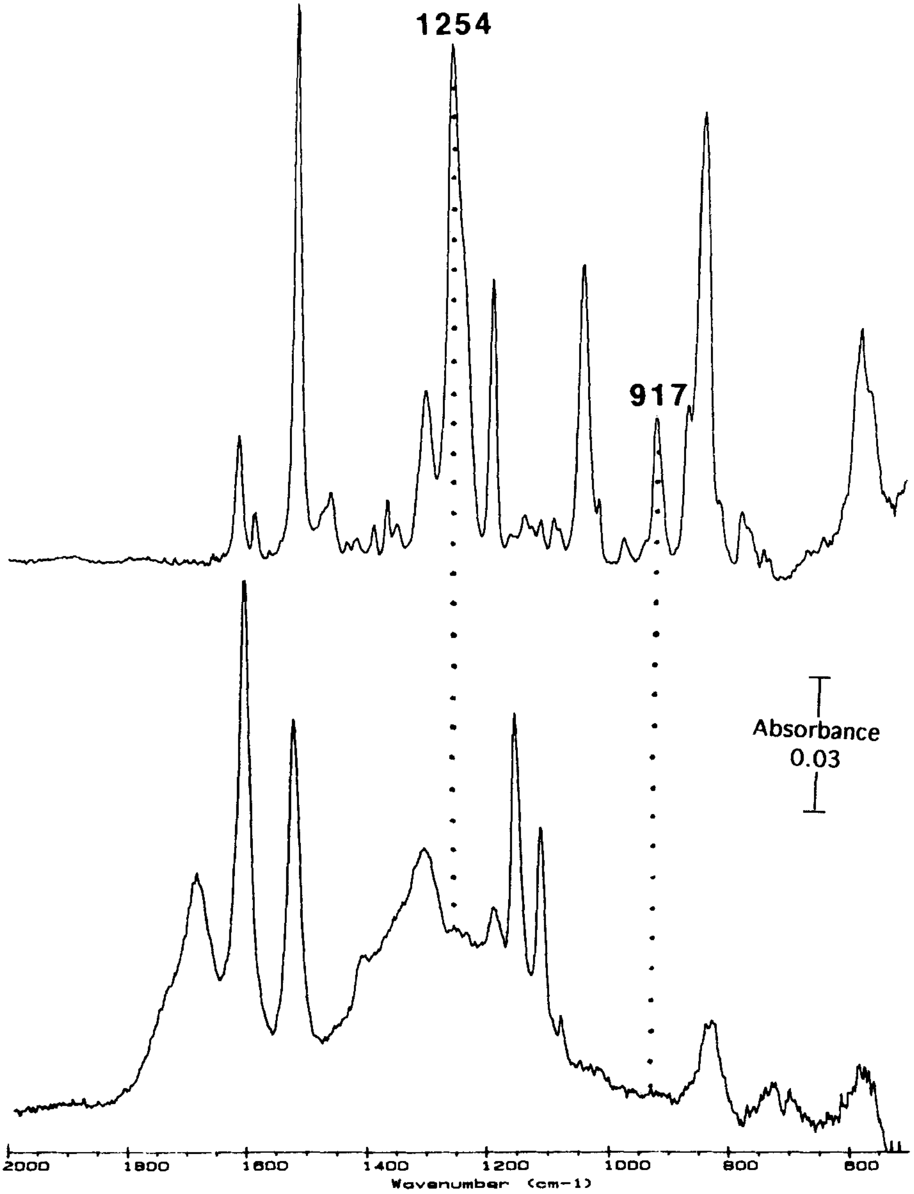

FIGURE 9 Comparison of EPON® 830 infrared spectrum and that of cured MY 720/HT 976 epoxy film, showing that the 1254 and 917 cm^{-1} peaks in EPON® 830 are not present in the MY 720/HT 976 epoxy spectrum.

