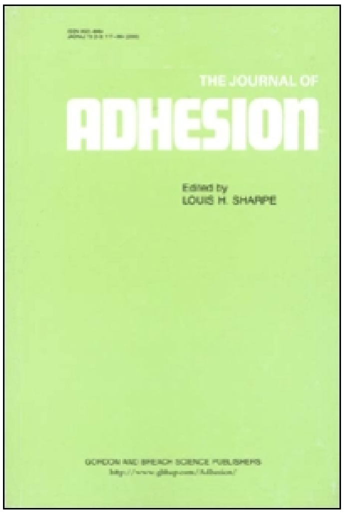

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Wells, J. C. , Thompson, B. T. and Dillard, J. G.(1995) 'The Effect of Surface Preparation and Exposure Environment on the Bond Failure Processes in Adhesively Bonded Sheet Molded Composite (SMC)', The Journal of Adhesion, 48: 1, 217 — 234

To link to this Article: DOI: 10.1080/00218469508028163

URL: http://dx.doi.org/10.1080/00218469508028163

J. Adhesion, 1995, Vol. 48, pp. 217–234
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The Effect of Surface Preparation and Exposure Environment on the Bond Failure Processes in Adhesively Bonded Sheet Molded Composite (SMC)

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(Received January 19, 1994; in final form August 9, 1994)

The durability of adhesively-bonded composites has been investigated using a wedge-type specimen. Polyester-resin, fiberglass sheet molded composite (SMC) was bonded with a commercial two-part polyurethane adhesive. The SMC composite received one of four different surface preparations: no treatment, abrasion, priming, or abrasion and priming. The wedge test was used to study the durability of the samples which were exposed to air and to the vapor above water, concentrated ammonium hydroxide, or methanol at 60°C. The crack length was measured during the experiments. The crack growth rate as a function of surface treatment varied in the manner: untreated $\approx$ abraded $>$ primed $\approx$ abraded and primed. The crack growth rate as a function of vapor changed in the manner: methanol $>$ ammonium hydroxide $>$ water $\approx$ air. The samples were removed at the conclusion of the test and the failure mode was determined visually, by scanning electron microscopy (SEM), and by X-ray photoelectron spectroscopy (XPS). Initial insertion of the wedge resulted in substrate failure (delamination of the composite). Exposure of untreated and abraded samples under stress to the test vapors promoted adhesive failure. Primed and abraded/primed samples under stress and exposed to methanol vapor debonded *via* cohesive processes.

KEY WORDS Composite bonding; durability; surface analysis; surface preparation; environmental exposure.

INTRODUCTION

Adhesively-bonded composites are widely used because of useful structural properties, ease of part preparation and low cost.[1] Composites are important structural components in the automotive, aerospace and marine industries.[2] Knowledge of the behavior of bonded structures in the presence of various vapors, cleaning solvents, and other fluids is of interest in developing an understanding of the chemical factors that influence durability.

Carre and Schultz[3] studied peel-type debonding processes for aluminum-elastomer specimens submerged in alcohols. Debonding of samples prepared using

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* Corresponding author.

sealed anodized aluminum was interfacial while failure occurred *via* a cohesive process for phosphated aluminum adherends. Interfacial failure resulted from a decrease in polar and dispersion type physical interactions at the interface. Cohesive failure was attributed to the loss of physical and chemical interactions. The decrease of physical interactions was the primary contributor to cohesive failure.

Cognard[5-7] has investigated the durability of adhesively-bonded steel in liquid and gaseous environments. No significant difference in the initial crack length or crack growth was noted when comparing the influence of the liquid or vapor environment. A change in failure mode from cohesive to interfacial failure was found for tests conducted in all liquids. Cognard[7] indicated that the failure behavior could be correlated with the permittivity of the liquid. It was also suggested that the influence of various liquids on the adhesive bond was related to the acid-base properties of the liquid (or gas), and that initial bonds between adherend and adhesive were affected by the chemical characteristics of the liquid (or gas) environment. A strain-induced reactivity was suggested to account for the observations.

In this investigation the goal was to examine the influence of gaseous vapors on the rate of debonding and on the mode of failure for adhesively-bonded composites. The effects of different environments and surface treatments on durability were studied using the wedge test.[4-7] The surface treatments were selected to represent a range of treatments where the surface chemistry was altered[8,9] and to correspond to treatments in common practice. The sheet molded composite (SMC) was a polyester resin, glass-fiber-reinforced composite. The bulk and surface properties of this type of SMC have been studied.[8,9]

EXPERIMENTAL

Panels of phase α-SMC, measuring 2.5 x 15.2 x 0.5 cm (1″ x 6″ x 0.200″), were obtained from Ashland Chemical Co, Columbus, OH. The SMC adherends received one of four different surface treatments before bonding: no treatment, surfaces wiped with a Kim-Wipe® tissue; abrasion with a methylene chloride soaked Scotch-Brite® pad; priming with a diisocyanate-based primer in methylene chloride (Ashland 6036; Ashland Chemical Co, Columbus, OH); or abrasion and then priming with Ashland 6036 primer. The composite panels were bonded with a two-part adhesive composed of Ashland 6600 urethane adhesive and 6611 curing agent (Ashland Chemical Co., Columbus, OH). The bond thickness was maintained by inserting 0.1 cm (0.037″) Teflon tabs at each end of the specimens. Non-bonded areas of 2.5 cm (1.0″) on one end and 1.25 cm (0.5″) on the opposite end of the sample were maintained so that the bonded area was approximately 2.5 x 11.4 cm (1″ x 4.5″). The adhesive was cured for one hour at room temperture in air and for one hour at 150°C in a forced air oven.

