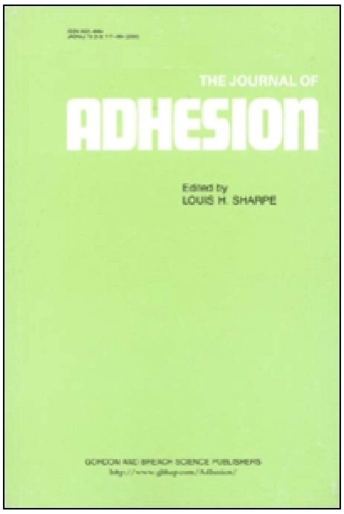

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The Effect of Immersion on the Breaking Force and Failure Locus in an Epoxy/Mild Steel System

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This paper presents the effects of immersion on the adhesion behavior in a polyamide-cured epoxy system immersed in sodium chloride electrolyte adjusted to three different pH values. The strength of lap shear joints was measured before and after exposure and after redrying. The failure locus was determined on a macroscopic and microscopic level. It was found that a large adhesion loss occurred upon immersion. Most of that loss was recovered upon redrying. All of the breaking force was recovered when the immersion fluid was distilled water. The locus of failure was primarily through the bulk of the adhesive before immersion. After immersion the failure was interfacial with a thin residue of polymer remaining on the metal surface. These results are discussed with respect to earlier work on the water absorption properties of the system.

KEY WORDS epoxy; wet adhesion; mechanical properties; lap shear joints; X-ray photoelectron spectroscopy.

INTRODUCTION

Durability and reliability of coatings and adhesives are of primary interest to end users and to producers of polymeric systems. A program of study is underway in our laboratories to understand better the environmental degradation of polymer/metal systems. The objectives of the study reported here are to determine the effect of immersion in salt solution on bond strength and to determine how the locus of failure changes with exposure as a function of pH. Alkaline pH values were chosen because that is typical of the environment present under polymer coatings when they are delaminating. The force necessary to fracture lap shear joints was recorded. The resultant fracture surfaces were then analyzed with X-ray photoelectron spectroscopy (XPS) to determine the locus of failure. The results are relevant to the reliability of structural adhesive joints.

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The lap shear test is a commonly-used method for evaluating adhesives and adhesion.[1,2,3] Its convenience stems from ease of preparation, exposure, and testing. Performing the lap shear test is straightforward and simple, but it must be done with highly reproducible samples because the apparent strength of the bond is a complex function of the overlap width and distance, and of the thickness of the adhesive layer.[4] These parameters all influence the degree to which the adhesive can deform when the bond line begins to rupture. The force needed to separate the bonds is measured. The locus of failure and relative areas of cohesive and interfacial failure are determined.

Lap shear testing is only one way to measure adhesion strength. Other adhesion tests use different parameters to evaluate adhesion. The epoxy button test consists of gluing a button of epoxy to the coating and pulling it off. If the cohesive strength of the epoxy and the bond between the epoxy and coating are stronger than the bond of interest, an adhesion strength can be measured. Area of delamination is the parameter of interest in the tape pull test. This test consists of sticking a tape to the surface of the coating after exposure and pulling the tape off with any coating which is loose.

Spadafora and Leidheiser[5] report that the adhesion of polymer coatings exposed to aqueous environments, as measured by the tape pull test, increases dramatically upon the addition of small amounts of sodium chloride to the electrolyte. They attributed increased adhesion in the tape pull test to the decrease in thermodynamic activity of water. The time until failure increased by almost 600 per cent in sodium chloride solutions of .001 molar to 1.0 molar as compared with distilled water. Failure time of the specimens was designated as the point at which 50% of the coating in contact with the tape was removed from the substrate.

Water can also have significant effects on the properties of the polymer itself. Many diluents affect the physical properties of polymers as they are absorbed. A common effect is the lowering of the glass transition temperature (T_g).[6] Lowering T_g results in decreased hardness and reduced strength of the polymer. The effect of diluents becomes more complex with liquids, such as water, which can participate in hydrogen bonding. Depending upon the specific interactions, the liquid environment may result in a greater decrease of T_g, crazing, and swelling.[7] Polyamide-hardened epoxy is known to be especially sensitive to permeation by water.[8] Earlier work by Shaw *et al.*[9] has shown that this epoxy polyamide system absorbs a quantity of water up to 30 weight per cent. The water is bound within the polymer and on the filler.

Another frequently used test is the peel test. This test is used in several different geometries to measure adhesive strength semi-quantitatively. A disadvantage of the peel test is that the force necessary to deform the adherends contributes to the total recorded force.

