

Assimilation of Oil from Metal Surfaces by Epoxy Adhesives: XPS and ATR Analyses

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SYNOPSIS

The oil displacing and absorbing behaviors of epoxy adhesives cured with amidoamine curing agents on oiled metal substrates were studied using X-ray photoelectron spectroscopy (XPS) and attenuated total reflection infrared spectroscopy (ATR). A simple XPS experiment demonstrated that amidoamine curing agents could displace an aliphatic oil from the cold-rolled steel (CRS) and the electrogalvanized steel (EGS) surfaces, but an epoxy resin based on bisphenol A could not. Results of ATR measurements showed that the oil was effectively displaced from the CRS surface and absorbed as deep as 2 μm into the epoxy adhesive cured with amidoamine with low amine numbers. But the oil was mostly present in the 0.3 μm thick adhesive layer near the CRS/adhesive interface for the epoxy adhesive cured with amidoamine with high amine numbers. The oil absorbing ability of the adhesive was worse on the oiled EGS substrate than on the oiled CRS substrate. It was also found that the pressure applied during cure could greatly facilitate the absorption of oil into the adhesive. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

An increasing number of adhesives have been applied in industry and commodity products to replace conventional fastening methods because of their relatively low cost, lack of corrosion, light weight, and good mechanical properties. Many of the current applications have required the adhesive systems to be capable of bonding to metal surfaces contaminated with treating oils or oils present in the ambient environment.¹⁻⁴ To form a strong adhesive bond with an oil-contaminated metal surface, the adhesive must penetrate through the oil and then contact with the metal surface underneath to form chemical or physical bonds. Accordingly, it should be capable of either displacing or absorbing the oil from the metal surface.⁴ Debski et al. indicated that an epoxy resin cured with dicyandiamide could absorb the oil from the metal surface.⁴

Rosty et al. conducted a series of studies on the adhesive bonding of the oil contaminated cold rolled

steel (CRS) substrate.⁵⁻⁷ The lap shear test was used to determine the effects of filler and curing temperature on the performance of the Epon-828/amidoamine (Versamid 140) adhesive on the oily CRS. The specimens cured at higher temperatures had greater lap shear strength because of the better assimilation of the oil by the adhesive and the greater extent of cure in the adhesive at elevated curing temperature.⁶ The viscosity of the oil was also found to adversely affect the lap shear strength of the joints.⁷

Bowen and Volkmann measured the bonding strengths of epoxy adhesives cured against AlMag #1564 oil coated CRS substrates.⁸ It was found that amidoamine curing agents cured epoxy systems were superior in tensile shear strength to those cured with aliphatic amine curing agents. They suggested that epoxies cured with amidoamine curing agents had greater affinity for the oily metal surface than those cured with simple amines because of the oleophilic character of the aliphatic fatty acid moieties in amidoamine curing agents.

Hong et al. characterized the failure surfaces of the joints with X-ray photoelectron spectroscopy (XPS) and found that an adhesive cured with ami-

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doamine curing agents with low amine numbers could displace the oil from the steel surface but the adhesive prepared with amidoamine with high amine numbers could not.^{9,10}

Natale studied the performance of three epoxy adhesive systems on oil contaminated automotive steel substrates by using lap shear specimens exposed to ambient conditions and accelerated corrosion cycles.¹¹ They indicated that the strength, strength retention, and failure modes of the adhesive bonds were dependent on the specific adherend/oil/adhesive used. Strength losses of lap shear joints were mainly attributed to corrosion at the adherend/adhesive interface. Similar conclusions were drawn by Ziane et al.¹²

Arnold studied the bonding durability of a modified one-part epoxy adhesive on mill oil contaminated CRS, electroplated, and hot-dipped galvanized steels.^{13,14} It was shown that the durability of the lap shear joints depended on the corrosion resistance of the substrate. Joints prepared using electrogalvanized steel (EGS) adherends had better durability than those prepared using CRS adherends due to the slower corrosion rate of the EGS.

Foister et al. also studied the performance of different epoxy adhesives on the clean and the oil coated electroplated and hot-dipped galvanized steels.¹⁵ Higher adhesive bonding strength and higher strength retention after water immersion were obtained on the EGS substrate than on the hot-dipped galvanized steel. It was found that a two part imidazole cured epoxy adhesive system and a one part dicyandiamide cured epoxy system had greater strength and strength retention values on the oiled ultrasmooth substrate than on a clean ultrasmooth substrate.

In a separate article, Foister et al. showed that poor adhesive strength and strength retention on hot-dipped galvanized substrates were related to their lower surface roughness and higher surface chemical heterogeneity compared to EGS substrates.¹⁶ Greater bond strength and durability were obtained on a more stable electroplated galvanized surface that mainly consisted of rough crystals of ZnO. The locus of failure was found to be identical for clean and reoiled surfaces for a given epoxy adhesive and the substrate. It was concluded that the initial bond strength was mainly influenced by surface morphology, but durability was mainly affected by the surface chemistry of the substrate. Similar conclusions were also reached by Holubka et al.¹⁷

Although many other studies of the performance of oil-accommodating adhesives on the oily CRS and EGS substrates, few were done to answer the question about how differently the adhesives could ab-

sorb the oil from the metal substrates.¹⁸⁻²⁰ In the current study, XPS and attenuated total reflection (ATR) infrared spectroscopy were used to investigate the oil-absorption ability of the epoxy adhesives on the oily metal surfaces.

XPS has been widely used for surface characterizations of the polymeric materials because of its relatively nondestructive nature comparing to other electron spectroscopy techniques. Not only the qualitative and the quantitative information of the chemical species on the outmost surface, but also the depth profiling analysis can be achieved by using XPS. As a result, XPS is used as a powerful tool to investigate surface related behaviors such as corrosion, wetting, friction, adhesion, and adsorption.²¹⁻³¹

The concept of XPS analysis is based on the fact that, when an atom is irradiated with X-rays with relatively low and monoenergetic energy, electrons from the core levels will be ejected with characteristic energies.³²⁻³⁶ By measuring the kinetic energy of the released electrons, the characteristic binding energy of the interested chemical element can be calculated. In this study, quantitative and qualitative information of the organic functional groups on the CRS and the Zn surfaces were obtained from XPS analysis in order to identify the type of chemicals near the metal surfaces.