A wedge measuring 2.5 x 2.5 x 0.4 cm (1″ x 1″ x 0.16″) was inserted 0.64 cm (0.25″) into the bonded composite panel in the 2.5 cm (1.0″) non-bonded region of the specimen to create a crack. Wedge insertion was accomplished by placing the sample and wedge in a vice and closing the vice. The samples were then placed in a closed test tube (Fig. 1) and exposed at 60°C to the vapors above water, concen-

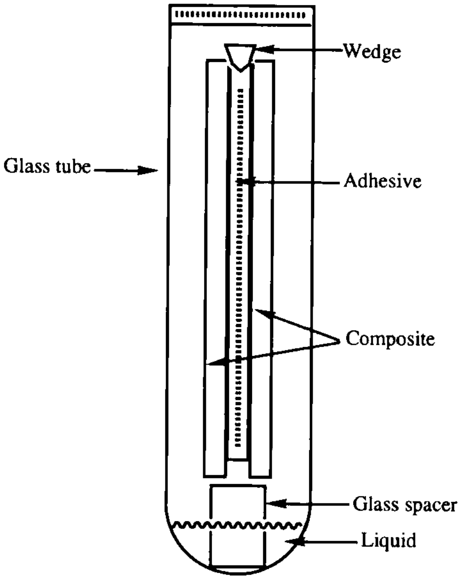


FIGURE 1 Sample Tube for Durability Experimental Tests.

trated ammonium hydroxide, and methanol. Samples were also tested in air at 60°C. For primed samples tested in methanol vapor, five samples were used. For all other experiments, three samples were tested in each vapor. Crack length was measured as a function of time. Crack length was measured as the distance from the contact point of the wedge with the sample to the end of the crack. The position of the crack was determined visually. Crack length on each side of the specimen was measured and the average of the two values taken as the crack length at that time. The crack growth curves show average crack lengths for the replicate number of samples for each type of specimen. The variation in crack length among each group of samples was: as received (no surface treatment), ± 0.6 cm; abraded, ± 0.6 cm; primed, ± 1.0 cm; abraded/primed, ± 0.8 cm. Samples which debonded during the test were removed from the test atmosphere and stored in a desiccator. At the end of the test, samples which had not debonded were force failed.

The surfaces of the failed specimens were characterzied visually, and *via* scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). SEM photomicrographs were obtained using an ISI SX-40 scanning electron microscope. Before analysis, the samples were cleaned by spraying the surface with helium and then the surface was lightly sputter-coated with gold. XPS measurements were made using a Perkin-Elmer PHI model 5400 X-ray photoelectron spectrometer. Photoionization was initiated using Mg K_α radiation ($h\nu = 1253.6$ eV), and the binding energy scale was calibrated by setting the C 1s hydrocarbon carbon peak at 285.0 eV.[9,10] The elemental compositional data are the average of measurements on two different areas of a specimen surface for two different samples. For specimens where it was difficult to determine the failure mode, additional measurements were made on several spots on several samples. The reproducibility of the measurements is ±15%.

RESULTS AND DISCUSSION

Samples Tested in Air, Water and Ammonium Hydroxide

The changes in crack length as a function of time for samples tested in air, water, and ammonium hydroxide are shown in Figures 2–4, respectively. The general behavior is that crack growth occurs for a period of time and eventually stops. The respective crack growth behavior for non-treated and abraded samples and for primed and abraded/primed specimens was similar. However, the extent of crack growth was greater for non-treated and abraded samples. The respective crack growth for abraded-, primed-, and abraded/primed-bonded samples was similar for specimens exposed to air, water, or ammonium hydroxide. However, in ammonium hydroxide, samples prepared using non-treated composite showed the greatest crack growth. That crack growth occurs faster and stops at a greater crack length for the untreated and abraded samples compared with primed and abraded/primed samples suggests that primer increases bond durability. Abrasion does not appear to increase the durability of the bond significantly.

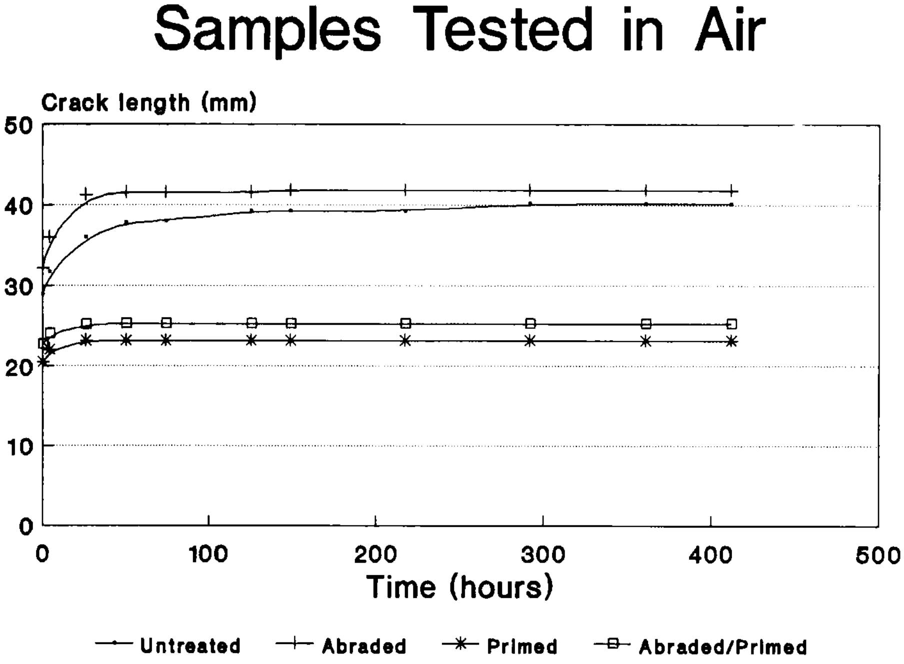


FIGURE 2 Crack Growth Behavior for Samples Tested in Air.

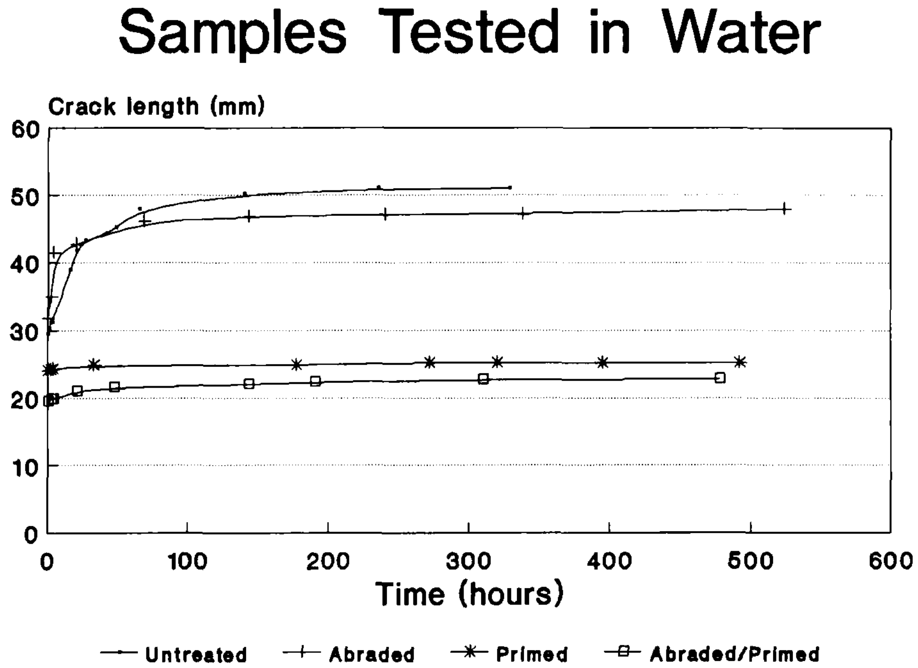


FIGURE 3 Crack Growth Behavior for Samples Tested in Water Vapor.