The failure locus of coated and adhesively bonded systems has been of continuing interest because it can provide evidence as to the mechanism of adhesion loss. Bikerman[10] theorized that true adhesive failure is not possible in adhesively bonded metals because a weak boundary layer is always formed along the interface. Until fairly recently, it was not possible to detect the remnants of this interfacial layer; however, advances in XPS technology have led to significant progress in this area.

A variety of polymer/metal systems have been studied. The systems have ranged from model systems chosen for simplicity of analysis, to more complex, commercial systems, used in real applications. Watts and Castle[11] were able to determine differences in the surface functionality of residues left on metal surfaces by different types of coatings, including different types of epoxy coatings. In tests conducted with the coated specimens immersed in water, the coatings they examined had delaminated both at rest potential and at cathodic potentials. In an earlier study, Castle and Watts[12] had found that polybutadiene delaminates from steel leaving carbonyl functionality on the steel surface. Dillingham and Boerio[13] examined the residues left on aluminum and epoxy after dry mechanical failure near the interface. They found that crack propagation was primarily through the oxide, with very little polymer remaining on the metal. Work by Dickie[14] showed that humidity-induced adhesion loss could also result in interfacial polymer remaining on a metal surface after fracture. His work indicated little chemical change in thermoset coatings as a result of, or leading to, adhesion loss. Hamadeh *et al.*[15] used XPS to investigate the cathodic disbonding of neoprene rubber from steel. They discovered that the primer degraded significantly upon exposure.

Interfacial analysis of debonded surfaces by XPS has been reported. This technique allows both quantitative chemical analysis and chemical state identification. Peak deconvolution is generally performed with the aid of a computer curve fitting routine. Assignment of these peaks can then be made based on *a priori* knowledge of the system.[16,17] Standards are prepared and analyzed in order to determine the peak characteristics of the functionalities of interest.

EXPERIMENTAL PROCEDURE

Materials

The adherends were clean and bare, aluminum-killed 1010 steel (GM 16-05E). The steel was degreased by immersion in acetone in an ultrasonic bath prior to bonding. The adhesive was formulated with 100 parts (by weight) Epon 828 (Shell Chemical) epoxide resin, 175 parts Versamid 140 (Henkel Corporation, La-Grange, Illinois, U.S.A.) polyamide curing agent, 100 parts Atomite (Thompson, Weinman & Co.) calcium carbonate filler, and trace amounts of fumed silica and diethylene glycol as viscosity enhancers to limit runout during cure. A small quantity of 125 micron glass beads were included in the mixture to maintain the joint thickness.

Lap shear specimens were prepared at Lord Corporation (Erie, Pennsylvania, U.S.A.) using two steel strips, each 100 mm × 25 mm. They were glued together with a 12 mm lap as shown in Figure 1. The joints were then cured at 90°C for twenty minutes. Adhesive flash was trimmed from the samples with a razor blade. The samples were coated with a proprietary cathodic electrocoat at PPG Industries (Cleveland, Ohio, U.S.A.) in order to prevent bulk rusting upon exposure. Electrocoating involved a cure at 175°C for 30 minutes. This coating procedure is typical of industrial practice. The electrocoat may have a significant effect on adhesion strength and bond durability by preventing corrosion product buildup at the interface, and on subsequent changes in electrolyte ingress. However, elimination of these variables aids in understanding and interpreting the effects of the electrolyte.

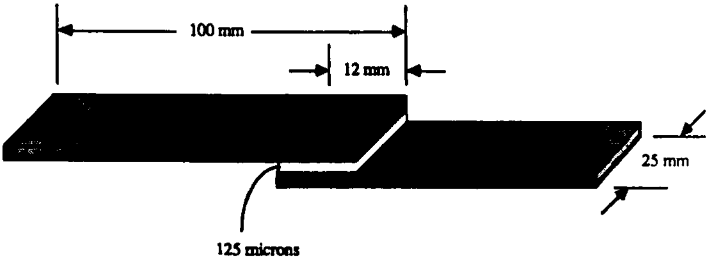

FIGURE 1 Geometry and dimensions of the lap shear joints.

