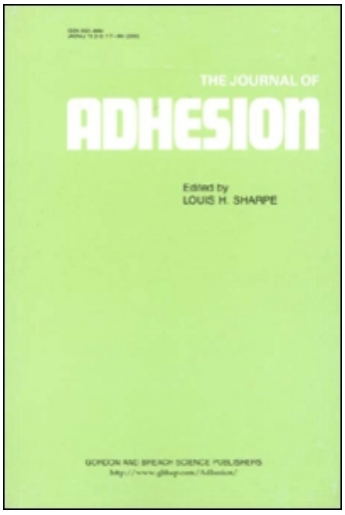

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James B. Hollenhead Jr.[a]; J. P. Wightman[a]
[a] Chemistry Department, Center for Adhesive and Sealant Science, Virginia Polytechnic Institute and State University, Blacksburg, VA

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The Adhesive Bonding of Steel with Polysulfone

JAMES B. HOLLENHEAD, JR. and J. P. WIGHTMAN

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

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The bonding of cold rolled steel with polysulfone, a thermoplastic adhesive has been studied. The single lap shear strength of bonded samples where the substrate was gritblasted was 40% lower than for the case where the substrate was hydrothermally oxidized. Both surface preparations resulted in diminished lap shear strength on exposure to high humidity conditions. However, the hydrothermally oxidized substrates resulted in more durable bonds.

KEY WORDS Cold-rolled steel; polysulfone; adhesive bonding of steel; hydrothermal oxidation of steel.

INTRODUCTION

As a means of joining structural components, adhesives are seeing widespread use in industry today. Several advantages of adhesives over conventional methods, such as welding, riveting, and bolting, have been noted. The advantages include improved stress distribution in the joint, the ability to join dissimilar materials, and the ability to join thin sheet materials efficiently.[1] In particular, the adhesive bonding of steel has taken place for over 40 years. Brockmann[2] notes that bonded steel joints are used in bridge construction, machine tools, and automobile bodies to name just a few applications.

The adhesive bonding of steel including the effect of surface preparation has been the subject of several recent reviews.[2–6] A number of papers have reported studies on stainless[7–9] or galvanized[10–13] steels. Only a limited number of papers have been concerned with cold-rolled steel.[10,11]

Although adhesive bonding has been practiced for many years, more information needs to be obtained concerning the durability of adhesive joints in their respective service environments.[14–16] Kinloch[1] has noted that water is one of the most hostile environments for structural adhesive joints. Moreover, he asserts that the long-term behavior of adhesive joints in high-moisture environments is one of the most important problems facing adhesive scientists. The one common denominator in the above referenced and other studies[17,18] is the use of thermoset or cross-linked adhesives.

The objective of this study is twofold. The first is to report the bondability of cold rolled steel with the thermoplastic adhesive, polysulfone, before and after hydrothermal oxidation of the steel substrate. The second objective is to examine the durability of cold rolled steel-polysulfone bonds in a moist and in a hot-moist environment.

EXPERIMENTAL

Materials. Udel P-1700 polysulfone was used as the adhesive. P-1700 is an engineering thermoplastic with a number average molecular weight of 26,000 g/mol and a polydispersity of 2.1.[19] The polymer was received as extruded pellets and was compression molded at 290°C into a 0.5 mm film. Following compression molding, the film was heat treated at 210°C overnight to relieve internal stresses due to pressing.

The steel adherends were cold rolled steel (CRS) obtained from Bethlehem Steel Co. Coupons measuring $25.4 \times 102 \times 1.6$ mm were used for assembling lap shear samples.

Adherend surface pretreatment. Adherends were given two surface pretreatments. For the first pretreatment, samples were grit-blasted with 100 grit silicon carbide, followed by an acetone wipe to remove loose grit. Care was taken to insure that the entire area to be bonded was evenly grit-blasted.

The object of the second pretreatment was to produce a structured oxide on the steel. First, gritblasted coupons were placed in 6N HCl for 5 minutes followed by a deionized water rinse and an acetone rinse. The coupons were heated to 450°C in a furnace through which flowed a stream of nitrogen which had been bubbled through water. The coupons were heated for 4.5 to 5 hours and the nitrogen flow rate was 2 liters/minute. This pretreatment is similar to that used by Evans and Packham.[20]

Lap shear samples. To prepare lap shear samples, coupons were assembled in a jig designed to allow for 25.4×12.7 mm overlap. Adhesive strips, cut from the compression molded film, were placed within the overlap portion of the coupons. The bond thickness was controlled using 0.1 mm wire spacers placed between the jig halves. The assembled jig and coupons were placed in a thermopress and heated to 290°C. After attaining this temperature, the pressure was slowly increased to 138 MPa. The samples were held at this temperature and pressure for 10 minutes. The samples were water cooled to room temperature under pressure and removed from the jig.