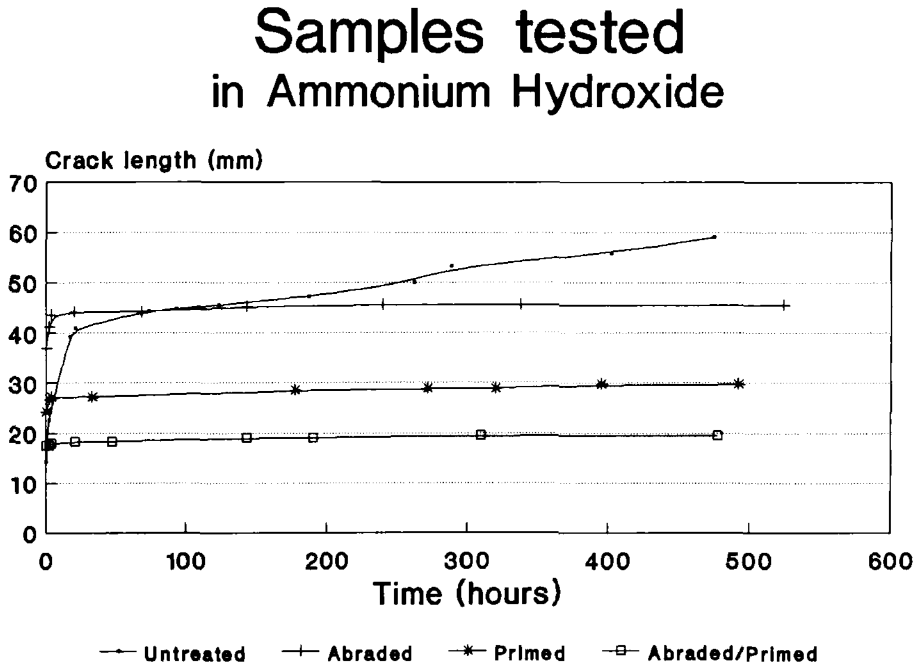


FIGURE 4 Crack Growth Behavior for Samples Tested in Ammonium Hydroxide.

After failure, the samples were examined visually to determine the failure mode. For non-primed samples, three different areas of failure were noted. Photographs showing representative failure surfaces for samples having had the treatments: non-treated, abraded, and primed, tested in water vapor are shown in Figure 5 to illustrate the changing nature of the failure process as a function of the surface treatment. Failure initiated by insertion of the wedge (left portion of the figures) occurred within the composite (substrate failure/delamination). The smooth area adjacent to the delamination region (toward the right of the delamination region) in the non-treated and abraded samples shows that failure occurs at the SMC-adhesive interface (adhesive failure) upon exposure to water vapor. The debonded area in the lower region of the specimens (right portion) shows that the

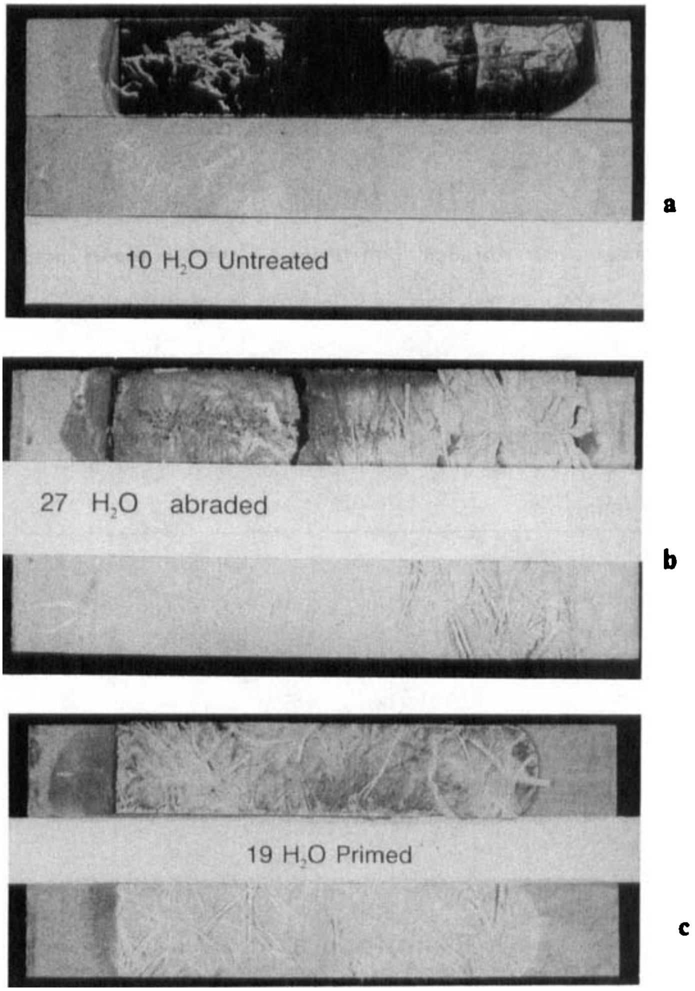


FIGURE 5 Failed Sample Specimens: Tested in Water Vapor: (a) non-treated sample surface; (b) abraded sample surface; (c) primed sample surface.

failure mode was substrate failure/delamination in the area where the samples were force failed. The region corresponding to adhesive failure is larger for non-treated samples than for samples bonded following abrasion or priming (see Fig. 5). Abraded/primed samples behaved in a manner similar to that for primed specimens and exhibited only substrate failure/delamination over the entire debonded region.