The ATR technique has also been used to study the absorption of liquids into solids by many investigators. Spasskova et al. applied ATR to investigate the absorption behavior of an epoxy resin in contact with the silicon rubber, and found a concentration gradient of epoxy resins in the silicon rubber.³⁷ Popov et al. and Lavrentev et al. studied the diffusion of the acetone into polyisoprene and polyisobutylene films by using ATR, respectively.^{38,39} The diffusion coefficient and the diffusion depth of the liquid into the solid material could also be determined with the ATR technique.^{40,41} In addition, ATR has been utilized to study the surface adsorption of proteins.⁴²⁻⁴⁴ Jensen et al. applied ATR analyses to determine the differences in the chemical compositions and the penetrations of various allylic ether resins in the wood at different depths from the wood surface.⁴⁵

In order to compare the relative intensities of the absorption bands of interest in the ATR experiment, the ratios of the absorbances between the bands of interest and a reference band in ATR spectra are calculated. Assuming the following equation can be applied⁴⁶:

$$A_x = \epsilon[C_x]d_e \quad (1)$$

where A_x is the absorbance of the band near $x \text{ cm}^{-1}$, ϵ is the molar extinction coefficient, C_x is the concentration of species having the absorption near $x \text{ cm}^{-1}$, and d_e is defined as the equivalent thickness of the film of the same material that is necessary to generate the same absorption for transmission at normal incidence and is described by^{47,48}:

$$d_e = [(n_2/n_1)E_o^2 d_p]/2 \cos \theta \quad (2)$$

where n_1 = refractive index of the internal reflection element (IRE); n_2 = refractive index of the sample; E_o = amplitude of the electric field of infrared light; d_p = depth of penetration; θ = angle of incident; and where the depth of penetration (d_p) is given by the following equation:

$$d_p = \lambda_1 / \{2\pi[\sin^2\theta - (n_2/n_1)^2]^{1/2}\} \quad (3)$$

λ_1 being the wavelength of incident light in the IRE.

Then the ratio of the absorbances of two absorption bands near $x \text{ cm}^{-1}$ and $y \text{ cm}^{-1}$ in an ATR spectrum can be obtained as⁴⁶:

$$A_x/A_y = [\epsilon_x C_x \lambda_x] / [\epsilon_y C_y \lambda_y] \quad (4)$$

where ϵ and λ are constants for a definite infrared absorption band assuming that the refractive index of the polymer film analyzed is constant. So the ratio of the absorbances of two absorption bands is proportional to the relative concentrations of the two species causing the observed infrared absorptions. This method is applied in order to know how well the oil can be absorbed into the adhesive from the metal/adhesive interface.

EXPERIMENTAL

Materials

Epon-828 epoxy resin and V-15, V-25, and V-40 curing agents (from Shell Chemical Co.) were used in this study. Epon-828 is a resin of type diglycidyl ether of bisphenol A (referred to as DGEBA). The substrates were 1020 CRS and EGS obtained from Armco, Inc. The oil used to "contaminate" the steel surface was the ship-out oil Ferrocote-61 (FC-61) manufactured by Quaker Chemical Co. Parco 338 and Parco 1500 cleaners, obtained from Parker Chemical Co., were used to clean the CRS and EGS substrates, respectively.

Metal Cleaning

The 1020 CRS substrates were cleaned in a 30 g/L Parco 338 solution at 60°C for 30 min and then ul-

trasonically cleaned in the same solution for 15 min. These steps were repeated and then the steel substrates were rinsed with deionized water.

The EGS substrates were cleaned in a 20.4 g/L Parco 1500 aqueous solution at 40°C for 3 min, ultrasonically cleaned in the same solution for 5 min, and then rinsed with deionized water. The effectiveness of these two cleaning processes was confirmed previously.^{9,10}

XPS

In order to measure the oil-displacing abilities of the adhesive constituents, the oil was dip-coated on the cleaned metal substrates first (oil thickness, about 20 μm). Then DGEBA, V-15, V-25, and V-40 were individually placed on the top of oiled EGS and CRS surfaces. After 48 h, the EGS and CRS specimens were immersed in liquid nitrogen to remove the excess organics from the metal surfaces. The exposed CRS and EGS surfaces were analyzed by using XPS to verify the oil-displacing capability of the adhesive constituents.

The XPS analyses were performed on a Perkin-Elmer Model 5300 ESCA system. Mg(K_{α}) X-rays, with a photon energy of 1253.6 eV, were used to generate spectra. In survey spectra, which were taken to obtain general information about the composition on the surface, 44.75 eV pass energy and 0.5 eV/step were used to scan the region from 0 to 1100 eV at a 45° take-off angle. In multiplex spectra, 17.9 eV pass energy and 0.05 eV/step were used to obtain more detailed information of each element of interest at a 45° take-off angle. Take-off angle was defined as the angle between the specimen surface and the optical axis of the analyzer in the instrument. The type of chemical species on the metal surface can be identified from XPS spectra. In applying the curve-fitting method, the full width at half maximum of constituent peaks in the multiplex spectrum was kept the same and the shape of fitting curves was determined by 90% Gaussian distribution (10% Lorentzian).

ATR Spectroscopy

CRS Substrates

In order to obtain good contact between adhesive films and the IRE, the CRS substrates were polished before the adhesives were applied. CRS substrates were cut into small coupons (1 × 2 cm), and polished down to 0.05 μm starting from 600 grit dry silicon carbide paper. After polishing, the mirror-like surfaces were rinsed with deionized water and blown dry with nitrogen gas.

Different adhesive systems were then applied to the polished substrates, which were either kept clean or coated with FC-61 oil (about 2 μm thick). After the adhesives were cured at room temperature for 18 h and postcured at 50°C for 5 h, the specimens were immersed in liquid nitrogen to expose the adhesive/CRS interface. Then the mirror-like adhesive side fracture surface was pressed against the IRE under a constant 32 oz-in torque, which was set by a torque wrench, and placed in an ATR accessory made by Harrick Scientific Co. Sixty scans were acquired at a resolution of 4 cm^{-1} from 4000 to 800 cm^{-1} . Three different kinds of parallelepiped IREs, Ge (60°), KRS-5 (60°), and KRS-5 (45°), were used. The intensities of the bands in the ATR spectra were calculated to obtain the concentrations of chemical groups as a function of penetration depth.

EGS Substrates

The procedures to obtain the ATR spectra from specimens prepared with EGS substrates were the same as those from CRS substrates except that as-received (unpolished) EGS were used. The EGS substrates were cleaned by methods described previously before applying the oil and the adhesive.

RESULTS AND DISCUSSION

XPS Analyses

Figure 1 is the XPS C(1s) spectra obtained from the oiled CRS specimens. The carbon peak consists of only one peak that has a binding energy near 284.6 eV, characteristic of C—H bonds, indicating that the oil is mainly an aliphatic compound. The atomic concentrations of this specimen showed that it contains 92.1% C, 6.5% O, 1.1% Fe, and 0.3% Ca. The

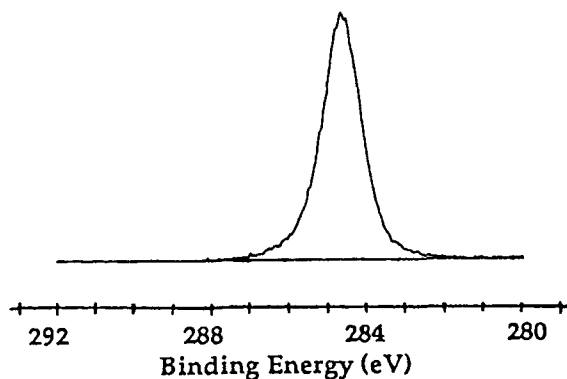


Figure 1 C(1s) spectrum obtained from oil-contaminated CRS surface.