Environmental exposure. Bonded samples were placed in three environments. The first was a room temperature desiccator; the second was a room temperature, 100% relative humidity environment; and, the third was an 80°C, 100% relative humidity environment.

Lap shear strength determination. Sample sets were removed from their respective environments at various intervals and their bond strengths determined on an Instron testing machine. The strain rate for all tensile testing was 1.27 mm/min. Six samples were tested for the determination of the initial lap shear strength. Therefore, only three samples were used in the exposure studies. Following sample fracture, 9.6 mm diameter pieces of the failure surfaces were punched from the adherends and analyzed using X-ray photoelectron spectroscopy and/or scanning electron microscopy.

X-Ray photoelectron spectroscopy. Samples of the failed adherend surfaces were analyzed at a 90° take-off angle using a Perkin-Elmer PHI-5300 spectrometer equipped with a Mg anode operated at 14 keV. The system pressure was nominally about 10^{-8} torr. Samples were mounted on stainless steel sample holders with a small piece of double-sided adhesive tape. After obtaining a survey spectrum of each failed sample, narrow scans were obtained from each of following regions: carbon 1s, oxygen 1s, sulfur 2p, iron 2p and silicon 2p. The binding energies of the photopeaks were referenced to the C 1s photopeak due to surface contamination taken at 285.0 eV. For samples pretreated in moist nitrogen, the nitrogen 1s region was also scanned. However, no significant peak was found for nitrogen on any of the samples.

Scanning electron microscopy. Scanning electron photomicrographs of the steel substrates and of the failure surfaces were taken with a ISI-SX-40 scanning electron microscope. To prevent charging, the samples were sputter coated with approximately 30 nm of gold. A 30 kV beam voltage was used to obtain images of 0° tilt and magnifications between 2,000 and 10,000 times.

RESULTS AND DISCUSSION

Substrate adherend analysis. The SEM photomicrographs shown in Figures 1 and 2 reveal the different topologies imparted to the steel surface by the two pretreatments. In Figure 1, the gritblasted surface appears rough and irregular; there are no visible grain boundaries or milling marks. Figure 2 is the steel oxide produced by heating under moist nitrogen. Contrary to the gritblasted case, the oxide produced under moist nitrogen is not irregular, but is comprised of blades or whiskers of oxide grown perpendicular to the surface. These features are identical to those noted by Evans and Packham.[20]

Table I lists the XPS results for pretreated steel adherends. Both surfaces are composed of carbon, oxygen, iron and silicon. The oxygen and iron are, of course, present on any steel surface. The source of the significant amounts of silicon on both surfaces is probably twofold. Small amounts (<2%) of silicon result from the metallurgy which produces cold rolled steel. The remainder of the silicon on the gritblasted surface arises from the use of silicon carbide as the grit. Since gritblasting was also the first step in preparing the samples which were given the moist nitrogen

