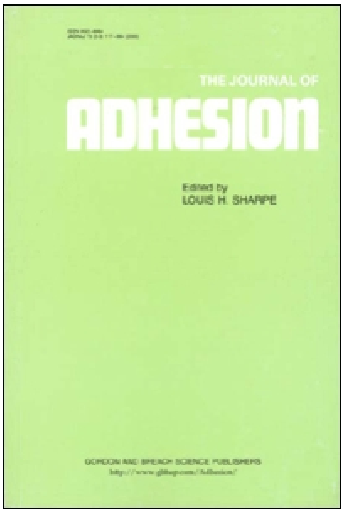

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Schmidt, R. G. and Bell, J. P.(1988) 'Investigation of Steel/Epoxy Adhesion Durability Using Polymeric Coupling Agents. II. Factors Affecting Adhesion Durability', The Journal of Adhesion, 25: 2, 85 — 107
To link to this Article: DOI: 10.1080/00218468808071252
URL: http://dx.doi.org/10.1080/00218468808071252

J. Adhesion, 1988, Vol. 25, pp. 85–107
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Printed in the United Kingdom

Investigation of Steel/Epoxy Adhesion Durability Using Polymeric Coupling Agents. II. Factors Affecting Adhesion Durability

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(Received May 22, 1987; in final form September 30, 1987)

Ethylene mercaptoester (EME) copolymers containing 23–90 wt% mercaptoester units were employed separately as coupling agents in steel/epoxy peel adhesion systems. As coupling agent functionality is increased the initial adhesion strength of the steel/EME/epoxy peel systems also increased, approaching a ten-fold improvement over controls for the EME 90 coupling agent. However, the degree of corrosion protection decreased significantly with increasing concentration of mercaptoester units. The best corrosion protection was obtained with the EME 23/epoxy resin system which protected the steel adherend for an average of 48 hours in 57°C water baths. Regardless of the coupling agent used, all of the peel specimens exhibited poor adhesion after 5–11 hours exposure to hot water. Information from hydrolysis stability, water absorption, locus of failure and internal stress analyses when pooled show that the observed adhesion loss is attributable to the effect of water on the epoxy resin used; failure occurred within the epoxy.

KEY WORDS Polymeric coupling agents; adhesion durability; 90 degree peel test; hydrolytic stability; water absorption; internal stress.

INTRODUCTION

All adhesion scientists will agree that water is a very destructive environment for metal/polymer adhesion systems. Several reviews

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have been written which address this problem.[1-4] In an attempt to improve adhesion durability, a number of researchers[5-11] have employed various low molecular weight coupling agents which have the ability to form chemical bonds "across" the metal/polymer interface. These ventures have met some success, but further improvements are desirable.

As we reported previously,[12] ethylene mercaptoester (EME) copolymers with various mercaptoester unit concentrations (23-90 wt%) have been synthesized and employed in steel/epoxy thick film adhesion systems. These semicrystalline copolymers exhibit good thermal stability. In addition, they have been shown to interact chemically with epoxide rings of epoxy resins and with free iron ions. These polymeric coupling agents promise to be tougher, more hydrophobic and less sensitive to thickness than their low molecular weight counterparts. It is believed that these features will result in a coupling agent region, and hence an adhesion system, with increased strength and durability.

The EME copolymer coupling agents are also attractive since they can be used as a tool to study the effect of various interfacial properties on adhesion durability. Varying the concentration of functional groups on the EME coupling agents not only has an effect upon the number of successful bonds formed across the steel/epoxy interface, but also influences the hydrophobicity and surface energy of the coupling agent region without changing the general chemistry of the adhesion system. Any of these factors could ultimately govern the durability of the interfacial region. The goal of this research is to gain an understanding of the effect of each of these factors on the steel/coupling agent/epoxy interphase. Although a specific steel/epoxy system is being used, it is believed that the information obtained will be applicable to metal/thermoset adhesion systems in general.

In the present study the effect of the coupling agent functionality on adhesion durability was analyzed in steel/EME/epoxy peel systems. The locus of failure of the peel samples, the hydrolysis stability of the EME copolymers and the wet strength of the epoxy resin were investigated to gain insight as to which factors control the strength loss in these systems in the presence of water. Also, the ability of the polymeric coupling agent to relieve interfacial stress was studied utilizing a bending beam apparatus.