IR-RAS analysis of the oxygen plasma-treated MY 720/HT 976 provide convincing evidence for the presence of hydroxyl, carboxylic acid, ester and ketone functional groups. Work with model compounds has shown that alcohols and phenols may react with glycidyl ethers to yield a variety of isomeric products containing hydroxyl

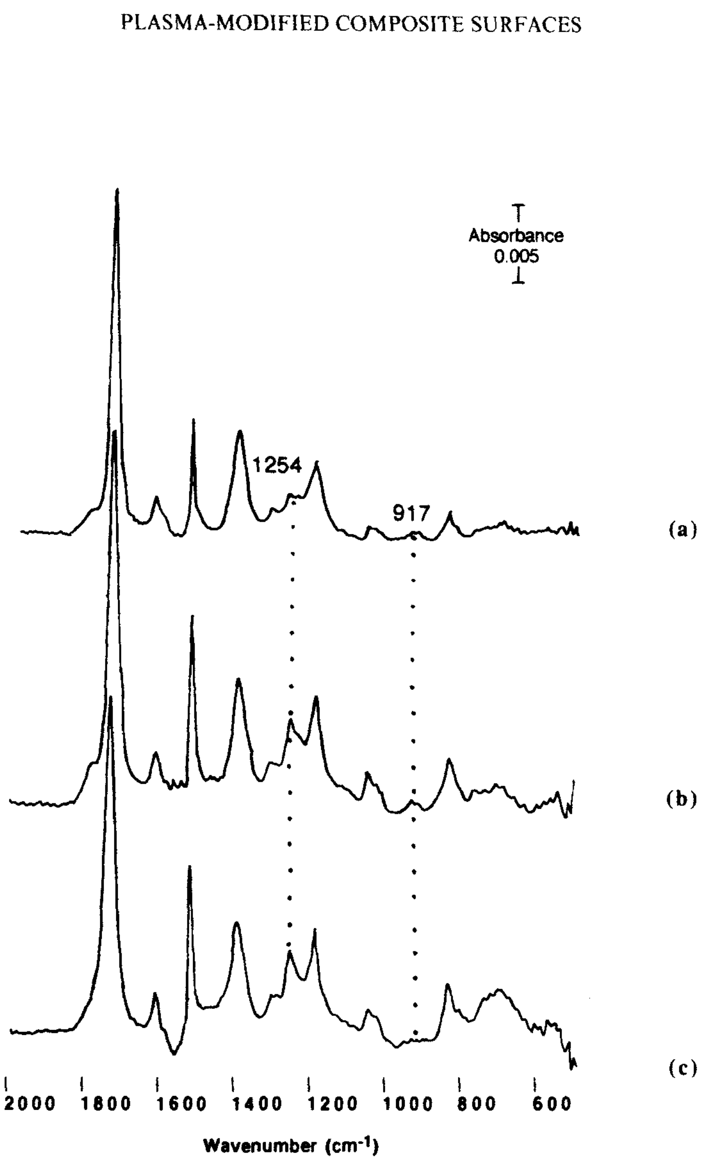

FIGURE 10 IR-RAS spectra of MY 720/HT 976 epoxy films following EPON® 830 immersion and solvent rinse. (a) unmodified film (b) oxygen plasma-treated film, immersed in EPON® 830 30–45 minutes after plasma treatment (c) oxygen plasma-treated film, immersed in EPON® 830 immediately after plasma treatment.

groups[31]. These hydroxyl groups are also capable of further reaction with epoxide groups to form polyethers. Carboxylic acid groups have also been observed to react with epoxide rings to form hydroxy-ester moieties[31]. Alternatively, the plasma-treated substrate may simply be serving as a catalyst for epoxy homopolymerization.

Matrimid® 5292 Surface

The EPON® 830 adsorption procedure was also carried out with the BMI model surfaces. Again, it was hypothesized that, following solvent rinsing of the immersed surfaces to remove physisorbed EPON® 830, a thin layer of more tightly bound or chemisorbed material would remain behind. Figure 11 shows a comparison of the EPON® 830 and cured Matrimid® 5292 spectra, in which it is evident that characteristic peaks of EPON® 830 at 1254 and 917 cm^{-1} are not present in the Matrimid® 5292 spectrum.