Scanning electron microscopy was used to characterize the failure mode better. Emphasis was placed on investigating the region where failure occurred due to the combined effects of stress and exposure to the gaseous environment. Non-bonded SMC samples that had been treated using the four surface preparations were studied in the initial characterization of the surfaces. Figure 6 shows photomicrographs of the composite following surface preparation using the four surface treatments. The as-received, non-treated surface (Fig. 6a) is relatively smooth with impressions of the sub-surface fibers showing in the photomicrograph. Dust particles are also visible on the untreated surface. The abraded surface (Fig. 6b) has a roughened appearance. The irregularities in the surface arise from the abrasive action of the Scotch-Brite® pad and the action of the solvent, methylene chloride. Fibers are not evident on the surface following the abrasion treatment. The primed (Fig. 6c) and abraded and primed (Fig. 6d) surfaces have a similar appearance. Each surface is relatively smooth and exhibits a few raised features as a result of the application of the primer.

Figure 7 presents photomicrographs of failure surfaces for a specimen prepared using as-received, non-treated SMC that was exposed to water vapor. These photomicrographs were taken in the region where the sample was judged by visual observation to fail at the interface. The smooth composite surface (Fig. 7a) and the smooth adhesive surface (Fig. 7b) support the notion that the sample failed interfacially. This result is typical of the findings obtained for other failed surfaces in regions characterized as adhesive failure.

A representative photomicrograph from an area of substrate failure for an abraded sample tested in water vapor is shown in Figure 8. Features characteristic of composite are present on both the SMC-side failure surface (Fig. 8a) and on the corresponding adhesive-side failure surface (Fig. 8b).

X-ray photoelectron spectroscopy was used to elucidate further the failure mode. Figure 9 shows the carbon 1s spectra obtained for five sample surfaces. Figure 9a is a spectrum for cured adhesive. The spectrum has two distinct peaks, the C—H/C—C hydrocarbon peak at 285.0 eV and a C—N/C—O peak at 286.4 eV. The C 1s spectrum for untreated, as-received SMC is shown in Figure 9b. The C—H/C—C photopeak, binding energy 285.0 eV, is the most significant feature in this spectrum. The photopeak at higher binding energy arises from the polyester functionality at the composite surface. The spectrum in Figure 9c was obtained in an adhesive-failure region for the adhesive-side failure surface of a sample prepared using as-received, non-treated SMC, tested in water vapor. In this spectrum, the C—N/C—O photopeak intensity is much smaller than that in Figure 9a. The lower C—N/C—O intensity indicates a reduced concentration of adhesive on the surface. This result suggests that composite constituents may be present on the surface and that failure is not completely adhesive but is likely mixed-mode.

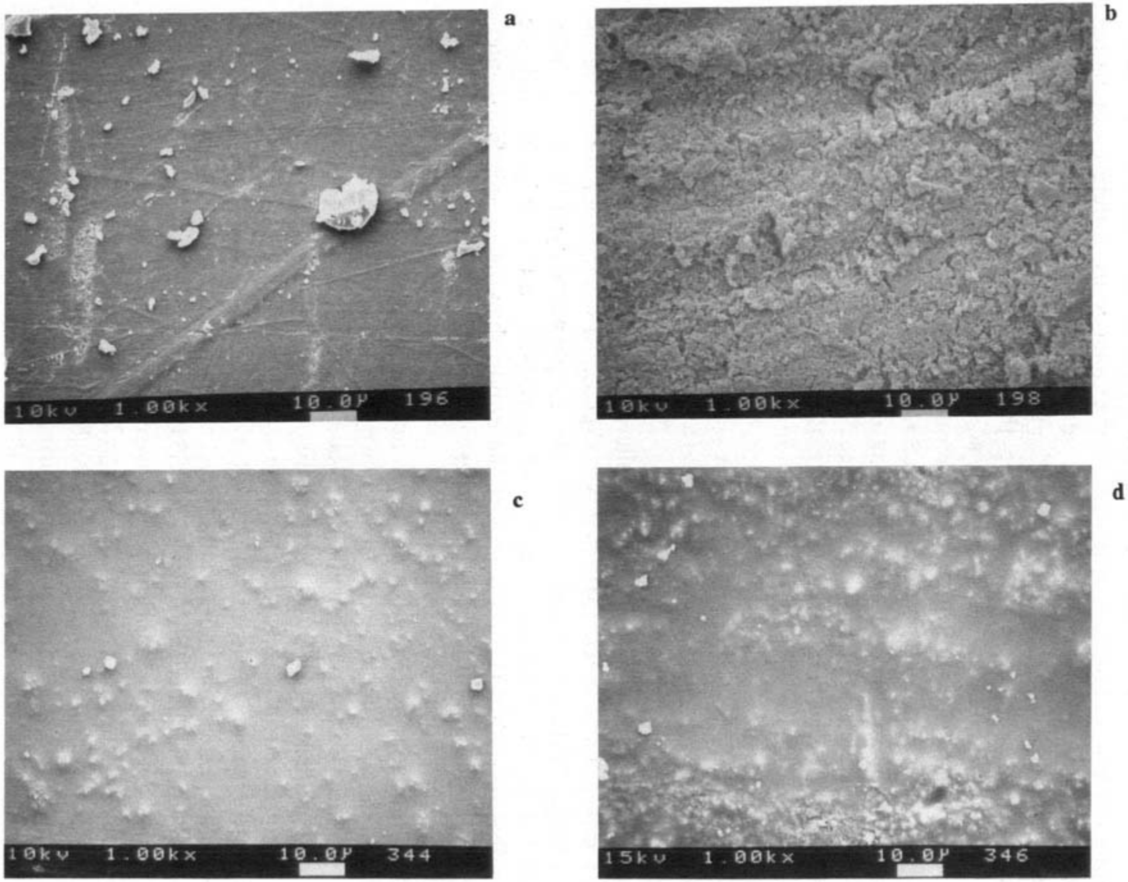


FIGURE 6 Scanning Electron Photomicrographs-Surface Treatments for SMC (a) as received, non-treated; (b) abraded; (c) primed; (d) abraded and primed.