EXPERIMENTAL

Materials

The EME copolymers used in this study were synthesized from ethylene-vinyl acetate copolymers as reported previously,[12] first by hydrolysis of acetate groups to the alcohol, followed by esterification with mercaptoacetic acid to give the mercaptoester copolymer. Peel adherends (1″ × 4″) were cut from 4″ × 12″ 1010 SAE 20 mil-thick carbon steel plates (Q Panel) using a squaring sheet metal shear blade. The plates were wiped with a damp cloth and acetone degreased before undergoing the specified pretreatments. A diglycidyl ether of bisphenol A type of epoxy resin (Epon 1001®, Shell Development Co.) was dissolved (40 wt% solids) in an equal weight solvent mixture of xylenes, Cellosolve ® and MIBK prior to mixing with Versamid 115® (Miller Stephenson Chemical Co.) (80 phr) polyamide curing agent. Pressure-sensitive polyethylene tape was obtained from 3M Co. Three-mil thick, 6″ × 5/16″ bending beam adherends were cut from 1010 CRS steel foil (Precision Brand) using a sheet metal shear blade. Trimethylolpropane trithioglycolate (TTTG), 95 + % low molecular weight mercaptoester coupling agent (Evans Chemetics) was used as received.

Peel sample preparation

To provide easy handling and insure identical treatments to every sample, the steel plates were placed in glass racks (capacity: 30 samples) prior to the pretreatment procedures. The 1″ × 4″ steel plates were prepared for bonding by first degreasing for 15 min in an acetone bath followed by 15 min exposure to a 70°C, 3 wt% aqueous citric acid bath with pH adjusted to 4.0 using ammonium hydroxide. A distilled water wash followed by immersion in a xylenes bath completed the pre-coupling-agent treatments. All pretreatments were carried out in a nitrogen-purged glove box. The pretreatments are designed to provide a fresh oxide layer for bonding. The EME coupling agents were applied to the steel plates from solution (0.25 wt% in xylenes/methanol) at 60°C under nitrogen. A one-min wash in a xylenes/methanol bath was the final pretreatment step. Ellipsometry and X-ray photoelectron spectroscopy results indicated that the coupling agent thickness was approximately 50–100 Å. Epon 1001/Versamid 115 (five-mil dry thickness) films were applied to the pretreated samples one hour after mixing at room temperature using a thin film applicator (Gardner Labs). Pretreated steel adherends were kept under an inert atmosphere until just prior to application of the epoxy film. The films were cured for 7 days in air at room temperature. Post curing for 9 hours at 80°C was found to be necessary to remove the residual solvent and complete the crosslinking reactions.[13] The back and sides of the samples were masked with polyethylene tape prior to exposure to a 57°C distilled water bath.

90 degree peel test

Following specified water exposures, samples were scribed to a width of 0.7 in. with a razor blade and immediately tested for adhesion strength using a 90° peel test apparatus designed in our laboratory (Figure 1). The 90° peel test fixture attaches to the crosshead of an Instron® tensile test machine. The sample stage slides freely on low friction bearings, enabling the peel angle to

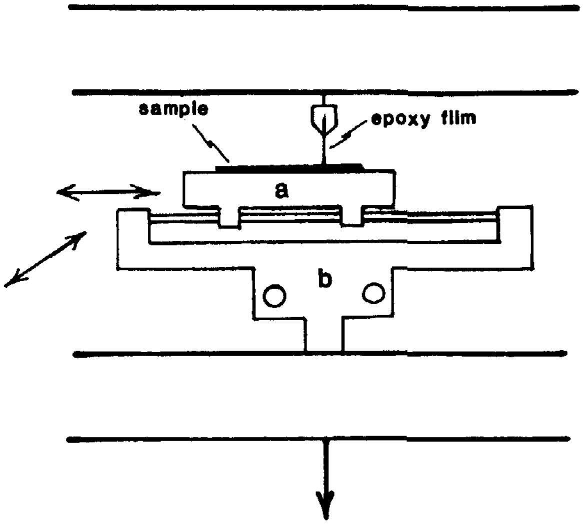

FIGURE 1 90 degree peel test apparatus.

remain at 90° as the crosshead moves downward. A TM-S Instron tensile tester equipped with either a 500 g, 2000 g or 50 lb load cell and a chart recorder was used to perform the measurements. The peel rate for all tests was 0.4 in/min. The average peel force was taken from the chart recorder output of peel force *vs.* debonded length. The values recorded are an average of at least four samples. All of the peel test variables (*i.e.* crosshead speed, peel angle, epoxy thickness, epoxy-composition) were chosen so as to eliminate as many extraneous contributions to the peel force as possible. Therefore, one should be careful when comparing other peel test results with the ones reported here.