Exposure and Mechanical Testing

The lap shear joints were immersed for three weeks in a) distilled water, b) aqueous solutions of 5% sodium chloride with the pH adjusted to 7 and 11, and c) one normal sodium hydroxide-5% sodium chloride at a temperature of 20 ± 3°C. All four of the solutions were exposed to air. Upon removal from solution, the samples were towel dried to remove excess moisture and pulled to fracture in tension using an Instron tensile testing machine at a strain rate of 50 mm/min. Unexposed samples were also fractured in this way. The maximum load at failure was recorded and the degree of interfacial failure was estimated visually. Tests were also performed on samples which had been exposed to aqueous environments and then allowed to dry at ambient temperature in a vacuum desiccator for eight weeks. Five unexposed samples were fractured. Seven samples were exposed to each of the solutions. Five of these were fractured prior to drying. Two were dried and then fractured.

Surface Analysis

Both surfaces of the fractured specimens were analyzed by X-ray photoelectron spectroscopy using a Perkin-Elmer PHI 5400 photoelectron spectrometer. Survey scans were recorded between 0 and 1000 eV using Mg Kα radiation and an analyzer pass energy of 89.45 eV. Multiplex spectra were recorded for carbon, nitrogen, oxygen, and iron using the Mg anode and an analyzer pass energy of 35.75 eV. Angle-resolved spectra were recorded in order to determine the thickness of the polymer residue remaining on the steel after interfacial failure. Spectra were recorded at 12 angles ranging from 15° to 90° to the surface (*i.e.* near grazing to normal incidence).

Interpretation of Angle-Resolved XPS

Angle-resolved data can be used to determine the thickness of the polymeric residue on the metal failure surface. The relative intensities of the peaks at different angles are determined. These data are interpreted using the following relationship derived from the fact that the photoelectron escape probability has an exponential dependence on depth.[18]

$$\ln(I_\theta/I_o) = d/\lambda[1 - \exp(-1/\sin\theta)]$$

θ is an arbitrary angle between the surface and the electron analyzer
I_θ is the intensity at arbitrary angle theta
I_0 is the intensity at the normal angle
d is the overlayer thickness
λ is the mean free path of the electrons

Since the acquisition angle is set, and the ratio of the intensities is measured, the quantity d/λ can be determined. Interpretation also relies upon making a reasonable assumption about the mean free path of the electrons. The electron escape depth was estimated using the work of Bailey and Castle.[19] They determined the mean free path of C1s photoelectrons through adsorbed organic vapors to be 4.6 nm.

Analysis of angle-resolved data from a substrate which is not perfectly flat should be considered semi-quantitative. Ridges and valleys on the surface can result in "shadowed" areas, which can not be seen by the detector, as well as areas which may be given undue emphasis. However, the trends in the data will give an accurate indication of the morphology of the overlayer. Since the intent of this study was to determine the approximate thickness over a large area and to determine the morphology of the residue, these effects have been neglected.

A plot of the log of the intensity ratio as a function of the reciprocal of the sine of the acquisition angle will be a straight line if the system has a homogeneous substrate covered by a uniform overlayer. If the thickness of the overlayer is inconsistent over the surface, the data will form a tail as the grazing angle is approached.

RESULTS

Mechanical Testing

Table I presents the breaking force of the lap shear joints (*i.e.* the load at fracture) in the unexposed condition and after exposure to the various environments discussed. Data from the exposed and dried specimens are also presented. The force required to break the unexposed specimens was nearly 5200 newtons. Table II shows the relative areas of cohesive and interfacial failure as a function of exposure. Fracture of the unexposed specimen occurred primarily through the adhesive. The

TABLE I
Breaking force of lap shear joints after 3 week exposure and subsequent drying. Followed by number of samples

	Breaking force of wet samples		**Breaking force of dried samples**	
Exposure	**(Newtons)**	**% of initial**	**(Newtons)**	**% of initial**
unexposed samples			5190 ± 285 -7-	100
distilled water	505 ± 55 (1σ) -5-	10	4930 -2-	95
5% NaCl, pH 7	145 ± 40 -5-	3	4560 -2-	88
5% NaCl, pH 11	135 ± 40 -5-	3	4500 -2-	87
5% NaCl, 1N NaOH	160 ± 105 -5-	3	4575 -2-	88

TABLE II
Effect of exposure and redrying on the locus of failure

Expsoure	**% Cohesive failure after exposure**	**% Cohesive failure after drying**
unexposed samples	85	
distilled water	0	60
5% NaCl, pH 7	0	30
5% NaCl, pH 11	0	30
5% NaCl, 1N NaOH	0	30

failure was estimated to be 85 per cent cohesive. The remainder of the failure was along the metal/polymer interface. The cohesive failure surface appeared jagged and corrugated.