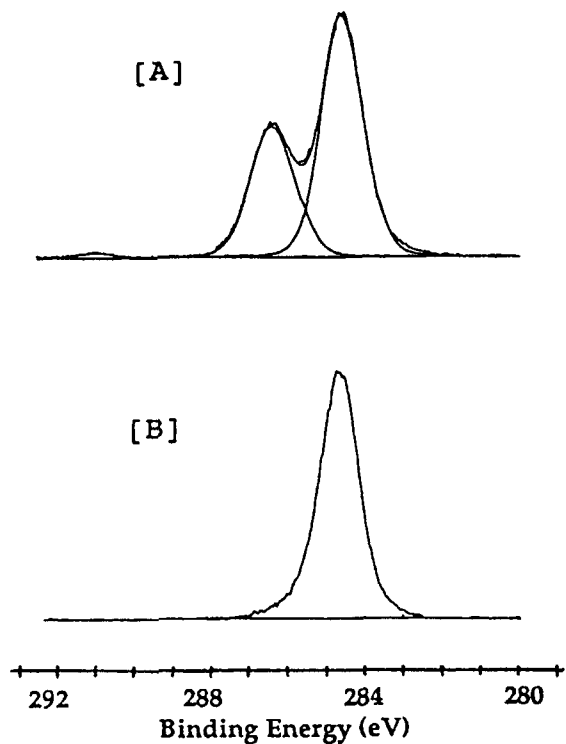


Figure 2 C(1s) spectra obtained from substrate fracture surfaces prepared by applying DGEBA on (A) clean and (B) oiled CRS.

oxygen detected comes from the iron oxide on the CRS and a calcium sulfonate additive in the oil.⁹

By comparing the XPS C(1s) spectra taken from DGEBA on clean and oiled CRS surfaces, the oil-displacing power of DGEBA was determined. Figure 2(A) is the XPS C(1s) multiplex spectrum obtained from DGEBA on the clean CRS surface. Three peaks are observed. The peak with binding energy near 284.6 eV is due to C—H in the resin. The peak with binding energy near 286.4 eV is due to the C—O—C in the epoxide ring, and the peak near 291.1 eV is due to the shake-up satellite of the aromatic ring in the DGEBA. The C(1s) spectrum obtained from DGEBA on the oiled CRS is shown in Figure 2(B). Only one peak near 284.6 eV was detected, indicating that the surface consists mostly of C—H bonds. Figure 2(B) is similar to the C(1s) spectrum of the oil shown in Figure 1. No C—O—C group from the epoxide ring was detected. The absence of C—O—C groups on the oiled CRS surface implies that DGEBA does not contact the CRS surface, that is DGEBA could not displace the oil from the CRS surface within 48 h.

Similar comparisons were made for curing agents and that proved to be capable of displacing the oil from the CRS substrates. The C(1s) spectra of spec-

imens prepared with V-15, V-25, and V-40 on clean and oiled CRS are shown in Figure 3. There are three peaks detected in each spectrum. The peak near 284.6 eV is due to C—H, the peak near 285.7 eV is from the C—N bonds of the amino groups, and the peak near 287.4 eV is due to the amide groups in the amidoamine curing agent. The spectrum shown in Figure 3(A1), V-15 on the clean CRS surface, is similar to Figure 3(A2), V-15 on the oiled CRS surface. The amino and amide groups detected on the oiled CRS surface are from V-15. If the oil is not displaced by V-15, then the spectrum in Figure 3(A2) would be similar to those shown in Figures 1 and 2(B). These results implies that V-15 could displace the oil from the CRS surface. In addition, the detection of amino and amide groups on the oiled

CRS surface and the similarities between Figure 3(B1) and 3(B2), and between Figure 3(C1) and 3(C2) also indicate that the oil is displaced from the CRS surfaces by V-25 and V-40 resins.

The displacement of the oil from the EGS surfaces by V-15, V-25, and V-40 was also investigated by the methods described above. It was shown that these three resins could displace the oil from the EGS surfaces. The XPS C(1s) spectra of specimens prepared with V-15, V-25, and V-40 on clean and oiled EGS surfaces are shown in Figure 4(A–C), respectively. Three peaks similar to those detected on CRS surfaces are also observed. Again, the spectrum shown in Figure 4(A1), V-15 on the clean EGS surface, is similar to Figure 4(A2), V-15 on the oiled EGS surface, indicating that V-15 could displace the

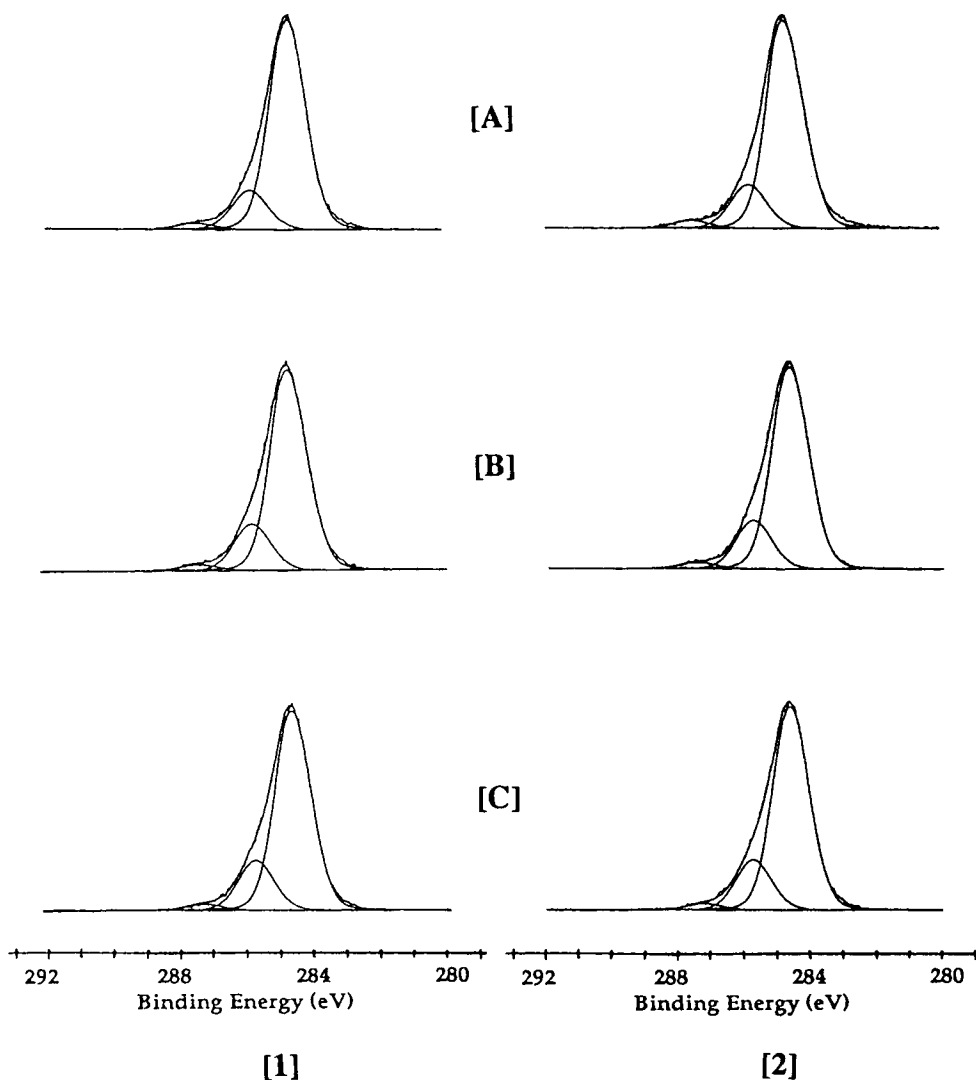


Figure 3 C(1s) spectra obtained from substrate fracture surfaces prepared by applying (A) V-15, (B) V-25, and (C) V-40 on (1) clean CRS, and (2) oiled CRS.