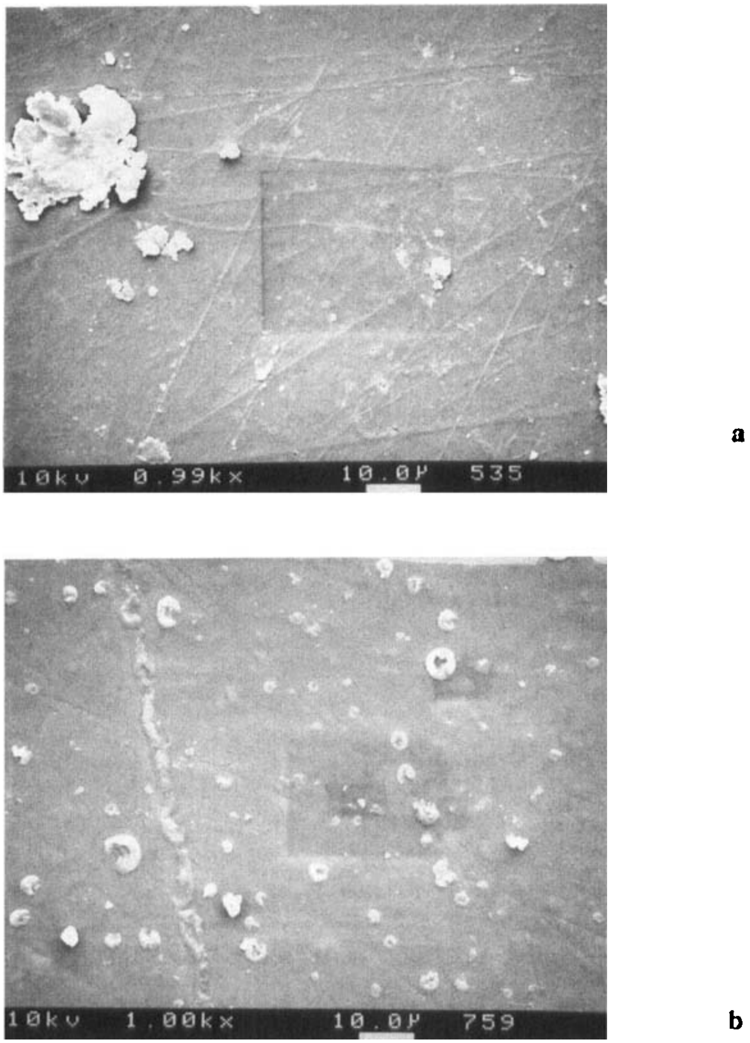


FIGURE 7 Scanning Electron Photomicrographs-Failure Surfaces-As-received, Non-treated SMC: Tested in Water Vapor (a) SMC-side failure surface; (b) adhesive-side failure surface.

Figures 9d and 9e are, respectively, spectra for the adhesive- and SMC-side failures for an untreated sample tested in air. Figure 9d, the adhesive side, exhibits C—H and C—N/C—O functionalities of approximately equal intensity. The spectrum in Figure 9e, the SMC side, is equivalent to that in Figure 9b, the spectrum for untreated, as-received SMC. That the adhesive-side failure is characterized as adhesive and the composite failure surface is evaluated to be SMC, clearly indicates that failure occurred at the adhesive-composite interface.

Substrate failure is a common failure mode for samples tested in these three vapors. Figure 10 shows the C 1s spectra obtained for abraded SMC (Fig. 10a) and

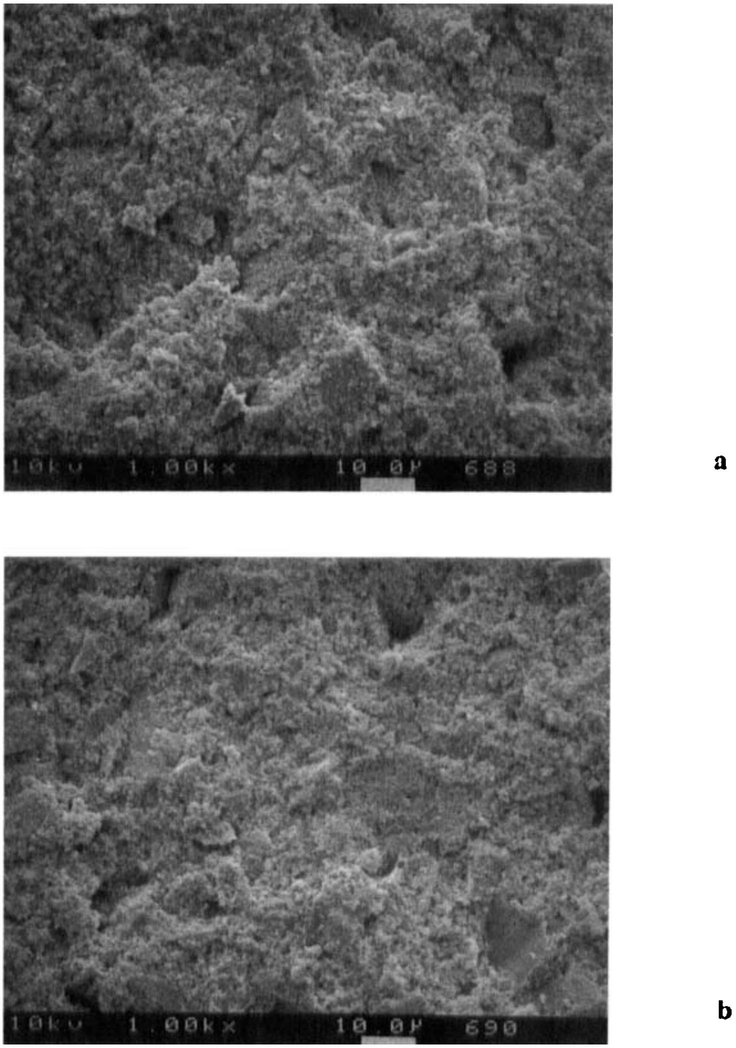


FIGURE 8 Scanning Electron Photomicrographs-Failure Surfaces-Abraded SMC: Tested in Water Vapor (a) SMC-side failure surface; (b) adhesive-side failure surface.

for a region of substrate failure (Fig. 10b) for a sample prepared with abraded SMC and tested in water. The spectra are equivalent and, in each spectrum, the principal C—H/C—C photopeak is evident and a small photopeak is noted at high binding energy, which is attributed to the ester functionality resulting from exposure of polyester matrix in the SMC. A summary of the failure modes for the samples tested in air, water and ammonium hydroxide environments is given in Table I. These failure mode results are based on the surface analysis results rather than on visual observations.