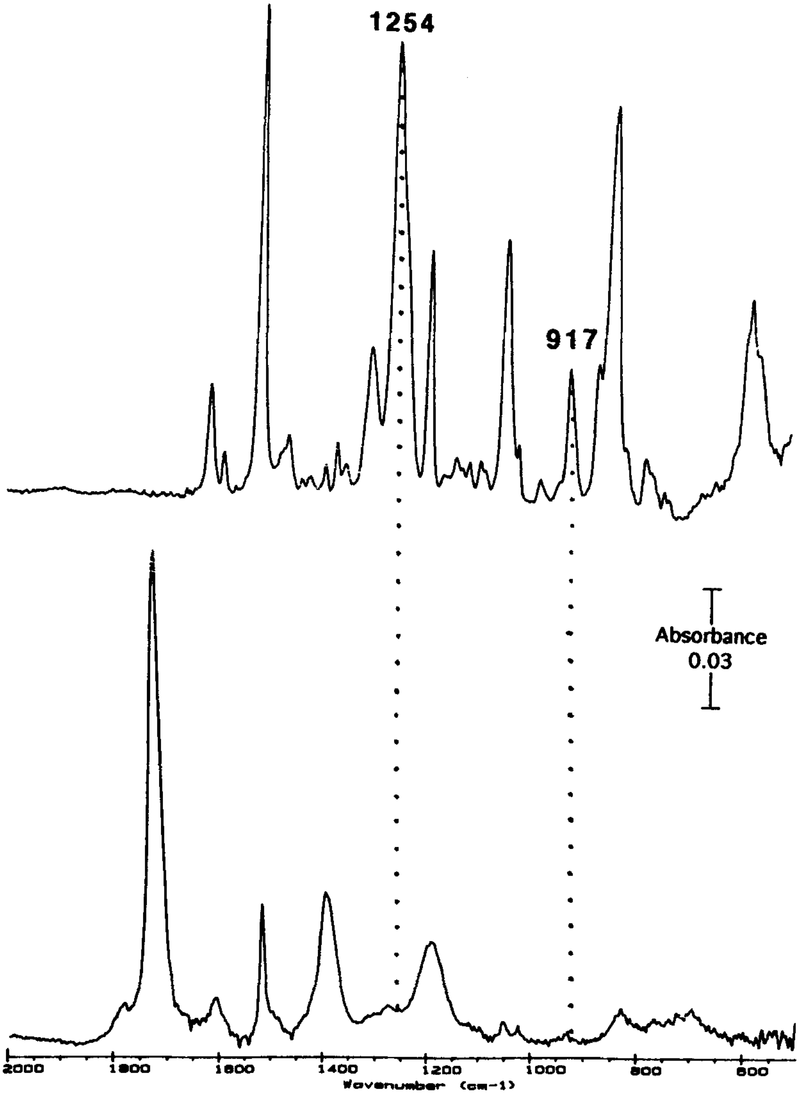

FIGURE 11 Comparison of EPON® 830 infrared spectrum and that of cured Matrimid® 5292 BMI film, showing that the 1254 and 917 cm^{-1} peaks in EPON® 830 are not present in the Matrimid® 5292 BMI spectrum.

Figure 12(a) shows the IR-RAS spectrum of a nonplasma-treated Matrimid® 5292 film following epoxy immersion and solvent rinsing. When compared with the original spectrum of Matrimid® 5292, new peaks are observed at 1254 and 920 cm^{-1}, corresponding to EPON® 830 C—O—C stretching and the epoxide ring vibration.

When the procedure is repeated using an oxygen plasma-treated Matrimid® 5292 substrate, the IR-RAS spectrum shown in Figure 12(b) results. This spectrum is virtually identical to the one shown in Figure 12(a) for the nonplasma-treated surface. Once again, the presence of the epoxy ring vibration at 920 cm^{-1} originating from the EPON® 830 indicates that no reaction has occurred between the surface and the neat epoxy resin. However, the intensities of the C—O stretch and O—H deformation