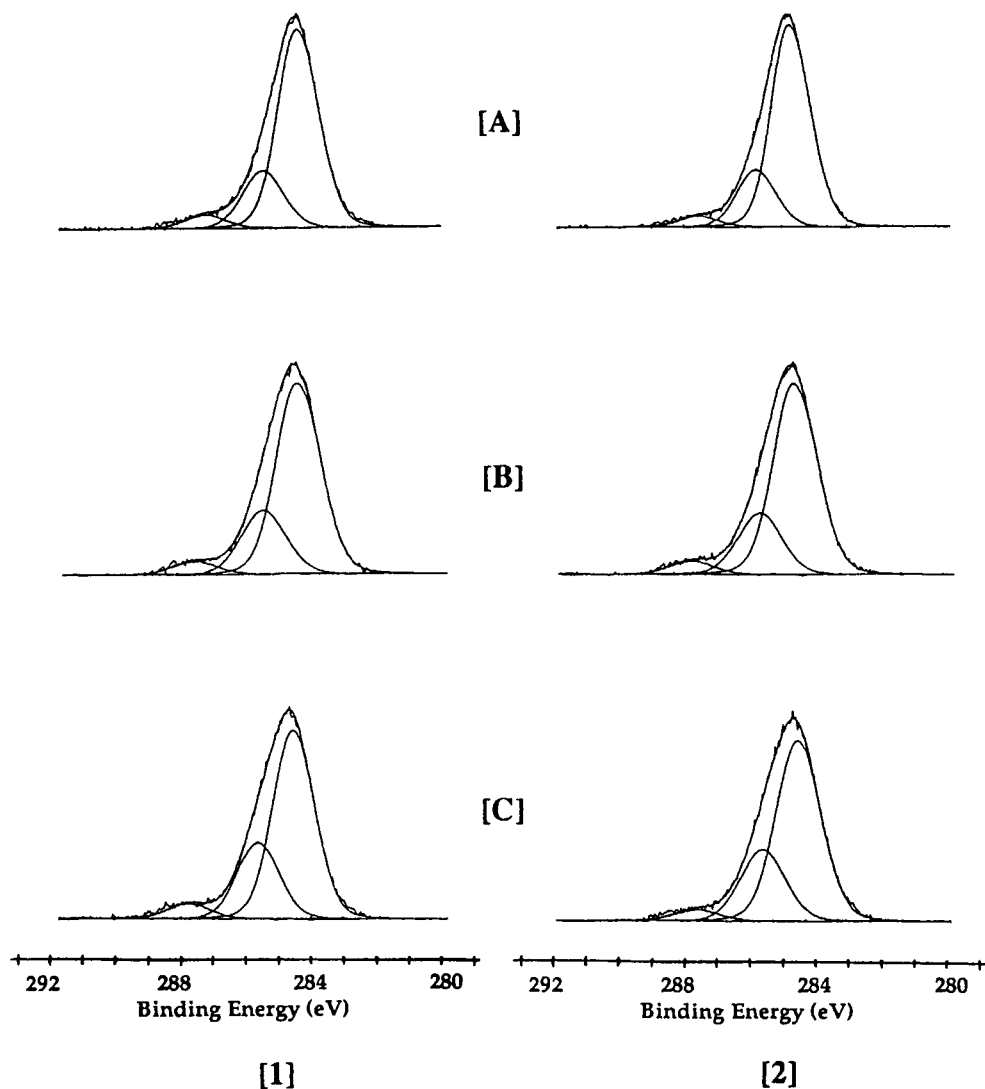


Figure 4 C(1s) spectra obtained from substrate fracture surfaces prepared by applying (A) V-15, (B) V-25, and (C) V-40 on (1) clean EGS, and (2) oiled EGS.

Table I Relative Concentrations of Components Found in C(1s) Spectra of Curing Agents

Curing Agent	Substrate	C—H (%)	C—N (%)	—CON— (%)	N/C (%)
V-15	Theoretical	83.6	13.1	3.3	8.2
V-25	Theoretical	80.5	15.5	3.9	10.8
V-40	Theoretical	78.8	16.9	4.2	12.3
V-15 (observed)	Clean CRS	82.1	15.5	2.4	9.4
	Oiled CRS	83.1	14.3	2.6	7.9
	Clean EGS	73.9	21.2	4.9	13.7
	Oiled EGS	75.0	21.0	4.0	12.4
V-25 (observed)	Clean CRS	79.4	18.2	2.4	10.5
	Oiled CRS	79.6	18.0	2.4	10.3
	Clean EGS	71.5	23.6	4.9	18.3
	Oiled EGS	71.5	22.7	5.8	18.3
V-40 (observed)	Clean CRS	78.1	19.5	2.4	10.8
	Oiled CRS	78.3	19.3	2.4	10.3
	Clean EGS	67.3	27.3	5.4	19.7
	Oiled EGS	68.8	27.2	4.0	18.2

Take-off angle was 45°.

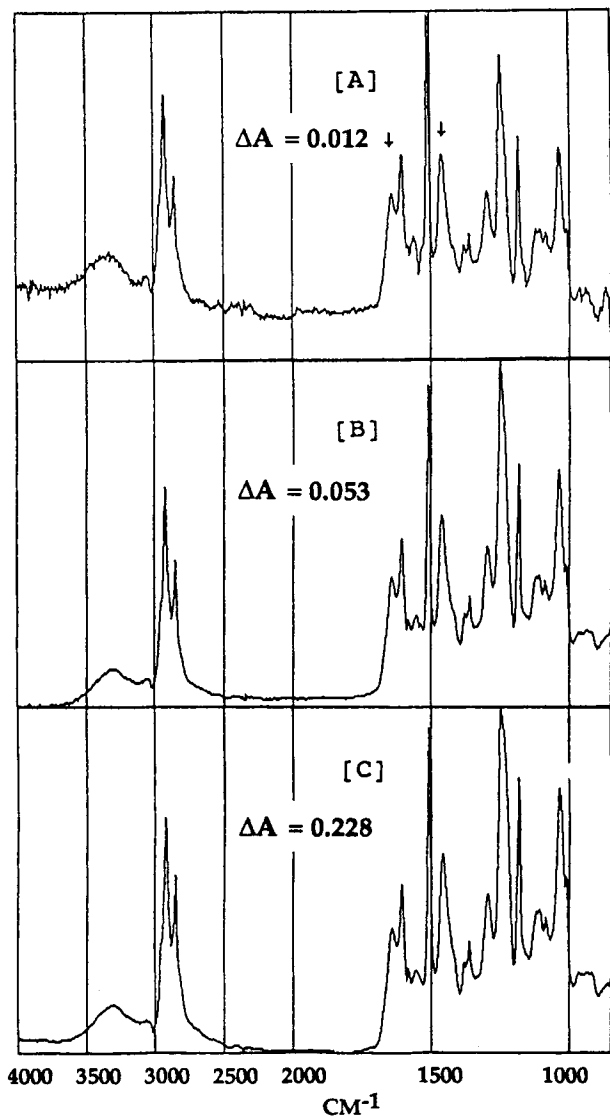


Figure 5 ATR difference spectra taken from the adhesive fracture surface of the specimen prepared by curing adhesive A on polished clean CRS using (A) Ge (60°), (B) KRS-5 (60°), and (C) KRS-5 (45°).

oil from the EGS surface. The similarities between Figure 4(B1) and 4(B2), and between Figure 4(C1) and 4(C2) also imply that the oil is displaced from the EGS surface by V-25 and V-40.