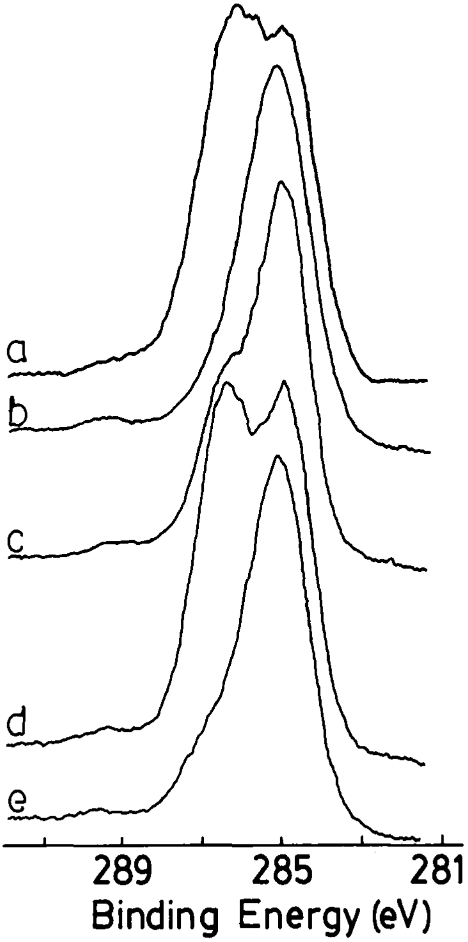


FIGURE 9 Carbon 1s X-ray Photoelectron Spectra (a) cured adhesive; (b) as-received, non-treated SMC; (c) adhesive-side failure surface; as-received, non-treated sample tested in water vapor (d) adhesive-side failure surface; as-received, non-treated sample tested in air (e) SMC-side failure surface; as-received, non-treated sample tested in air.

TABLE I
Failure Mode for Samples Tested in Air, Water, and Ammonium Hydroxide

Region	Untreated	Abraded	Primed	Abraded/Primed
wedge	substrate	substrate	substrate	substrate
vapor	mixed/adhesive	mixed/adhesive	substrate	substrate
force	substrate	substrate	substrate	substrate

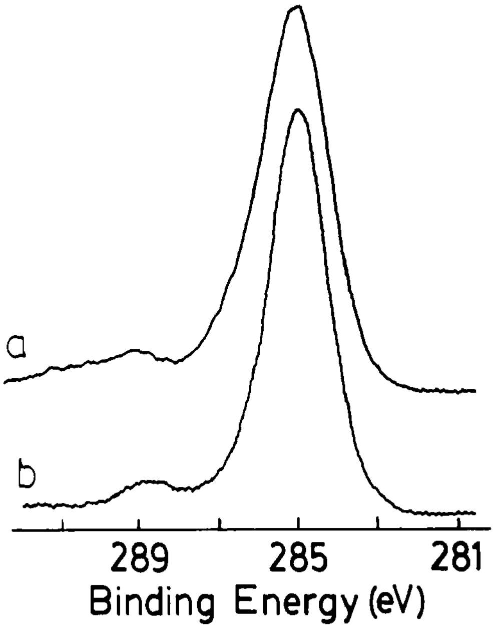


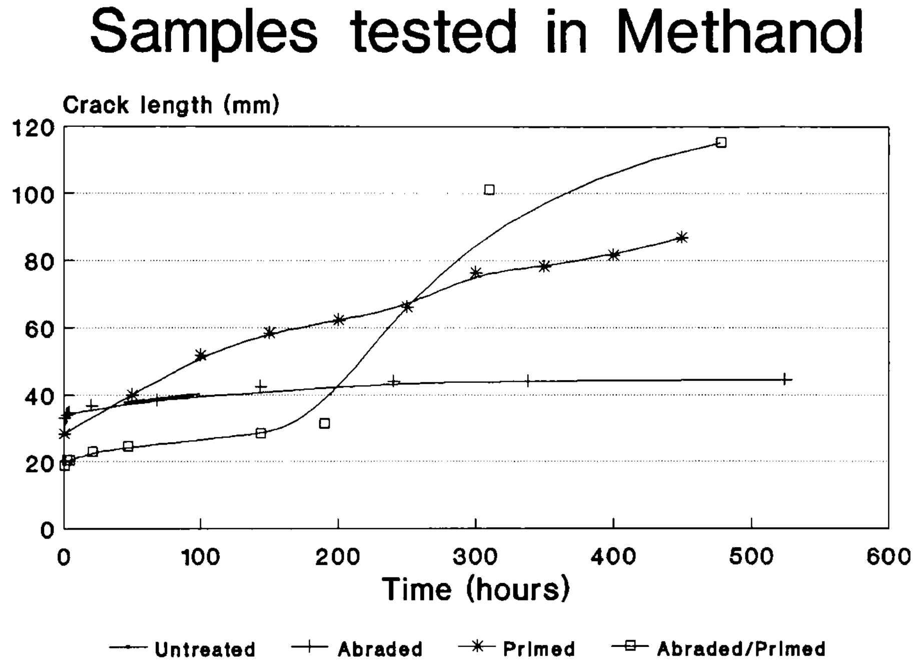
FIGURE 10 Carbon 1s X-ray Photoelectron Spectra (a) abraded SMC; (b) SMC-side failure surface; abraded sample tested in water vapor.

Samples Tested in Methanol

A plot of crack length *vs.* time for samples tested in methanol is given in Figure 11. All untreated samples debonded within 24 hours. Two of the three abraded samples debonded within 68 hours. The third abraded specimen did not fail during the test. None of the primed or abraded/primed samples debonded during the test, but the samples did show significant crack growth. Although primer aids in increasing bond durability, methanol vapor accelerates debonding of primed and abraded/primed samples compared with the effect noted in the other vapors.

The crack growth behavior for the primed and abraded/primed specimens exposed to methanol vapor is unlike that found for samples exposed to the other test vapors. In methanol vapor, crack growth extends to greater than 60 mm within 200–250 hrs., whereas crack growth in the other vapors is 25–30 mm for an equivalent exposure time. Furthermore, crack growth for primed and abraded/primed samples exposed to methanol increases as a function of time, while crack growth for equivalent samples exposed to the other vapors is arrested within about 50 hrs. On the other hand, crack growth behavior for primed and abraded/primed specimens in methanol is not exactly the same (see Fig. 11), although the failure mode is equivalent. Such behavior could be the result of heterogeneity in the bonded specimens. A complete explanation for this observation is unavailable at the moment.