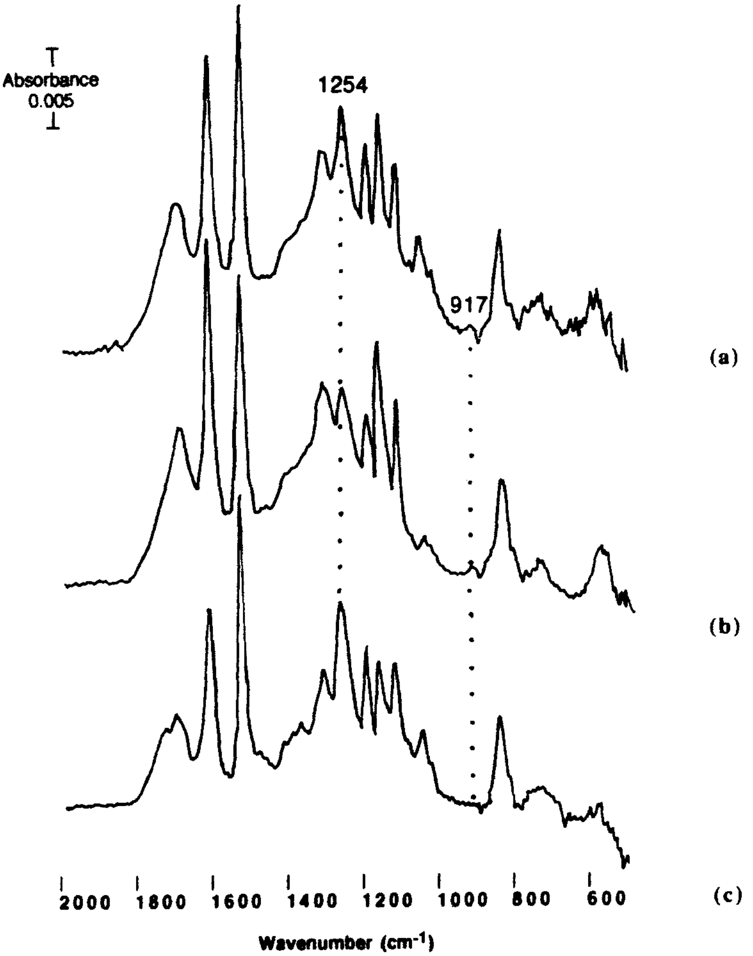

FIGURE 12 IR-RAS spectra of Matrimid® 5292 BMI films following EPON® 830 immersion and solve- nt rinse. (a) unmodified film (b) oxygen plasma-treated film, immersed in EPON® 830 30–45 minutes after plasma treatment (c) oxygen plasma-treated film, immersed in EPON® 830 immediately after plasma treatment.

peaks at 1048, 1022 and 1300 cm^{-1} are increased relative to the nonplasma-treated surface. This could indicate that some degree of epoxy ring-opening has taken place.

As was also done with the epoxy model surfaces, the plasma-treated Matrimid® 5292 surfaces were then *immediately* submerged into the EPON® 830 bath following plasma treatment. The IR-RAS spectrum shown in Figure 12(c) reveals the results. The peak at 1254 cm^{-1} is evident, again confirming that adsorption of the EPON® 830 has occurred. However, in this instance, *no peak* is seen at 920 cm^{-1}, indicating that the epoxide rings have indeed undergone ring-opening. This result once again provides evidence for some type of specific chemical interaction between the plasma-treated surface and the liquid epoxy resin. As discussed above for the model epoxy surface, similar reactions between the functional groups found on the plasma-treated BMI surface and EPON® 830 are theoretically possible.

This evidence seen for covalent interaction between both the plasma-modified epoxy and BMI surfaces and a liquid epoxy resin can be correlated with the improved hot/wet resistance exhibited by oxygen plasma-treated composite-to-composite bonds[8,9]. Specific interactions or covalent bonding in the interphase region of a bond have often been cited as factors which increase moisture durability in other bonding systems[32–34]. The functional groups incorporated into the composite surface by plasma treatment are also now shown to be capable of participating in reactions which potentially increase hot/wet bond durability.

CONCLUSIONS

As analyzed by XPS, both oxygen plasma-treated epoxy and BMI films displayed increases in the concentration of oxygen-containing functional groups following plasma treatment. IR-RAS analysis of the plasma-treated surfaces also revealed the presence of oxygen-containing functional groups such as carboxylate/ester, carbonyl and hydroxyl. These results are consistent with the findings of XPS and illustrate the complementary nature of these two techniques.

Adsorption of a liquid epoxy, EPON® 830, was seen to take place on both the model epoxy and model bismaleimide surfaces. Infrared bands characteristic of the liquid epoxy were observed in the spectra of nonplasma-modified and oxygen plasma-modified substrates after immersion and solvent rinsing. However, epoxy ring-opening reactions, as evidenced by the disappearance of the epoxy ring vibration at 917–920 cm^{-1}, were only observed in the case of oxygen plasma-treated substrates immersed immediately into the liquid epoxy bath after plasma treatment. The fact that this reaction is only observed when a minimal time elapses between plasma treatment and initial contact with the adhesive resin emphasizes the short-lived reactivity of the plasma-treated surface.

The disappearance of the reactive epoxide functional group in the vicinity of a plasma-treated polymer surface provides evidence for some type of specific or covalent interaction in the interphase region. The correlation of these findings with the observed hot/wet durability improvement in plasma-treated composite-to-composite bonds serves to elucidate the mechanism for temperature and moisture resistance in the interphase region.

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