The oil-displacing behavior could also be observed from atomic concentrations obtained from the CRS and EGS fracture surfaces. Table I lists the relative concentrations of functional groups found on different CRS and EGS surfaces and theoretical values calculated from the curing agents. Few differences in N/C ratios and intensities under C—H, C—N, and amide peaks are detected between specimens prepared with clean and oiled CRS substrates, indicating that similar amounts of curing agents are

on clean and oiled CRS surfaces, and little oil was present near the CRS surfaces. Similar results could be obtained from clean and oiled EGS substrates.

It is worth mentioning that on all CRS and EGS specimens analyzed, small amounts of metal elements (from the metal substrates under the organic layers) are always detected indicating that the organics analyzed are close to the CRS and EGS surfaces and the conclusions drawn above are valid.

ATR Measurement

The ATR difference spectra (using clean IRE crystals as the references) taken from the adhesive fracture surfaces of the specimens prepared with ad-

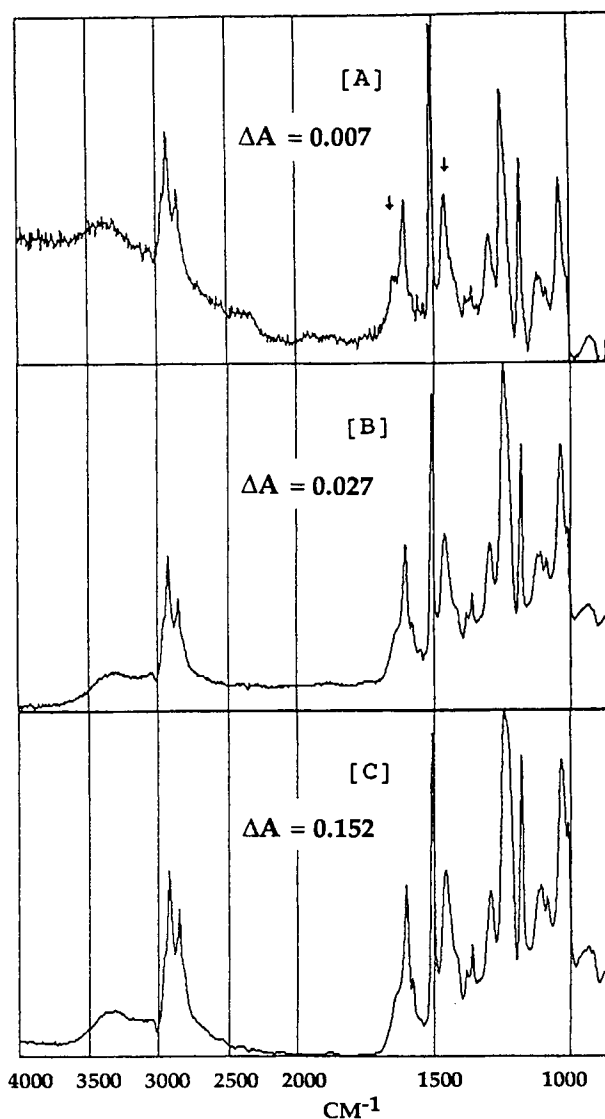


Figure 6 ATR difference spectra taken from the adhesive fracture surface of the specimen prepared by curing adhesive C on polished clean CRS using (A) Ge (60°), (B) KRS-5 (60°), and (C) KRS-5 (45°).

Table II Absorbance Ratios Calculated from ATR Spectra Obtained from Various Adhesive Fracture Surfaces

Adhesive	CRS Substrate	d_p	A(1645)/A(1510)	A(1458)/A(1510)
A	Clean	1	0.40	0.53
		2	0.39	0.59
		3	0.38	0.62
	Reoiled	1	0.40	0.67
		2	0.39	0.67
		3	0.43	0.72
B	Clean	1	0.31	0.49
		2	0.28	0.56
		3	0.31	0.62
	Reoiled	1	0.31	0.74
		2	0.28	0.67
		3	0.34	0.72
C	Clean	1	0.20	0.46
		2	0.18	0.52
		3	0.19	0.57
	Reoiled	1	0.22	0.82
		2	0.18	0.62
		3	0.23	0.66

d_p : 1-Ge (60°), 2-KRS-5 (60°), 3-KRS-5 (45°).

hesives A and C on the clean CRS surfaces using different IRE crystals are shown in Figures 5 and 6, respectively. The band near 1645 cm^{-1} is characteristic of the stretching vibration of amide groups in the curing agents. The band near 1458 cm^{-1} is due to the scissor vibration of $-\text{CH}_2-$ groups in the aliphatic oil and adhesives. The band near 1510 cm^{-1} is characteristic of aromatic ring stretching from the epoxy resin.

In order to understand the distribution of the functional groups as a function of the penetration depth, the ratios of the absorbances of bands near 1645 and 1458 cm^{-1} to the absorbance of the band near 1510 cm^{-1} are calculated. Assuming the refractive index of the epoxy film is 1.6, using eq. (3) and known refractive indices of the Ge ($n = 4.0$) and KRS-5 ($n = 2.38$), the d_p 's of Ge (60°), and KRS-5 (45°) are near 0.34 , 0.81 , and $2.01\text{ }\mu\text{m}$, respectively, for an infrared radiation with λ near $6.62\text{ }\mu\text{m}$ (1510 cm^{-1}). The absorbance ratios obtained are listed in Table II.

The results of Table II indicate that the adhesive A specimen has the most amide and aliphatic $-\text{CH}_2-$ groups near the CRS surface, and the adhesive C specimen has the least, indicating that more amide containing aliphatic chains are near the CRS surface for the adhesive A specimen than the adhesives B and C specimens. These trends are shown more clearly in Figures 7 and 8. It was shown from previous results that the V-15 curing agent had more amide groups than V-25 and V-40, and V-40 had the least amide groups.⁹ The difference in amounts of curing agents used and difference in amide contents result in these differences.

It was also observed that the adhesive layers farther away from the CRS surface contain more $-\text{CH}_2-$ groups than those closest to the CRS surface. Figure 8 shows that the A(1458)/A(1510) ratios increase with an increase in d_p for all three different adhesive specimens, indicating that more $-\text{CH}_2-$ groups are present farther away from the adhesive/CRS interfaces.