Visual analysis of failed untreated samples revealed two areas of failure as shown in the cartoon representation of failure surfaces in Figure 12a. In the region where



Two abraded samples debonded by 68 hours

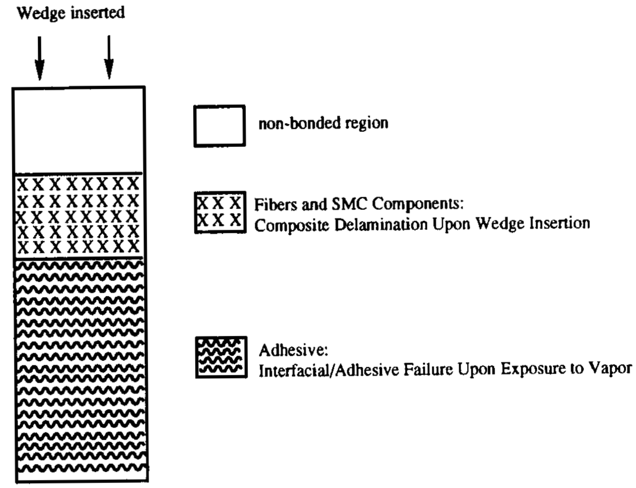
FIGURE 11 Crack Growth Behavior for Samples Tested in Methanol Vapor.

the wedge was inserted, substrate failure occurred. Beyond the initial substrate failure region, failure occurs at the SMC-adhesive interface and this mode of failure occurs exclusively until the specimen debonds completely (Fig. 12a).

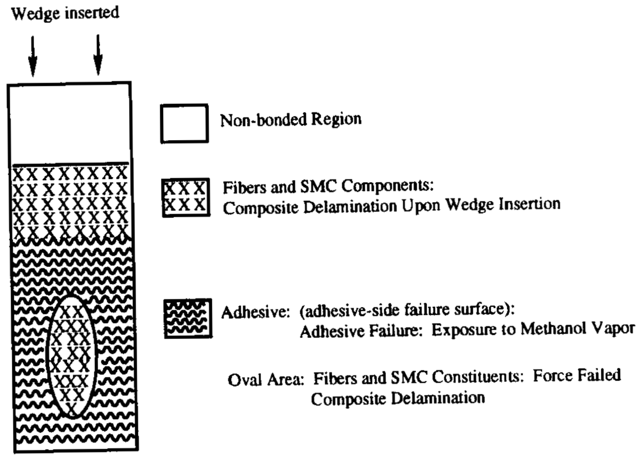
The behavior of abraded samples upon exposure to methanol vapor resulted in a unique failure pattern. A cartoon to represent an adhesive-side failure surface for an abraded sample is shown in Figure 12b. An area of substrate failure caused by wedge insertion occurs at the top of the sample. Further down the sample, an area of adhesive failure is apparent which is adjacent to the region of substrate failure (wedge insertion). In the lower portion of the sample, where the specimen was force failed, a region of adhesive failure surrounds an oval-shaped region of substrate failure/delamination. It is reasonable that the area of adhesive failure in the lower portion of the sample was caused by methanol vapor diffusing into the interfacial region of the sample and promoting debonding.

Methanol was the only vapor which significantly affected the failure mode for primed and abraded/primed samples. In all other environments, the only failure mode for primed and abraded/primed samples was substrate failure/delamination. Samples tested in methanol vapor exhibited a change in the visually-determined mode of failure from substrate failure/delamination caused by insertion of the wedge to cohesive failure.

A summary of the failure modes for samples tested in methanol is given in Table II. X-ray photoelectron spectroscopy was used to analyze the failure regions



Untreated SMC: Tested in Methanol Vapor
(a Adhesive Side - Failure Surface



Abraded/SMC: Tested in Methanol Vapor
(b Adhesive - Side Failure Surface

FIGURE 12 Representative Cartoon Figures Showing Failure Surfaces (a) adhesive-side failure surface; as-received, non-treated sample tested in methanol vapor. (b) adhesive-side or SMC-side failure surface; abraded sample tested in methanol vapor.

that were produced while the specimens were under stress and exposed to the test vapor. A representative C 1s spectrum for an adhesive-side faliure surface for an untreated sample tested in methanol, where adhesive failure was suggested from visual observations, is shown in Figure 13a. The two strong photopeaks at 285.0 and 286.4 eV indicate that adhesive is present on the surface. A typical C 1s spectrum for

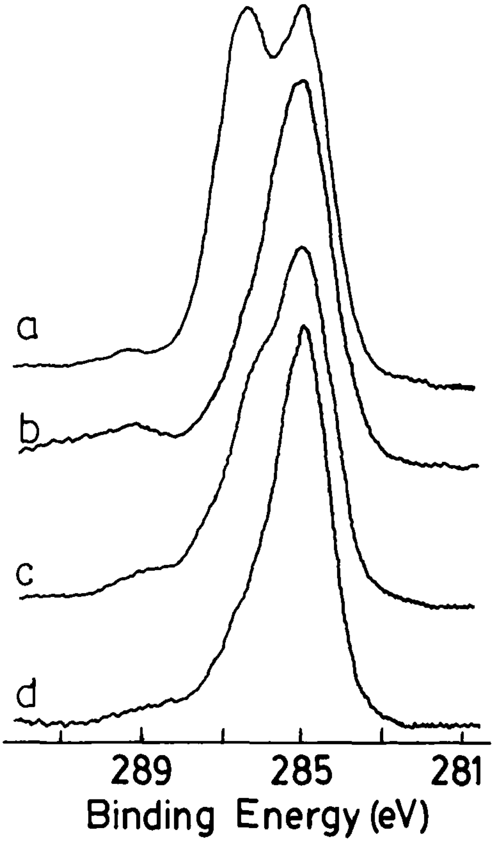


FIGURE 13 Carbon 1s X-ray Photoelectron Spectra (a) adhesive-side failure surface; as-received, non-treated sample tested in methanol vapor. (b) SMC-side failure surface; as-received, non-treated sample tested in methanol vapor. (c) adhesive-side failure surface; abraded sample tested in methanol vapor. (d) adhesive-side failure surface; primed sample tested in methanol vapor.