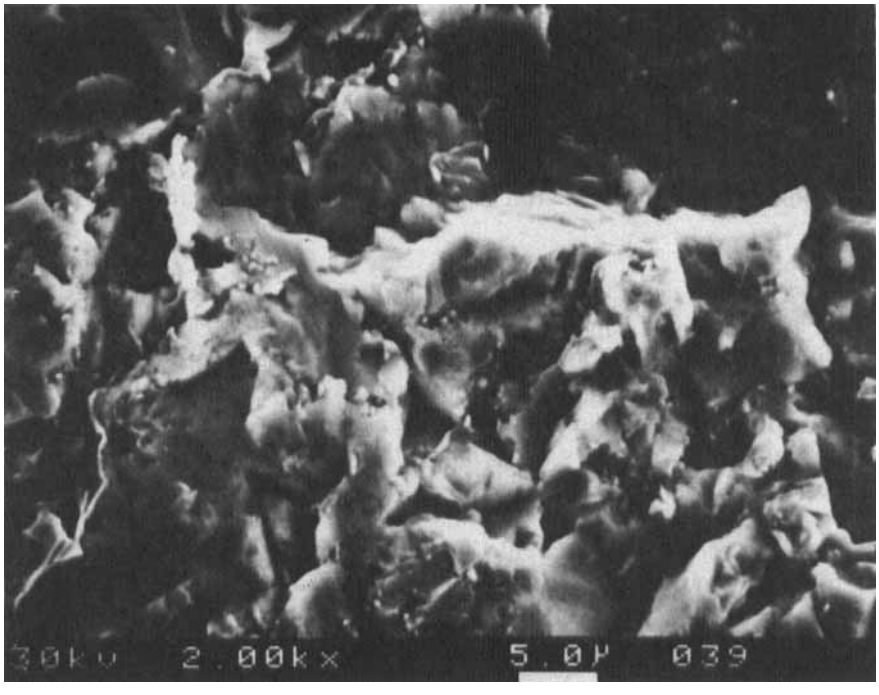

FIGURE 1 SEM photomicrograph of gritblasted steel (2000X).

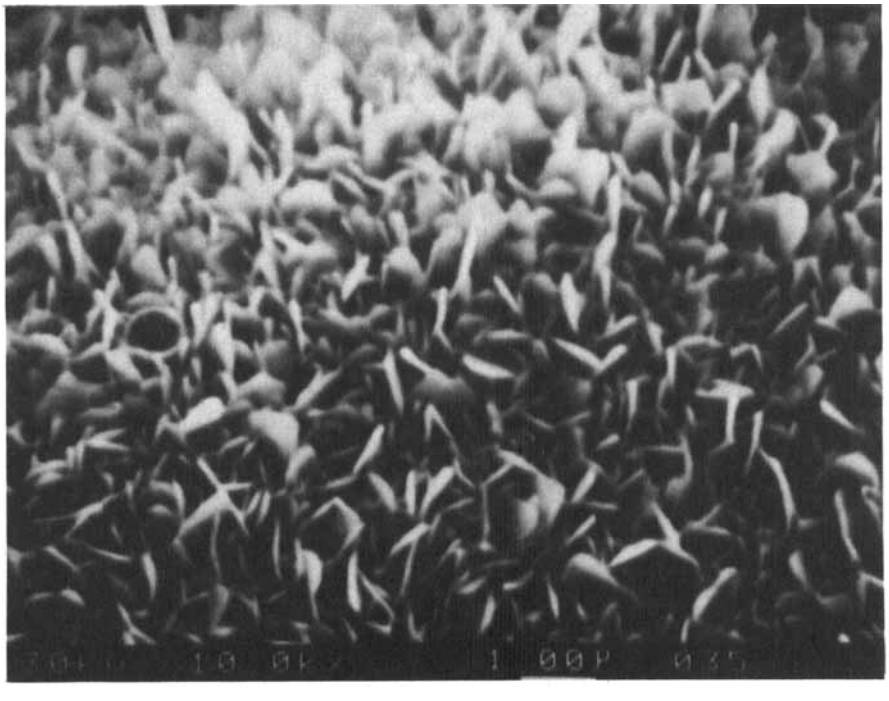

FIGURE 2 SEM photomicrograph of steel heated under moist nitrogen at 450°C (10,000X).

TABLE I
XPS results for pre-bond adherends

Element	Atomic concentration (%)	
	Gritblasted	Moist Nitrogen
Carbon	47.	20.
Oxygen	38.	51.
Iron	7.2	18.
Silicon	7.0	10.
Nitrogen	nsp	nsp

nsp—no significant peak

treatment, silicon appears on that surface too. The larger amount of carbon on the gritblasted adherend stems from hydrocarbon contamination accumulated during specimen handling. The analyses of the steel heated in moist nitrogen were performed on freshly prepared samples, so less contamination was present and the percent carbon by XPS is lower. Further, it is interesting to note that no nitrogen was detected on the steel surface heated above 450°C for 45 hours in a nitrogen atmosphere. In short, the narrow scan spectra for the Fe 2p and O 1s regions of the grit-blasted and hydrothermally treated steel did not differ significantly.