It is worth mentioning that although Carlsson and Wiles indicated that the force applied on the polymer film against an IRE crystal could affect the

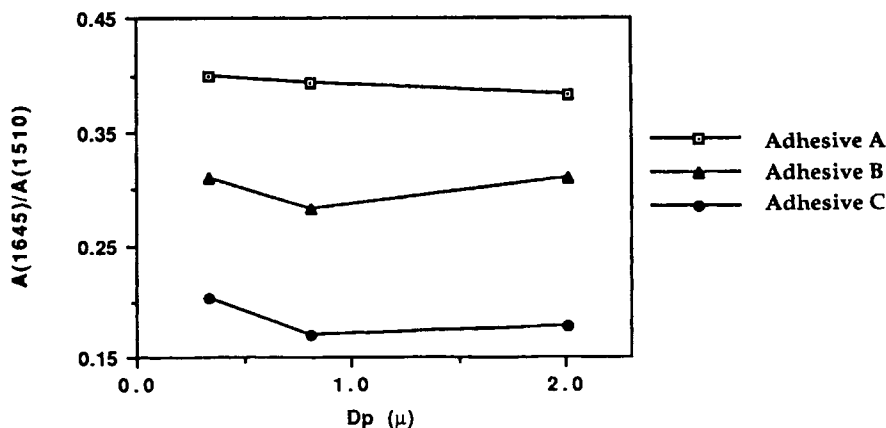


Figure 7 The ATR absorbance ratios of A(1645)/A(1510) obtained from specimens prepared by curing adhesives on polished clean CRS.

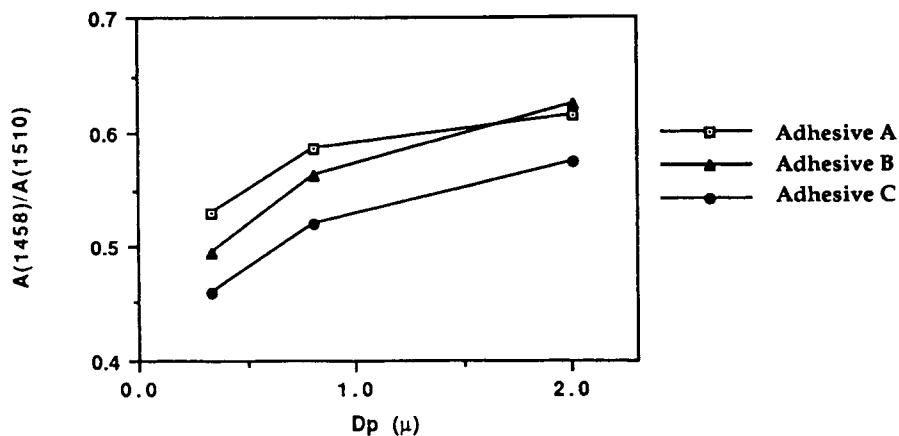


Figure 8 The ATR absorbance ratios of $A(1458)/A(1510)$ obtained from specimens prepared by curing adhesives on polished clean CRS.

intensity measured and the absorbance ratio calculated in the ATR spectrum, no such effect was observed in this study.⁴⁹ In addition, different methods of drawing baselines have no influence on the trends of calculated absorbance ratios either.

The ATR spectra taken from the adhesive fracture surface of the specimen prepared with adhesive A on the oiled CRS using different IRE crystals are shown in Figure 9. The ratios of $A(1458)/A(1510)$ calculated are shown in Table II and Figure 10. By comparing the ratios of $A(1458)/A(1510)$ shown in Figures 8 and 10, it is determined that the ratios of $A(1458)/A(1510)$ increase in the presence of oil because of aliphatic oil absorbed into adhesive A. However, the relatively similar values of $A(1458)/A(1510)$ ratios between different penetration depths imply that the oil is relatively evenly distributed in the adhesive layer analyzed. The oil probably penetrates into adhesive A as deep as 2.0 μm (see Fig. 10).

From previous XPS analyses, it was also known that there was no oil detected on the substrate fracture surfaces of specimens prepared with adhesive A on oiled CRS substrates.⁹ From these observations, it was concluded that the oil is effectively absorbed into adhesive A from the oiled CRS surface.

A different oil distribution was observed from the specimen prepared with adhesive C on the oiled CRS surface. The ATR spectra taken from the adhesive fracture surface of the specimen prepared with adhesive C on the oiled CRS substrate using different IRE crystals are shown in Figure 11. The ratios of $A(1458)/A(1510)$ are also shown in Table II and Figure 10. From a comparison of Figure 8 and 10, it is determined that the ratios of $A(1458)/A(1510)$ calculated from different penetration depths all increased significantly. The greatest increase of the

$A(1458)/A(1510)$ ratio is observed from the spectrum taken with Ge (60°), indicating that oil is mostly present in a surface layer with thickness about 0.34 μm for the specimen prepared with adhesive C on the oiled CRS substrate. As a result, the oil does not penetrate into adhesive C as deep as into adhesive A, that is, adhesive C does not absorb oil from the CRS surface as effectively as adhesive A. These results are consistent with those obtained previously, where a layer of oil was detected on the substrate fracture surface of the specimen prepared with adhesive C on an oiled CRS substrate.⁹

The $A(1458)/A(1510)$ absorbance ratios calculated from the ATR spectra taken from the adhesive fracture surface of the specimen prepared with adhesive B on an oiled CRS surface are intermediate between those of specimens prepared with adhesives A and C (see Table II and Fig. 10). The magnitude of change of $A(1458)/A(1510)$ from adhesive B specimen is between those of adhesives A and C specimens (see Fig. 10). This indicates that the effectiveness of oil absorbed by adhesive B is intermediate between those of adhesives A and C.

In the previous article it was shown that the curing reaction of adhesives still occurred in the presence of oil.⁹ This was also observed from the ATR spectra taken from the specimens prepared with oiled CRS substrates (Figs. 9, 11). The absence of a significant absorption band near 910 cm^{-1} , characteristic of the epoxide group, in Figures 9 and 11 implies that the curing reaction proceeds to a great extent even in the presence of the oil.

The oil absorbed by the adhesives could also be observed from the absorption bands near 2920 cm^{-1} , which is characteristic of C—H stretching in the aliphatic chains. The ratios of $A(2920)/A(1510)$ obtained from the ATR spectra taken from the ad-