Hydrolytic stability

EME copolymers were cast from xylenes solutions on CaF_2 plates. The samples were immersed in either distilled water ($pH = 6.5$) or aqueous NaOH ($pH = 11.6$) baths at 57°C. Hydrolytic stability of the copolymers was monitored using a Nicolet 60SX FTIR spectrometer.

X-ray Photoelectron Spectroscopy (XPS)

XPS data were obtained with a Leybold-Heraeus LHS-10 electron spectrometer employing MgKα exciting radiation (1253.6 eV). The X-ray power supply was run at 13 kV and 10 mA. The chamber pressure was maintained at approximately 3×10^{-9} torr during the scans. Elemental mole fractions were determined from band areas and empirical atomic sensitivity factors.[14]

Depth profiling was accomplished by argon ion ($E_{Ar+} = 5000$ eV) sputtering in conjunction with XPS. A rastered beam (8 mm × 8 mm) with an emission current of 10 mA and a beam current density of 5–10 $\mu A/cm^3$ was used for this study. A beam angle of 30° and a chamber pressure of 4×10^{-7} torr were maintained during the sputtering.

SEM

A 1200 B Amray Scanning Electron microscope equipped with a Polaroid camera (Type 55 film) was employed to obtain micrographs of the peel sample fracture surfaces. Prior to analysis the samples were mounted on aluminium stages and gold/palladium coated in a high vacuum chamber.

Water absorption

Five-mil thick Epon 1001/Versamid 115 films were cast, using a doctor blade, onto steel adherends treated with a mold release agent. The resin was cured for 7 days at room temperature followed by a 9 hour 80°C post cure. The epoxy film was gently removed from the steel adherend and cut into one-inch squares. The films were dried in a vacuum oven and weighed prior to immersion in separate 57°C water baths. The samples were removed from the baths at specified times and their water absorption was measured gravimetrically. Before weighing, excess surface water was removed by gently blotting the samples with a dry laboratory napkin.

Tensile properties

Dog bone specimens were stamped from epoxy films prepared identically to the water absorption samples. A TM-S Instron tensile tester equipped with a chart recorder and an extensiometer were used to measure the tensile modulus and yield stress of epoxy samples immediately following specified 57°C water immersion. All measurements were carried out with a crosshead speed of 0.2 in/min.

Internal stress measurements

Ten-mil thick Epon 1001/V115 films were cast on precut 1010 CRS 6″ × 5/16″ × 3-mil thick strips with a doctor blade. Prior to coating, the steel strips either underwent coupling agent pretreatments (identical to peel specimens) or solvent degreasing in acetone. Five strips held together by a polyethylene tape backing were coated simultaneously to ensure an even coating over the entire width of each sample. Following a 7-day room temperature cure the backing was carefully removed (peeled at 180 degrees to avoid bending the sample). The samples were post cured for 9 hours at 80°C on the bending beam apparatus which is similar to that used previously by

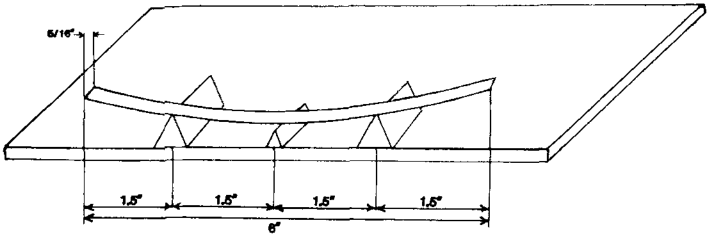

FIGURE 2 Bending beam apparatus.