Initial lap shear strengths and failure surface analysis. Bonded lap shear samples of both surface pretreatments were failed 1 day after bonding. During this 24 hour period, the bonds were stored in a room temperature dessicator with a relative humidity of less than 3%. The average lap shear strength of the gritblasted samples was 3600 psi. The standard deviation of the six values averaged to give this result was 380 psi or about 10.5%. The average lap shear strength of the samples pretreated in moist nitrogen was 6300 psi with a standard deviation of 480 psi. The fact that gritblasting produced a bondable surface is not surprising. Brockmann[2] noted that sandblasting was the best pretreatment for bonding steel with an epoxy resin in that it gave the highest lap shear strength of several pretreatments. However, pretreating the steel adherends in a furnace under moist nitrogen results in bonds with a significantly higher lap shear strength over the gritblasted case. Even though Evans and Packham[20] found that this pretreatment improved peel strength in steel-polyethylene systems, there was no evidence that lap shear strength would be influenced. In fact, Filbey and Wightman[21] determined that the initial lap shear strength was insensitive to surface pretreatment of Ti-6-4 adherends bonded with FM-300, an epoxy adhesive. Nevertheless, for steel bonded with polysulfone, the lap shear strength is sensitive to pretreatment of the steel substrate in moist nitrogen at 450°C.

The failure mode in these initial lap shear bonds was mainly cohesive for both pretreatments. Although to the naked eye the adhesive appeared visually to have pulled away from one adherend, XPS analysis revealed the presence of polymer on both sides of a failed bond. Table II lists the XPS results for a failed bond which was gritblasted. Also shown in Table II is the analysis of a neat polysulfone film. The presence of sulfur in polysulfone provides a convenient tag for assigning an average failure plane. Both sides of this failed bond contain significant amounts of sulfur, almost as much as in the neat film. However, there are substantial amounts

TABLE II
XPS results for failed lap shear sample
Pretreatment: gritblast
Environment: room temperature desiccator

Element	Atomic concentration (%)		
	Side 1	Side 2	Neat film
Carbon	65.	70.	82.
Oxygen	26.	23.	15.
Sulfur	2.0	2.2	3.0
Iron	4.8	3.5	nsp
Silicon	2.0	1.2	nsp

of iron and silicon on the surface, indicating that at some point the polymer either pulled away from the surface or was thinner than 10 nm. XPS typically analyzes the top 5–10 nm of a surface. Again, both pretreatments gave rise to bonds which fractured with a large amount of cohesive failure. Figure 3 is an SEM photomicrograph of a failed adherend which was pretreated in moist nitrogen. The tufted structure of the polymer gives evidence as to why this pretreatment gave higher lap shear strengths than gritblasting, even though both failed within the polymer. The presence of the blade-like oxide caused local yielding at the polymer interface. This local yielding dissipates the fracture energy into the bulk of the polysulfone, resulting in a higher shear strength. Such dissipation could not occur in the case of

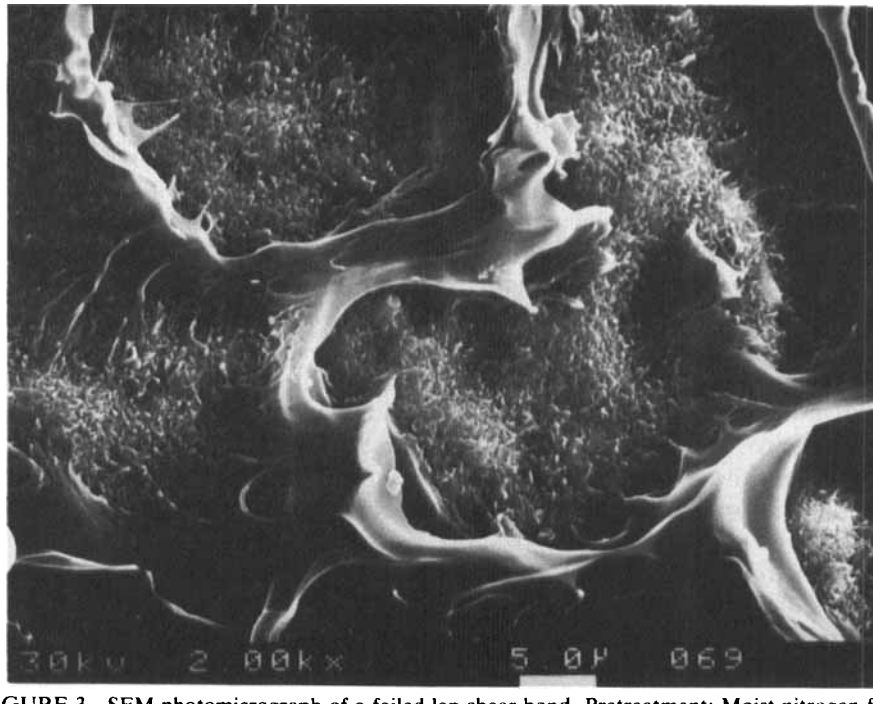

FIGURE 3 SEM photomicrograph of a failed lap shear bond. Pretreatment: Moist nitrogen furnace Environment: 1 day in desiccator (2000X).

a gritblasted surface where the possibility of oxide-polymer interlocking was not as great. SEM photomicrographs of adherends from which the polymer was dissolved reveal that the bladed oxide structure is intact after bonding. These results serve to reinforce the point made earlier by Sharpe[22] that "because an adhesive joint is a system of materials with complex responses, we should be very careful about broad-based extrapolation of single cause and effect relationships which derive from application of a single analytical technique."