Three weeks exposure to any of the salt solutions dropped the breaking force well below 200 newtons, approximately 3% of the original. Exposure to distilled water reduced the breaking force to about 500 newtons, approximately 10% of the original. Drying the samples in a vacuum desiccator returned the breaking force of the sample exposed to the distilled water to 95% of the pre-exposure value. Samples exposed to the electrolyte solutions only recovered to 88% of their initial breaking force upon drying. The differences between the salt solutions did not cause statistically different changes in the breaking force of the lap shear joints. There was no visual difference among the samples exposed to salt solution and those exposed only to distilled water. All of the exposed samples exhibited 100 per cent interfacial failure as judged by visual examination.

This epoxy system absorbs up to 30 weight per cent water.[9] This water interacts with the polymer, causing a large degree of plasticization, which is responsible for the large drop in the strength of the adhesive. In the wet condition, the polymer can be easily deformed without causing the polymer to crack. In the dry state the polymer is brittle. It undergoes little deformation before fracture, and has a jagged fracture surface. The plasticization phenomenon is reversible. After the drying cycle, the polymer is once again strong and brittle. The specimen exposed to distilled water showed greater than 60 per cent cohesive failure after drying as compared with 85 per cent prior to exposure. Those specimens, exposed to salt solution and then dried, exhibited about 30 per cent cohesive failure.

Failure Mode

The fracture surfaces from the exposed samples display one hundred per cent interfacial failure. The metal surface appeared shiny and bright as it had before the joint was formed. Surface analysis indicated the presence of carbon, nitrogen, oxygen, and iron on the steel side of the fractured specimen. A representative XPS survey from the metal side of the interfacial failure is shown in Figure 2. The shape of the carbon peak envelope and the presence of nitrogen on the surface indicate the presence of polymer on the metal side of the interfacial failure. No iron was found on the polymer side of the interfacial failure. No chemical conversion of the steel surface has occurred as a result of curing the adhesive or the exposure to the electro-

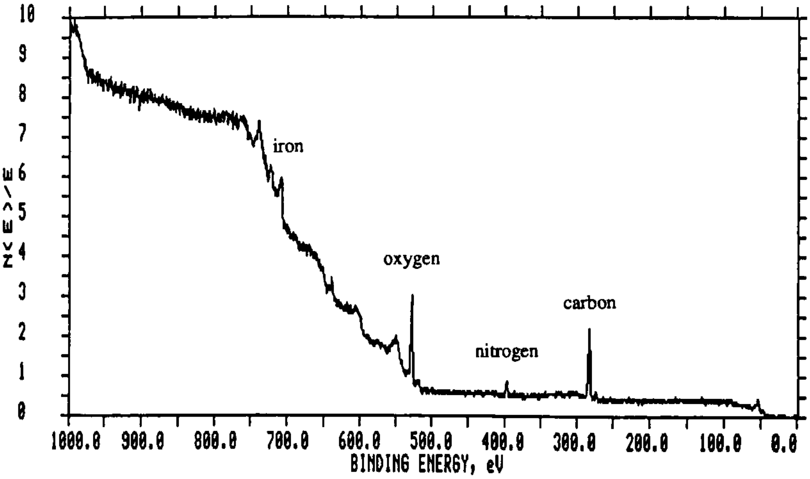

FIGURE 2 Typical XPS survey from the metal side of an interfacial failure. The elements present are iron, oxygen, carbon, and nitrogen. The nitrogen is an easily recognizable sign of the polymer remaining on the surface.

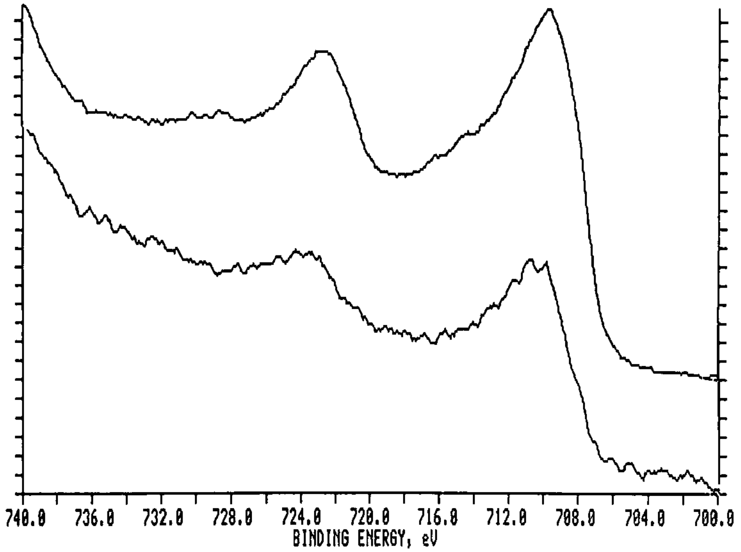

FIGURE 3 Comparison of iron spectra from unbonded steel (top) and steel which was bonded, exposed, and fractured. The peak positions and shapes are very similar. The spectrum from the exposed sample has lower intensity due to the remaining polymer layer.