Dannenberg[15] (Figure 2). By placing a large dish of anhydrous calcium sulfate in the oven all the measurements were carried out at approximately zero humidity. A constant rate of cooling of approximately −1°C/min was obtained using liquid carbon dioxide. As the sample was cooled from its post curing conditions it began to curve due to the excess thermal contraction of the resin. The deflection of the beam from horizontal was measured with a Gardner microscope cathetometer positioned outside the glass window of the oven. As long as the elastic limits of the steel and epoxy were not exceeded, the radius of curvature of the sample could be related to the contractive stress in the resin through Eq. (1) presented by Dannenberg.[15]

$$S = P/bh_1 = (E_2h_2^3/12h_1(8d/LH)(F(m, n)) \qquad (1)$$

where

S = stress through the resin cross sectional area,
P = total contractive force,
b = width of beam,
E_1 = Young's modulus of resin,
E_2 = Young's modulus of steel beam,
h_1 = thickness of film,
h_2 = thickness of steel foil,
H = thickness of resin + foil,
d = deflection of beam center,
L = length of beam between supports,
$m = E_1/E_2$
$n = h_1/h_2$ and

$$F(m, n) = ((1 - mn^2)^3(1 - m))/(1 + mn)^3 + ((mn(n + 2) + 1)^3 + m(mn^2 + 2n) + 1)^3)/(1 + mn)^3$$

The moduli of elasticity of the epoxy resin at the test temperatures were measured by the method suggested by Inoue and Kobatake.[16] The samples used were similar to those described above, but coated evenly on both sides so that no bending was induced upon thermal treatment. Small weights were placed on the ends of the samples and the observed deflection was related to the modulus through an equation. Sample calculations are shown in the appendix.

Contact angle measurements

Using the sessile drop method, advancing and receding contact angles of four test liquids were measured on polymeric surfaces which were dip coated onto steel plates. An IMASS® contact angle analyzer which projects an enlarged image of the drop on a calibrated screen was used for the measurements. The test liquids consisted of tritolyl phosphate, methylene iodide, formamide, and glycerol which were obtained in purities exceeding 99.5% or distilled. These liquids were chosen due to their relatively low vapor pressures and the wide range of polar and dispersion components of surface energy which they span. The test liquids and samples were stored, and the measurements were completed, at the equilibrium temperature of the contact angle analyzer (38°C).

From the measured values, the equilibrium contact angle from each of the four test liquids was calculated (assuming a roughness factor of unity) and paired in all possible combinations (*i.e.* 1–2, 1–3, 1–4, 2–3, 2–4, 3–4).[17] Similar to the findings of Kaelble,[18] pairs with very similar polar and dispersion components of surface energy gave unreasonably high values. Kaelble proposed that in order to be included in the analysis, the absolute value of D for any pair must equal or exceed 10 mJ/m^2 where

$$D = \{(\gamma_L^d)_i(\gamma_L^p)_j\}^{1/2} - \{(\gamma_L^d)_j(\gamma_L^p)_i\}^{1/2} \qquad (2)$$

Only the pairs which passed this restriction were used and the mean of the resulting surface energy values are reported.

RESULTS

Adhesion durability

Table I lists the 90° peel adhesion values for wet and redried samples prepared with acetone degreasing (controls), three different

TABLE I
90° peel strengths (g/in) of wet and (redried) steel/EME/epoxy systems following specified exposures to 57°C water baths, peel rate: 0.4 in/min.

		Peel strength (g/in) Immersion time (hrs 57°C water)					Corrosion protection (hrs)
Treatment	0	1	3	5	11	24	
Control	78	69	17	9	4	2	14
		(57)	(30)	(24)	(16)	(5)	
EME 23	47	26	16	11	10	9	46
		(40)	(31)	(26)	(23)	(19)	
EME 47	284	139	47	36	16	13	32
		(196)	(83)	(71)	(57)	(44)	
EME 90	729	319	36	24	16	11	20
		(543)	(311)	(187)	(66)	(30)	
TTTG	684	106	28	11	8	3	16
		(650)	(180)	(17)	(19)	(9)	

† Samples dried 1 hr under vacuum at 50°C.