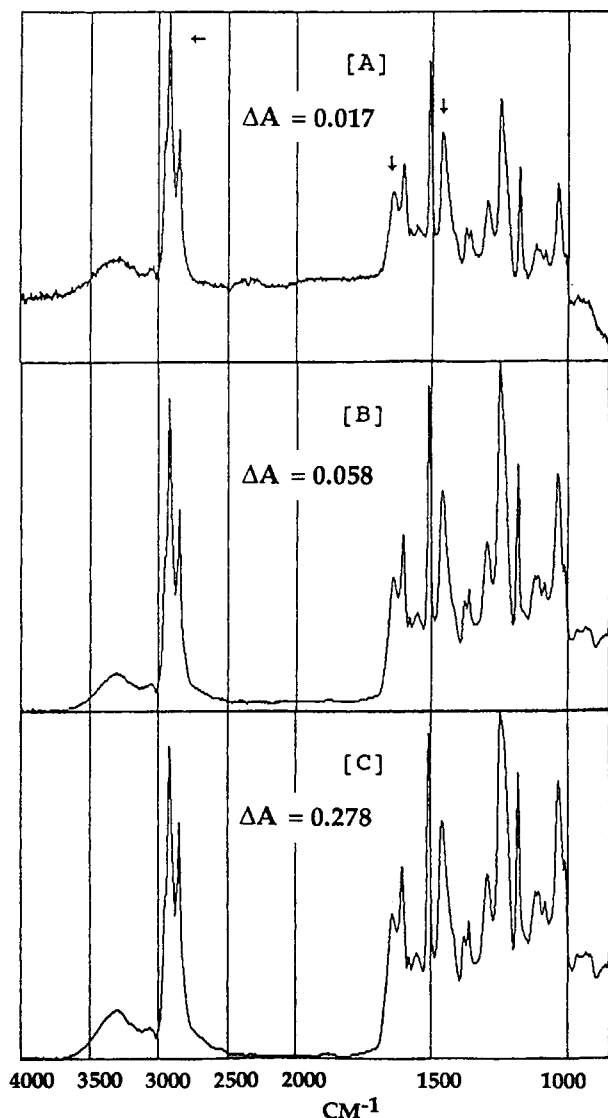


Figure 9 ATR difference spectra taken from the adhesive fracture surface of the specimen prepared by curing adhesive A on oiled CRS using (A) Ge (60°), (B) KRS-5 (60°), and (C) KRS-5 (45°).

hesive fracture surface of the specimen prepared with adhesive A on oiled CRS are 1.20, 0.92, and 0.90 using Ge (60°), KRS-5 (60°), and KRS-5 (45°), respectively. Because d_p is dependent on the wavelength, d_p 's for an infrared radiation with wavenumber near 2920 cm^{-1} are 0.17, 0.42, and $1.04\text{ }\mu\text{m}$ for Ge (60°), KRS-5 (60°), and KRS-5 (45°), respectively. Apparently, the oil is more abundant in the $0.17\text{ }\mu\text{m}$ layer than in the 0.42 and $1.04\text{ }\mu\text{m}$ layers on the adhesive fracture surface. Although it is shown that the oil is effectively absorbed deep into adhesive A, it is reasonable that the adhesive layer

closest to the CRS surface contains more oil than that farther away.

The ratios of $A(2920)/A(1510)$ calculated from the ATR spectra taken from the adhesive fracture surface of the specimen prepared with adhesive C on the oiled CRS substrate are 1.46, 0.89, and 0.73 from Ge (60°), KRS-5 (60°), and KRS-5 (45°), respectively. Most of the oil was just present on the thin adhesive fracture surface layer. The results obtained here are consistent with the results obtained from the ratios of $A(1458)/A(1510)$. Therefore, from absorbance ratios calculated from different absorption bands, the distribution of oil in the adhesive can be obtained.

The results obtained from the ATR experiments seem to be contradictory to the results obtained from the XPS experiments, in which V-25 and V-40 curing agents are proven to be as effective as V-15 in displacing the oil from both the CRS and EGS surfaces. This discrepancy is believed to partly result from the different amounts of curing agents used in the adhesives and mainly from different curing rates of the adhesives prepared with these three curing agents. For stoichiometric balance, V-15, V-25, and V-40 were added as 120, 90, and 75 phr, respectively. Because DGEBA is not compatible with the oil, the amount of oil absorbed by the epoxy adhesive would depend only on the curing agent. Increasing levels of curing agents would, therefore, allow more available curing agents to assimilate the oil.

Moreover, the gel times of V-25 and V-40 cured epoxy resins are near 45–60 min, which are shorter than the gel time of V-15 cured epoxy resin (1–2 h). Therefore, the oil and V-15 have more time to diffuse mutually into each other, that is V-15 cured adhesive has longer time to absorb and assimilate the oil from the metal surfaces than V-25 and V-40 cured adhesives. It was shown previously that V-25 and V-40 could displace the oil from either CRS or EGS surfaces effectively within 48 h. This fact indicates that V-25 and V-40 “alone” could displace the oil from both oiled CRS and EGS surfaces if enough diffusion time is available, while V-25 and V-40 cured “adhesives” could not because of a faster curing reaction resulting in insufficient time allowed for mutual diffusion of the oil and the curing agent.

In order to determine the amounts of oil absorbed by the epoxy adhesives during cure, the following experiment was performed. Oil was placed on top of the different epoxy adhesive films during cure and then the amounts of oil absorbed by adhesive films were weighed and determined after cure. It is found that the oil with thicknesses about 29, 15, and $15\text{ }\mu\text{m}$ were absorbed by adhesives A, B, and C per cm^2

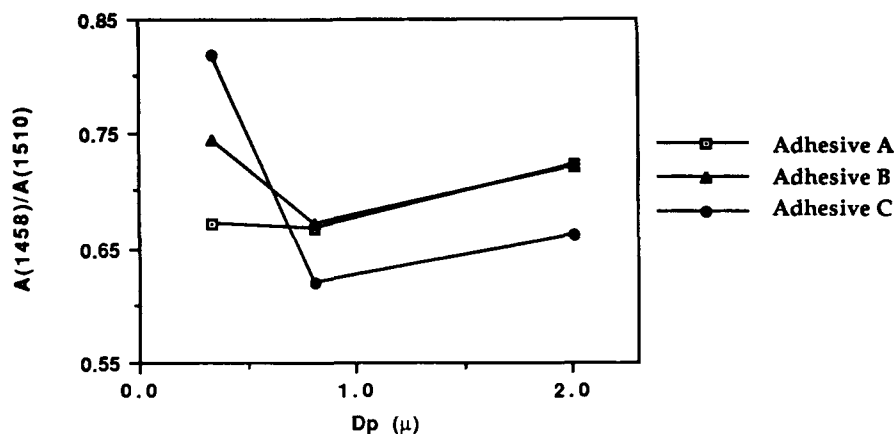


Figure 10 The ATR absorbance ratios of A(1458)/A(1510) obtained from specimens prepared by curing adhesives on oiled CRS.

with the standard deviation about $2 \mu\text{m}$, respectively. In spite of the different amounts of curing agents added in the epoxy resins, adhesive A absorbs about twice as much oil as adhesives B and C, but adhesives B and C absorb nearly the same amount of oil during cure. This implies that the speed of curing may significantly affect the oil-absorbing behavior of such adhesive systems.

In the case of oiled EGS specimens, ATR results indicate that significant amounts of oil are present in the $0.3 \mu\text{m}$ thick layer of adhesive A near the adhesive/EGS interface. Appreciable amounts of oil on the fracture EGS surface could be observed. This implies that adhesive A absorbs oil from the oiled CRS surface better than from the oiled EGS substrate, which is consistent with the previous analyses of fracture metal surfaces.¹⁰ In trying to obtain good adhesive bond with the oiled EGS substrates, the adhesive/oiled EGS system cured under pressure was tested.

Effect of Pressure

Pressure applied during cure could provide better wetting and spreading of the adhesive, help the adhesive fill in the porosity of the rough substrate, minimize imperfections resulting from the volatile products generated during cure, and retain the uniformity of the bond line by forcing the excess adhesives out of the joint.⁵⁰ To study the effect of applied pressure on the oil-displacing behavior of the epoxy adhesive, adhesive A cured against oiled EGS substrates under pressure-free and pressurized conditions were analyzed.