lytes. This is shown in Figure 3, which compares an iron spectrum taken prior to bonding with one taken after adhesive failure. The peak positions are identical; the shapes are very similar. The lower spectrum, from the bonded and fractured sample, has a lower intensity due to the presence of a polymer overlayer. Trace amounts of chlorine were seen in the survey scan indicating the migration of chloride along the interface.

A typical C1s spectrum from the metal side of the interfacial failure is shown in Figure 4. The overall carbon peak envelope is a combination of several component peaks which are due to aliphatic carbon, carbon-nitrogen bonds, carbon-oxygen bonds, and carbon double-bonded to oxygen atoms. These peaks are indicated in the figure. Single bonds between oxygen and carbon are present from the epoxy itself. Amine (C—N) and carbonyl (C═O) bonds are present from the hardener. The carbon spectra from the polymer residue were found to be very similar to the spectrum from the bulk adhesive, but the spectra from the interface had a greater proportion of the peak envelope attributable to the hardener. This may be due to isolated areas containing high concentrations of hardener, or to higher levels of hardener throughout the interphase region. Spot-to-spot differences were not observed, indicating that the distribution was uniform with respect to the spatial resolution of the XPS instrument, *i.e.* the one square millimeter spot size used in this analysis.

The locus of the failure within the interfacial polymer is also of interest. Montages of the iron and oxygen spectra obtained in the angle-resolved mode are shown in Figures 5 and 6, respectively. The iron spectra can be seen to decrease in magnitude as the grazing angle is approached. Similarly, the low binding energy component of the oxygen peak, due to the oxide, decreases in intensity as the grazing angle is approached. The normalized peak intensity at each angle was plotted as a function of angle to the surface for each of the two elements. This data is shown in Figure 7. For such a plot, both the slope and the intercept are functions of the thickness of the overlayer and the escape depth of the electrons. The plot for both of the peaks "tails off" as angles approach grazing. This indicates that there is a patchy or uneven character to the residue remaining on the surface. An even overlayer would have resulted in a straight plot. Based on these data, the overlayer has an average thickness of about 2.5 nm.

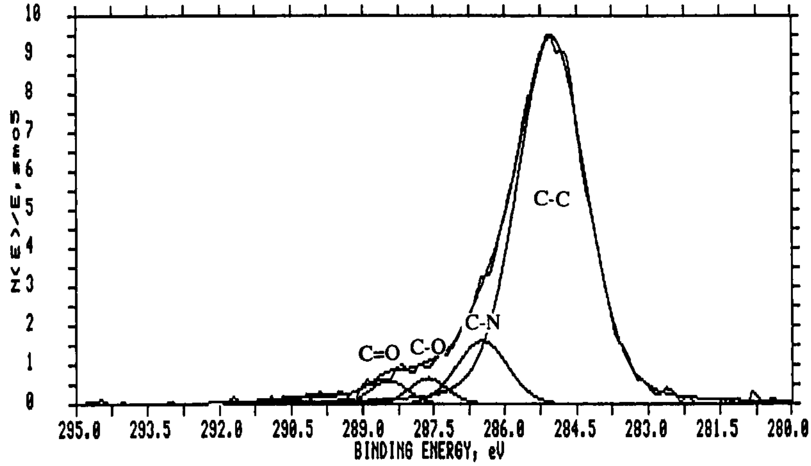

FIGURE 4 The C1s spectrum indicates the presence of carbon in four forms, each of which is attributable to the polymer. They are C—C bonds, C—N bonds, C—O bonds, and O—C—O bonds.