Lap shear strengths and failure surface analysis of exposed bonds. Figure 4 is a plot of lap shear strength versus time of exposure in two 100% relative humidity environments for bonds pretreated by gritblasting. The results for samples exposed at room temperature are indicated by the solid symbols while those exposed at 80°C are represented by the open symbols. The initial lap shear strength of 3600 psi is greatly reduced after just one day in either moist environment, although the reduction is greater in the hotter environment. The average lap shear strength for bonds in both environments continue to decrease non-linearly with exposure time. The strength of bonds exposed to the hot, moist environment decreases for 17 days and then levels off. The strength of bonds exposed to the room temperature environment decreases less rapidly, but after 30 days the bond strength has converged with the results for the 80°C case. Thus the effect of 30 days exposure to a moist environment is to decrease the lap shear strength of gritblasted samples to one third of the initial value. The observation that the decrease in lap shear strength tends toward the same value indicates that the effect of water at the bondline is the same in both environments. Elevated temperature only accelerates the effect of water on the bondline.

Whereas the average failure plane of gritblasted samples was mainly cohesive for unexposed bonds, exposure to moist environments produces a different failure

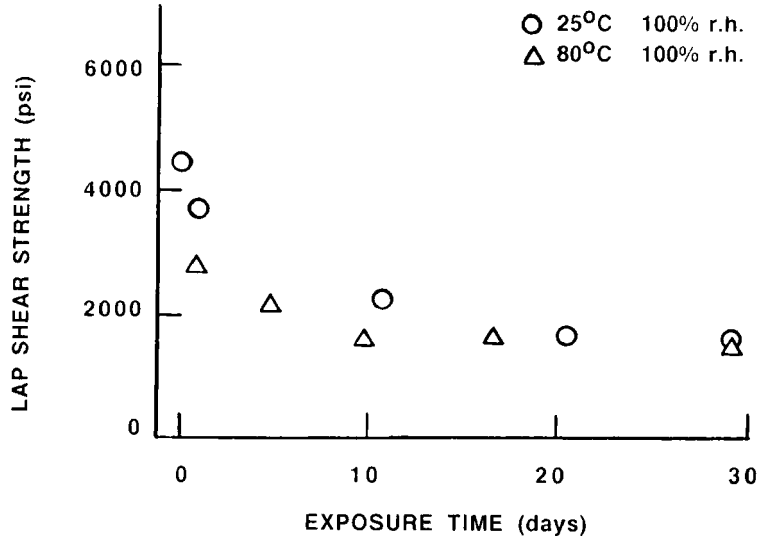

FIGURE 4 Lap shear strengths of gritblasted steel samples as a function of time.

TABLE III
XPS results for failed lap shear sample
Pretreatment: gritblast
Environment: 25°C, 100% relative humidity, 30 days

Element	Atomic concentration (%)	
	Side 1	Side 2
Carbon	29.	68.
Oxygen	47.	23.
Sulfur	0.8	2.5
Iron	5.3	0.2
Silicon	7.5	1.7

mode. Table III lists the XPS results for a gritblasted sample exposed to room temperature, 100% r.h. environment for 30 days. The lack of an appreciable amount of sulfur on side 1 and the presence of 2.5% sulfur on side 2 suggests failure at the polymer/steel oxide interface. Further evidence for this failure mode is the absence of iron on side 2, making side 2 the polymer failure surface and side 1 the metal failure surface. Interfacial failure between polymer and oxide was characteristic of all samples exposed to moisture. The observation that failure shifts to the interface upon environmental exposure was noted by Kinloch[1] as a general occurrence in many systems. Specifically, Filbey and Wightman[21] noted a similar shift in failure locus for an epoxy/titanium bond exposed to a hot, moist environment under stress.