EME polymer coupling agent/citric acid and TTTG (low MW coupling agent)/citric acid pretreatments. The samples were soaked in 57°C water for the times indicated. Also, the average amount of time that the coupling agent/epoxy resin systems protected the steel adherends from corrosion under these conditions is reported. The appearance of an average of three or more pits per sample was used as the criterion for the presence of significant corrosion. All of the pits were black in color.

The following conclusions may be drawn from these peel data:

1) Presence of the coupling agent/citric acid treatments enhanced both the adhesion durability and corrosion protection beyond that of the controls.

2) Both the initial and redried adhesion strengths increased significantly with an increase in coupling agent functionality.

3) The ability of the coupling agents to protect the steel substrates from corrosion decreased with an increase in coupling agent functionality.

4) Within 11–24 hours of exposure to 57°C water the wet adhesion strengths of all the coupling agent samples dropped to essentially equal values.

Possible explanations will be given in the Discussion section.

Hydrolytic stability

FTIR spectroscopy was used to monitor the stability of the EME copolymers in 57°C deionized water (pH = 6.5) and 57°C dilute

TABLE II
Hydrolytic stability of EME copolymers as monitored by carbonyl stretching to C—H bending IR absorption ratios

	Exposure time (days)						
	Water				Naoh soln		
Polymer	0	1	7	28	1†	7†	28†
EME 23	1.49	1.41	1.35	1.27	1.25	1.25	1.08
EME 31	2.75	2.49	2.42	2.33	2.22	1.95	1.92
EME 47	3.24	2.67	2.86	2.30	2.29	2.35	1.97

† Additional exposure time following 28 days in 57°C water.

NaOH solutions (pH = 11.6) (hydroxide ions would be present in these systems if corrosion reactions were taking place on the steel surface). Since the relative number of carbonyl groups present as compared to CH bonds will diminish as hydrolysis proceeds, the C=O stretching (1731 cm^{-1}) and C—H bending (1463 cm^{-1}) absorption bands can be used to analyze the hydrolytic stability of the copolymers. Table II lists the ratio of carbonyl stretching to C—H bending absorption magnitudes at various exposure times for each of the copolymers tested.

The EME copolymers were somewhat susceptible to hydrolysis, as indicated in Table II by the decreasing trend in C=0/C—H bending absorption ratios with exposure to the 57°C baths.

Locus of failure

X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) were used to obtain both quantitative and qualitative analyses of the peel specimen failure surfaces. In the XPS analyses, iron atoms in the steel, sulfur atoms in the coupling agent and nitrogen atoms in the epoxy curing agent served as natural tags and greatly enhanced the ability of this technique to identify the region in which failure occurred. XPS is a very surface sensitive technique. The maximum escape depth of a photoelectron is approximately 50 Å. Table III indicates the mole fractions of each of the elements (C, O, N, S, Fe) that were detected on both the epoxy and steel failure surfaces by XPS. Carbon, oxygen and nitrogen were the only elements present in a significant quantity on all of the steel side and epoxy side failure surfaces. This coupled

TABLE III
Surface compositions of steel/EME/epoxy failure surfaces as determined using XPS: (top) epoxy side, (bottom) steel side

	Mole fractions				
Epoxy side	X_C	X_O	X_N	X_S	X_{FE}
EME 23 0 hr	0.81	0.15	0.04		
5 hr	—	—	—	—	—
EME 47 0 hr	0.80	0.16	0.04		
5 hr	—	—	—	—	—
EME 90 0 hr	—	—	—	—	—
5 hr	0.82	0.15	0.03		0.004
Steel side					
EME 23 0 hr	0.55	0.37	0.04		0.04
5 hr	0.51	0.40	0.04		0.05
EME 47 0 hr	0.53	0.37	0.04	0.0008	0.05
5 hr	0.68	0.28	0.02		0.03
EME 90 0 hr	—	—	—	—	—
5 hr	0.50	0.40	0.03		0.06
Epoxy theoretical					
Epon 1001/V 115	0.84	0.11	0.05		

with the fact that significant concentrations of sulfur were absent from all of the failure surfaces suggests that failure occurred primarily through the epoxy resin in all cases. Table III shows that a small amount of iron and an increased oxygen concentration was detected on the steel failure surfaces. Considering the maximum photoelectron escape depth, this indicates that failure occurred in the epoxy very near the interface. It is also possible that small regions were present on the sample surface where iron oxide was exposed due to migration or surface protrusions. SEM micrographs of the steel and epoxy failure surfaces of EME 47 samples after 5-hour exposures to 57°C water are shown in Figure 3. The presence of plastic deformation regions (consistent with polymeric morphology) on the failure surfaces supports the XPS data indicating failure occurred within the epoxy resin in these systems.