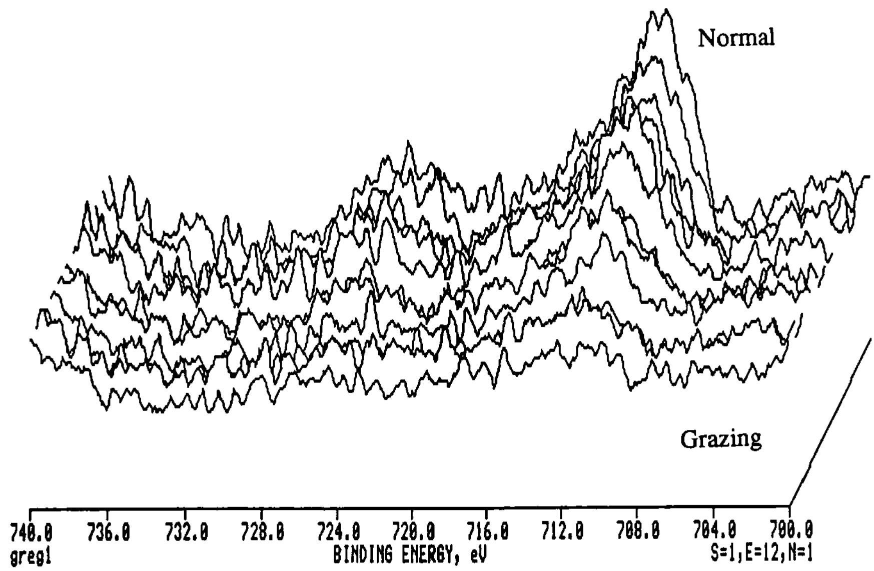

FIGURE 5 The montage of the angle resolved spectra for the Fe2p peak shows a decrease in the intensity of the iron signal as the grazing angle is approached.

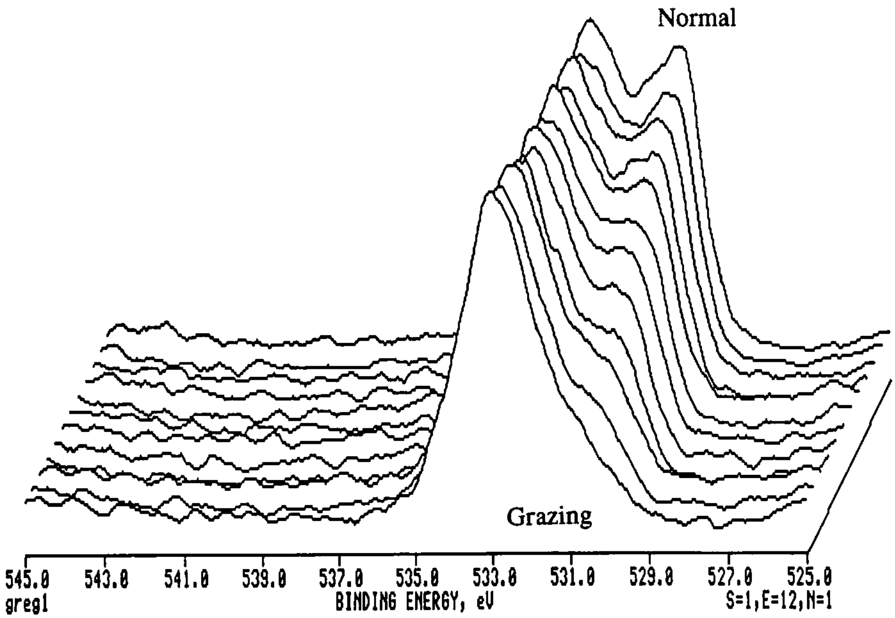

FIGURE 6 The montage of the O1s angle resolved spectra indicates the presence of oxygen in two forms. The high binding energy component is due to the oxygen in the polymer. The lower binding energy component is due to the oxygen present as iron oxide. The latter peak decreases in intensity as the grazing angle is approached.

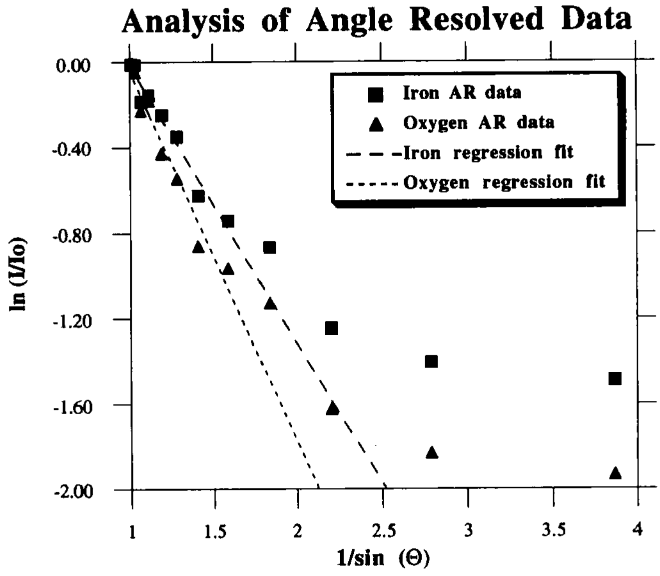

FIGURE 7 The natural log of the relative intensity is plotted as a function of reciprocal sin θ for the angle resolved data. The regression lines for the first eight points is also plotted. The slope and intercept of the regression line are directly related to the thickness of the polymer residue on the surface. The "tails" indicate that the residue has a patchy or uneven morphology.