Upon exposure to a moist environment, samples pretreated under moist nitrogen exhibit a decrease in lap shear strength similar to that of the gritblasted case. Figure 5 is a plot of lap shear strength versus time of exposure to a 100% r.h. environment.

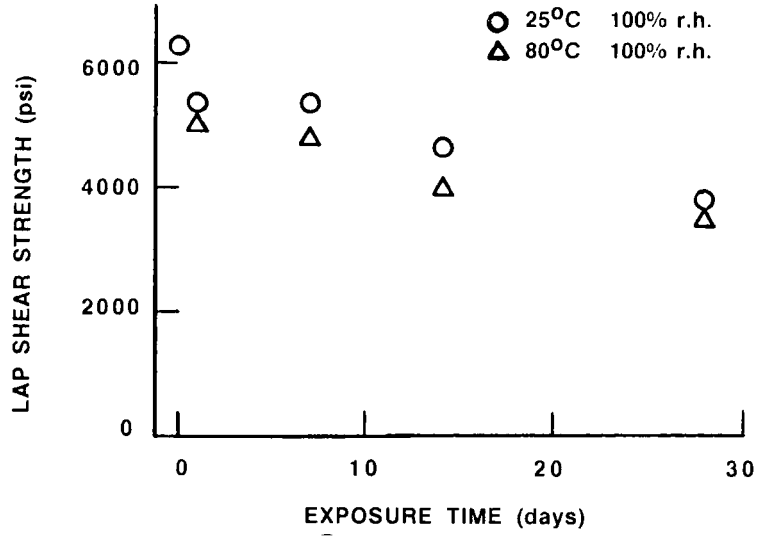

FIGURE 5 Lap shear strengths of moist nitrogen treated steel samples as a function of time.

TABLE IV
XPS results for failed lap shear sample
Pretreatment: moist nitrogen
Environment: 80°C, 100% relative humidity, 28 days

Element	Atomic concentration (%)	
	Side 1	Side 2
Carbon	20.	22.
Oxygen	54.	50.
Sulfur	0.2	0.3
Iron	25.	27.
Silicon	1.5	1.3

Again, the solid symbols indicate results following room temperature exposure, while the open symbols represent the results for 80°C exposure. One day of exposure in either environment produces a significant decrease in lap shear strength. In this case the added effect of temperature is less apparent than for the gritblasted samples. Results for samples exposed at 80°C are only slightly lower than the room temperature case. The decrease in lap shear strength is nonlinear in both environments. However, the lap shear values do not reach a plateau as they did for gritblasted, exposed samples. The values for the two environments do converge after 28 days to a lap shear strength around 3800 psi, which is only a 40% loss in initial lap shear strength. It is interesting to note that the weakest moist-nitrogen treated bond was stronger than the initial lap shear strength of the gritblasted samples.

The failure mode of the exposed moist-nitrogen treated bonds was not cohesive as was the unexposed failure mode, nor was it an interfacial failure as observed for the gritblasted, exposed samples. Table IV lists the XPS results for a sample exposed for 28 days to 100% r.h. at 80°C. The lack of an appreciable amount of sulfur on either side, combined with large amounts of iron and oxygen on both sides indicates that this bond failed within the oxide layer. This shift of failure within the oxide layer was obtained after only one day of environmental exposure. Indeed, the failure must have occurred well within the oxide since both sides have almost exactly the same atomic composition. Oxide failure was observed for all the moist-nitrogen treated samples exposed to moisture, whether at room temperature or 80°C. No evidence of blade-like morphology was observed on any of the failure surfaces.

SUMMARY

Bonding gritblasted steel with polysulfone results in reproducible bonds which exhibit mainly cohesive failure. Exposure of gritblasted bonds to moist environments results in a drastic decrease in lap shear strength after 30 days. The average failure plane shifts from cohesive failure in the polysulfone to the oxide-polysulfone interface as evidenced by XPS.

Growing a bladed oxide on the steel prior to bonding improves the lap shear strength significantly over the gritblasted case. The increase in shear strength is due to the dissipation of fracture energy from the interface into the bulk of the polymer.

Polymer yielding is evident from SEM photomicrographs of failed samples. Exposure of moist nitrogen treated bonds to moist environments results in a 40% loss in lap shear strength over 28 days. The locus of failure shifts from cohesive for the unexposed case to oxide failure in exposed samples.

The lap shear test distinguished between the two surface pretreatments and gave good qualitative information about the durability of steel polysulfone bonds. XPS proved to be invaluable in assigning the average failure plane which could not simply be observed visually.

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