In an attempt to gain additional information, a depth profile of the steel failure surface of the 50 Å EME 90 one-hour water exposure sample was completed utilizing ion beam sputtering. Figure 4 shows that the Carbon (1s) content decreases and the Fe($2p^{1/2}$, $2p^{3/2}$) surface content increases as the surface is sputtered.

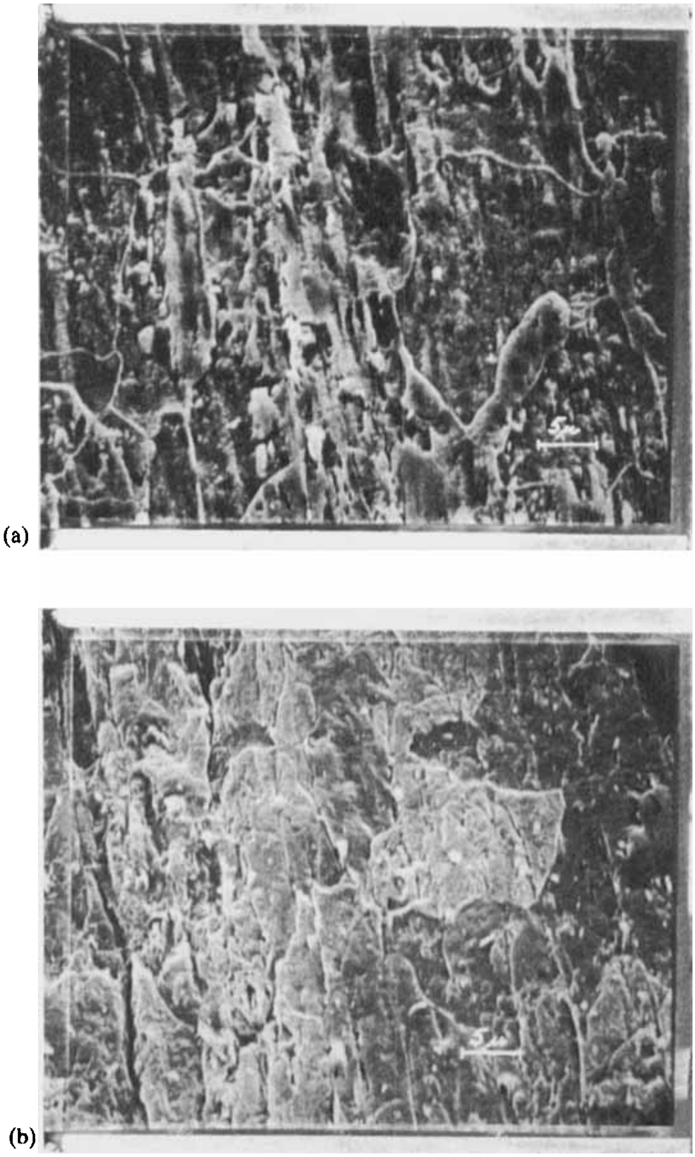

FIGURE 3 SEM micrographs of, (a) steel side and, (b) epoxy side 90° peel failure surfaces from samples treated with EME 47 and exposed to 57°C water for 5 hours prior to testing.

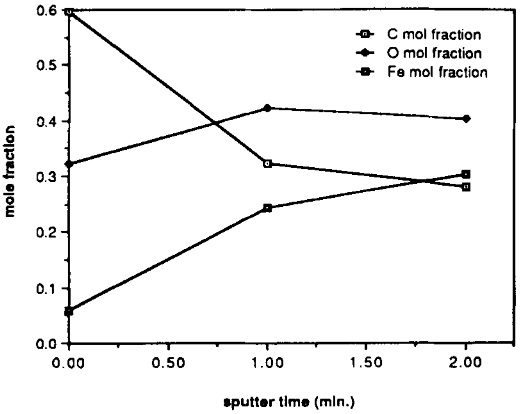

FIGURE 4 Depth profile analysis of steel/EME90/epoxy failure surface (C, O, Fe): steel side.