In this experiment a thick oil layer, about $70 \mu\text{m}$, was coated on the EGS surfaces first. Then speci-

mens were prepared using adhesive A cured against these heavily oiled EGS substrates both freely and under a pressure of 14 psi. The cured specimens were fractured in liquid nitrogen to expose the substrate and adhesive fracture surfaces that could be analyzed by using XPS and ATR, respectively.

It is shown that less aliphatic groups are present on the adhesive fracture surface of the sample cured under pressure than those of the sample cured freely. The ratios of A(1458)/A(1510) obtained from ATR spectra are shown in Figure 12. The ratios of A(1458)/A(1510) from pressure-free cured sample are 2.29 from Ge (60°), 1.03 from KRS-5 (60°), and 0.91 from KRS-5 (45°). The ratios of A(1458)/A(1510) from a sample cured under 14 psi were 0.73 from Ge (60°), 0.63 from KRS-5 (60°), and 0.75 from KRS-5 (45°). The aliphatic groups, due to unabsorbed oil, are mostly present in the layers less than $0.34 \mu\text{m}$ thick near the adhesive/EGS interface from the free-cured sample, but are evenly distributed in the bonding interface of pressure-cured specimen. In addition, the oil is seen on both substrate and adhesive fracture surfaces of free-cured specimens. But this is not observed from the specimen cured under pressure. As a result, the oil is effectively absorbed into the adhesive as deep as $2 \mu\text{m}$ when the specimen was cured under a pressure of 14 psi. It is evident that the pressure applied during the curing process could facilitate the epoxy adhesive to absorb the oil from the oiled EGS surface.

The beneficial effect of pressure on oil absorbing is also confirmed by XPS analysis. The XPS atomic concentrations obtained from the substrate fracture surface of the specimen cured under pressure are 66.9% C, 24.7% O, 4.8% N, and 3.6% Zn at 15° take-off angle. The N is from the curing agents in the

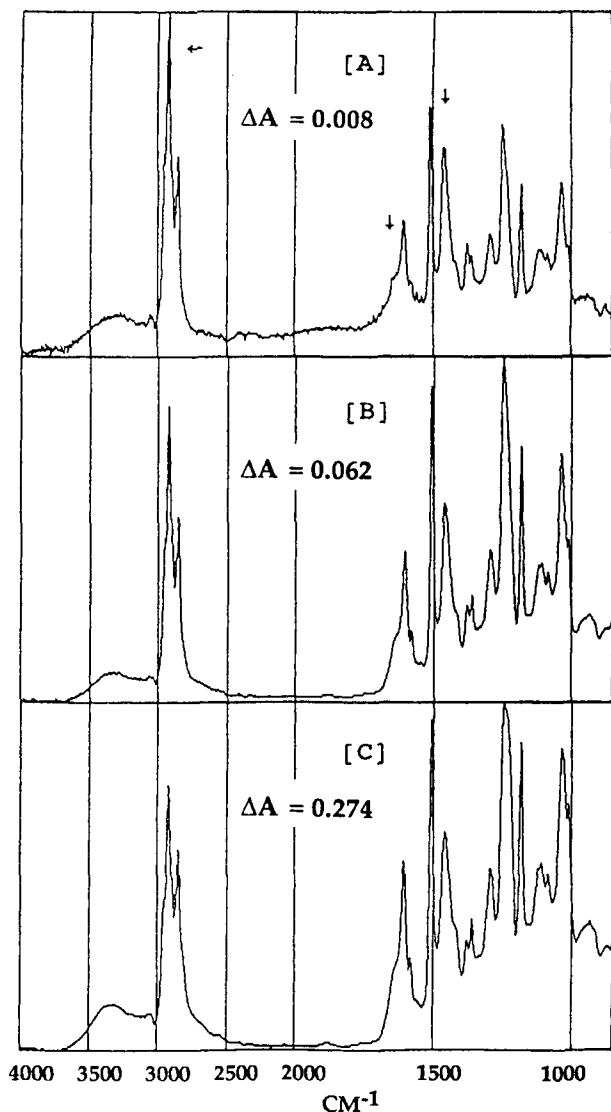


Figure 11 ATR difference spectra taken from the adhesive fracture surface of the specimen prepared by curing adhesive C on oiled CRS using (A) Ge (60°), (B) KRS-5 (60°), and (C) KRS-5 (45°).

adhesive and Zn is from the EGS substrate. The N/C ratio is 0.071, which is close the N/C ratio of the bulk adhesive A (0.063). This indicates that little oil was left on the EGS surface. Accordingly, the pressure applied during cure greatly facilitates the oil-absorption capability of adhesive A on the oiled EGS substrates.

It is believed that the pressure applied would force the excess adhesives and oil out of the bonding interface and facilitate the mutual diffusion between the oil and the adhesive. It was indicated by Tang et al. that the pressure applied during cure could

facilitate the resin flow during the curing process.⁵¹ Without using the pressure, the increase in viscosity during cure would retard the resin flow and inhibit the oil absorption.

CONCLUSIONS

A simple XPS experiment verified that V-15, V-25, and V-40 could displace the oil from the CRS and EGS substrates within 48 h, but DGEBA resin alone could not displace the oil from the CRS surface. The miscibility between the resin and the oil could play an important role in determining the effectiveness of the resin in displacing the oil.

The results of ATR measurements indicated that the oil could be absorbed into adhesive A as deep as $2\ \mu\text{m}$. But the oil was mostly present in the $0.3\ \mu\text{m}$ adhesive layer near the CRS/adhesive interface for specimens prepared with adhesives B and C. Accordingly, adhesive A was more effective in displacing the oil from CRS surfaces than adhesives B and C. In addition, the oil could be absorbed by the adhesive more easily from the CRS surface than from the EGS surface. However, the oil-absorption power of the adhesives can be greatly enhanced when the adhesive systems cure under pressure.

It is proposed that the oil-absorbing ability of the adhesive systems used is related to the amounts of curing agents added and the competitions between the oil-diffusion rates and the curing rates in the adhesives.

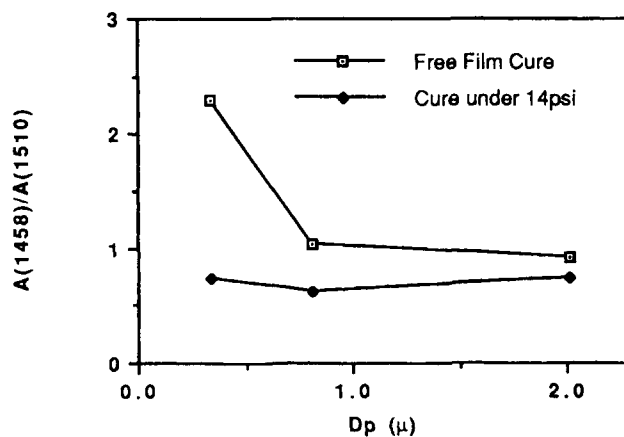


Figure 12 The ATR absorbance ratios of A(1458)/A(1510) obtained from specimens prepared by curing adhesive A on oiled EGS under different conditions.

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Received March 21, 1994

Accepted June 27, 1994