DISCUSSION

Mechanical Properties

The breaking force is degraded by two mechanisms. Most is lost in a reversible process: drying the samples after exposure leads to recovery of 88% of their initial breaking force. Irreversible degradation of the joints also occurs. The irreversible degradation is largely due to the presence or the effect of the salt in the solution since similar samples exposed to distilled water showed 95% recovery.

The study previously cited, by Spadafora and Leidheiser,[5] had contrary results. It was similar to this one in that samples exposed to salt solution were compared with those exposed to distilled water. The former study indicated increases in time-to-failure of nearly 600 per cent for samples immersed in 0.1 molar sodium chloride as compared with those in distilled water. This behavior was attributed to a decrease in the thermodynamic activity of the water. In 0.1M NaCl solution the activity of water is reduced by .4 per cent as compared with distilled water.[20] The degradation observed in this epoxy/polyamide system overwhelms any strengthening mechanism due to the limited decrease in the activity of water.

The reversible portion of the degradation is due to the water alone. Large amounts of absorbed water in the system plasticize the adhesive, reducing the amount of externally applied force necessary to fracture the specimen by approximately 90%. The water forms hydrogen bonds with the polar groups (amines, carbonyls, and epoxides) causing the plasticization and consequent reduction of the overall strength of the joint. This phenomenon has been previously recognized.[21] Plasticization results in the loss of hardness and strength observed in the exposed samples. When removed from the electrolyte, the water desorbs from the polymer, returning the polymer to its stiff, and stronger, condition. This phenomenon occurs throughout the bulk of the polymer. Rigid, strong epoxy becomes pliable and easily torn after immersion.

The second component of the degradation is irreversible. The specimens exposed to salt solution have a lower wet breaking force than those exposed to distilled water. Furthermore, they do not fully recover their initial breaking force upon drying as do the samples exposed only to distilled water. In the wet condition, the salt-exposed samples are approximately 360 newtons weaker than the water exposed samples. After redrying the difference is about 380 newtons. The difference in breaking force between those samples exposed to salt water and those exposed to distilled water is approximately equivalent in both the as-exposed condition and the dried condition. The salt effect may be due to small quantities of water retained at the interface as waters of hydration of the salt known to be at the interface.[14] It is uncertain how much salt would be required at the interface for this mechanism to be effective. There is a trace amount of chlorine visible in the survey spectra from the interface, demonstrating that chloride ions can migrate to the interface during exposure.

The pH of the solution did not have an observable effect on the strength of the joints. The conclusion is that the main mechanisms of degradation were due to the ingress of water and chloride. Chemical reaction with hydroxyl ions and degradation of the polymer were not observed as a function of pH.

Failure Mode

A variety of failure modes have been reported in polymer/metal systems. Some systems have been reported to display interfacial mixed-mode failure.[22] In an acrylic/brass system the bond rupture line wandered between the oxide and the polymer, indicating that the oxide and the polymer interphase were of comparable strength. Other systems have been reported in which the failure locus was primarily in the oxide interphase region.[23] Either of these cases would be indicated by the presence of iron oxide in the spectra obtained from the polymer side of the interfacial failure. In the epoxy/polyamide system studied here, there was no indication of iron or iron oxide on the polymer failure surface. This, along with the presence of polymer residue on the metal failure surface, indicate that the failure occurred in the interfacial layer of the polymer.

The specimens displayed primarily cohesive failure in the polymer prior to electrolyte exposure. All displayed interfacial failure in the polymer after exposure to any of the aqueous solutions. However, upon drying some of the cohesive failure mode was regained. The difference in recovery of cohesive failure mode between samples exposed to salt solution as compared with those immersed in distilled water (30% *versus* 60%) is further evidence that the presence of salt in the electrolyte contributes to damage. The change in the relative amount of interfacial failure indicates that the interfacial strength is degraded more than the bulk strength. If they degraded equally, it would be expected that the failure locus would remain the same, but that the stress necessary to initiate failure would be decreased.