TABLE II
Failure Mode for Samples Tested in Methanol

Region	Untreated	Abraded	Primed	Abraded/Primed
wedge	substrate	substrate	substrate	substrate
vapor	adhesive	adhesive	cohesive	cohesive
force	failure	adhesive/substrate	substrate	substrate

the corresponding composite-side failure surface is shown in Figure 13b. That the C—H/C—C peak and the ester photopeak are present indicates that this surface is principally SMC. These XPS analysis results confirm interfacial failure for specimens bonded using as-received non-treated SMC.

Figure 13c shows the C 1s spectrum for the adhesive-side failure surface for a bonded abraded sample tested in methanol. The surface analyzed corresponds to a region where visual examination indicated adhesive failure. The important characteristic of this spectrum is that the intensity of the C—N/C—O peak at 286.4 eV is significantly less than that found for the pure adhesive. The diminshed C—N/C—O peak intensity is taken to indicate the presence of composite on the adhesive surface. These results lead to the interpretation that failure is mixed-mode, *i.e.*, substrate and adhesive failure take place, or that a thin layer of composite is present on the adhesive failure surface.

Primed and abraded/primed specimens failed cohesively during exposure to methanol vapor. A possible explanation for the change in mode of failure was obtained by comparing X-ray photoelectron spectra for the failed adhesive-side surface with the spectrum for pure adhesive. The C 1s spectrum for the adhesive-side failure surface of a primed sample tested in methanol is shown in Figure 13d. In this spectrum the C—H/C—C photopeak is more intense than that corresponding to C—O/C—N functionality. The C 1s spectrum for pure adhesive is shown as Figure 9a. The relative intensities for the C—H/C—C and C—O/C—N contributions on the failure surface are in contrast to the intensities found for the pure adhesive. It is not reasonable that the decrease in C—O/C—N intensity is due to the presence of composite on this failure surface, since visual examination of the two failure surfaces indicated the presence of adhesive on each surface. The decrease in the relative C—O/C—N intensity suggests that methanol interacts with the adhesive in

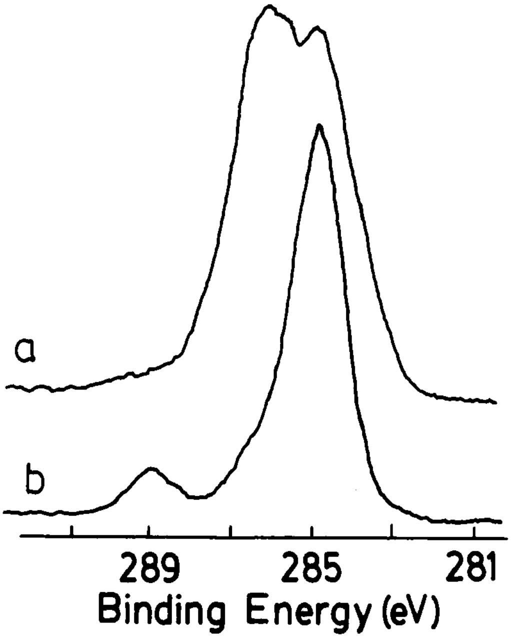


FIGURE 14 Carbon 1s X-ray Photoelectron Spectra (a) adhesive failure surface formed by insertion of the wedge into an adhesive specimen. (b) adhesive failure surface formed by crack growth in an adhesive specimen under stress while exposed to methanol vapor.

the specimen under stress in the gaseous environment. It appears that methanol weakens the adhesive by attacking the urethane functionality which may contribute to bond failure in the urethane adhesive.

To examine possible reactions of methanol with the urethane adhesive, specimens of urethane adhesive under stress in the presence and absence of methanol vapor were studied, and the surfaces of failed adhesive were characterized using XPS analysis methods. Adhesive specimens were placed under load in air by inserting a wedge into a crack in the adhesive. Following crack initiation, the adhesive specimens were immediately exposed to methanol vapor. Crack growth occurred and was eventually arrested.

Surface analysis characterization results are shown in Figure 14 for these adhesive specimens. The carbon 1s spectrum for a failure surface produced by insertion of the wedge in the adhesive in air is shown in Figure 14a. The two prominent photopeaks are characteristic of the urethane adhesive, and the spectrum is equivalent to the spectrum in Figure 9a. These results demonstrate that adhesive failure in the absence of methanol vapor yields a surface that is essentially pure adhesive. The carbon 1s spectrum in Figure 14b was obtained for an adhesive sample tested in methanol vapor. The spectrum was measured in the region of failure that occurred upon exposure to methanol vapor. In Figure 14b the characteristic urethane carbon photopeak at 286.5 eV is significantly reduced and a new peak at about 289.0 eV is evident. The photopeak at 289.0 eV is indicative of the presence of carboxylate carbon. These findings indicate that alteration of the adhesive surface chemisty has occurred. A reasonable interpretation of these results is that degradation of the stressed adhesive takes place *via* reaction of methanol with the urethane adhesive under the conditons of the experiment.

SUMMARY AND CONCLUSIONS

Methanol caused the most rapid bond failure. The crack growth rate as a function of surface treatment varied in the manner: untreated $\approx$ abraded $>$ primed $\approx$ abraded/primed. Crack growth rate as a function of vapor changed in the manner: methanol $>$ ammonium hydroxide $>$ water $\approx$ air. The initial mode of failure in adhesively-bonded composite samples caused by insertion of the wedge was always substrate failure/delamination. After exposure to gaseous test environments, the as-received, non-primed samples exhibit a change in failure mode either to adhesive or mixed-mode failure. Abrasion increased bond durability slightly but the failure mode was unchanged compared with samples prepared using non-treated composite. Priming the composite increased bond durability. Except for specimens tested in methanol, primed and abraded/primed samples exhibited only susbtrate failure/composite delamination. Samples prepared using primed composites that were tested in methanol vapor debonded *via* cohesive failure.

Acknowledgements

Thanks are expressed to the Center for Adhesive and Sealant Science, the Adhesive and Sealant Council, the National Science Foundation-Science and Technology Center (DMR-9120004), Ashland Chemical

Company and the Commonwealth of Virginia for providing financial support for this study. Thanks are also expressed to Frank Cromer who was instructive in the operation of the surface analysis instrumentation. JCW and BTT were supported by undergraduate research grants provided by the Adhesive and Sealant Council, Inc., and by the National Science Foundation, respectively.

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