The carbon peak envelope on the metal surface after interfacial failure contained the same components as the spectrum of the bulk polymer. However, inspection of the spectrum from the interface indicates that there is a greater proportion of hardener at the interface. This was determined by comparing the relative areas of the C—N and C—O peaks. The C—N peaks are only present from the polyamide hardener, the C—O only from the epoxy resin. The bulk adhesive had a C—N to C—O peak area ratio of approximately 1.6. The interfacial adhesive residue had a C—N to C—O peak area ratio of 2.8. The presence of greater amounts of hardener at the interphase could account for the fact that the failure became entirely interfacial upon exposure to aqueous environments. The double-bonded oxygens and the amine groups, being the most polar, would most readily hydrogen bond with the water, decreasing the local strength of the joint disproportionately. The higher free volume of the softer material at the interface may also lead to greater local water accumulation. This provides a rationale for the generally-accepted view that water tends to accumulate at the interphase when adhesive joints are exposed to wet or moist environments.[22]

Residue Thickness

A description of the locus of the interfacial failure aids in understanding the mechanism by which failure occurred. The angle-resolved data were used to determine that the thickness of the polymeric residue on the metal failure surface was approximately 2.5 nm. The intensity ratios for both the iron peak and the low binding energy portion of the oxygen peak (due to the metal oxide) taken near a grazing angle "tail off" from the straight line made by those points obtained closer to normal incidence. This indicates that the residue has a patchy or uneven morphology. This may mean that there are areas which are covered by the thin overlayer of polymer adjacent to areas where the oxide is bare; or it may mean that the polymeric residue has an uneven thickness distribution over the entire surface. It may cover the entire surface, but be relatively thick in some areas and much thinner in other areas. Comparing the data from the iron peak and from the oxygen peak it was concluded that the average thickness of the overlayer was approximately 2.5 nm.

As a first estimate, it was concluded that most of the overlayer was thin, and covering a fairly large area. The rationale for this stems from the dependence of the peak intensity on angle. If the overlayer were patchy and thick (relative to the escape depth of the electrons) the signal from the substrate would be relatively constant. This is because the exposed substrate would contribute equally at all angles. Since that is not the case, most of the overlayer must be on the order of, or thinner than, the escape depth of the electrons originating in the substrate.

The overall mechanism of interaction between the polymer/metal system and the aqueous environments is believed to be the combined result of the ingress of chloride and water and the dissolution and migration of the calcium carbonate filler. The latter was previously discussed.[9] It was concluded that the buffering effect of the calcium carbonate dominated the electrochemical properties of the system. The mechanical properties, however, are dominated by the water, when the system is wet, and by the presence of the chloride, which migrates in during immersion, when it is dry. The overall breaking force of the joint is more severely degraded in the vicinity of the interface due to the excess hardener present there. The uneven thickness of the polymeric residue remaining after interfacial failure may be a result of the inhomogeneous distribution of the hardener. This distribution may also be responsible for clustering of water at the interface which could further lead to localized damage at the interface.

CONCLUSIONS

The epoxy/polyamide system studied was exposed to sodium chloride solutions of varying pH for three weeks. The mechanical properties of adhesive joints were evaluated and the mode of failure was analyzed. Those samples exhibiting interfacial failure were analyzed to determine the loci of failure.

- The breaking force of lap shear joints decreased by 90 per cent when exposed to distilled water for three weeks. This loss was almost fully recovered upon drying.
- The breaking force of lap shear joints exposed to salt solution declined by 97 per cent. This loss was largely, but not completely, recovered upon drying.
- The fracture locus changed, upon exposure to aqueous environments, from cohesive in the polymer to interfacial in the polymer regardless of the electrolyte. Some of the cohesive fracture mode was regained upon drying, more for the samples exposed to distilled water (60% cohesive) than for the samples exposed to salt solutions (30% cohesive). It is interesting to note that while a large portion of the failure locus (70%) remained interfacial after salt exposure and drying, nearly 90% of the breaking force was recovered.
- Two distinct mechanisms are involved with the degradation of adhesion: a reversible mechanism believed to be associated with water-induced plasticization and an irreversible degradation associated with the presence of salt in solution.
- A polymer residue remained on the steel surface in the areas where interfacial failure was observed.
- A greater amount of hardener was present at the interface than in the bulk polymer. The combined effects of the increased local polarity and greater free volume combine to increase the local concentration of absorbed water. In turn, this leads to the accelerated degradation of the interphase as compared with the bulk.
- XPS was further used to characterize the chemistry and morphology of the polymer residue remaining on the metal surface after interfacial failure. The interfacial polymer layer was found to be of uneven thickness over the surface with an average thickness of approximately 2.5 nm.

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