Oxygen (1s) which is present in both the organic films and in the iron oxide remains fairly constant during sputtering.

In the steel/EME/epoxy peel systems, nitrogen atoms and sulfur atoms, although present in relatively small concentrations, should serve as natural tags for the epoxy and EME coupling agent phases respectively. Figure 5 indicates that primarily nitrogen, and hence epoxy, is present on the failure surface initially. However, as

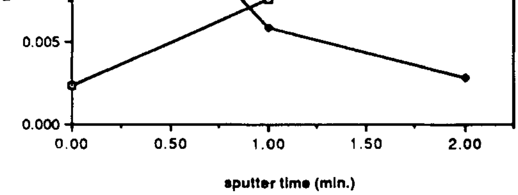

FIGURE 5 Depth profile analysis of steel/EME90/epoxy failure surface (N, S): steel side.

sputtering continues, the nitrogen concentration of the surface decreases as the sulfur concentration increases, suggesting that the EME coupling agent layer remains intact on the steel surface during failure. Also, the fairly gradual increase in sulfur and decrease in nitrogen indicates that some interdiffusion between the epoxy and EME 90 phases likely exists.

Wet epoxy properties

Figure 6 shows the effect of a 57°C water immersion on the water absorption, tensile modulus and yield stress of 5-mil thick Epon 1001/V115 films. The data indicates that the equilibrium water absorption under these conditions was approximately 3–3.5% by weight. The decrease in tensile modulus and yield stress associated with the water absorption was 66% and 70% respectively. The majority of the water absorption and resulting decline in tensile properties occurred within the first hour of water immersion. This is consistent with the property losses after water exposure that were presented in Table I.

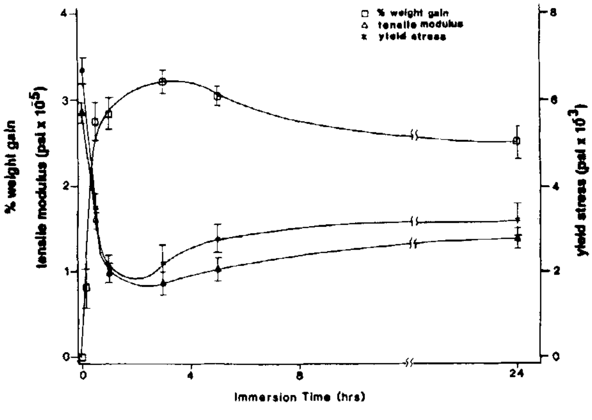

FIGURE 6 Effect of 57°C water immersion on percent weight gain, tensile modulus, and yield stress of Epon1001/V115 epoxy resin system.

Internal stress

Bending beam experiments were completed to obtain a semi-quantitative measure of the level of stress that develops in steel/Epon 1001/V115 adhesion systems. Upon cooling from the post cure temperature of 80°C, thermal stresses were created in the steel/epoxy interphase due to the large differences in their thermal expansion coefficients.[19] Dannenberg[15] and Shimbo *et al.*[19] have shown that for thin coatings (<5 mil), as long as the epoxy resin is above its glass transition temperature (*Tg*), the polymer molecules have sufficient mobility to relieve the stresses as they develop. At the *Tg* of the resin the mobility of the polymer molecules are severely restricted. Therefore, as the temperature decreases below *Tg*, stresses develop which cannot be readily relieved and hence can reduce the adhesion strength of the system.

By using a thin (3 mil) metal adherend strip the contractive stresses developed at the interface of the steel/epoxy samples can be observed as a concave curving of the sample on the bending beam apparatus. Through the use of a series of equations developed by Inoue and Kobatake,[16] the magnitude of the contractive stresses can be calculated from the measured deflection of the beam from its stress-free state and the epoxy and steel tensile properties.

Figure 7 shows the measured deflection as a function of temperature of steel/epoxy samples with and without a thin polymer coupling agent (EME 47) applied to the adherend. These data reveal that the polymeric coupling agent was effective at delaying the onset of interfacial stress in the system by approximately 7–10°C.

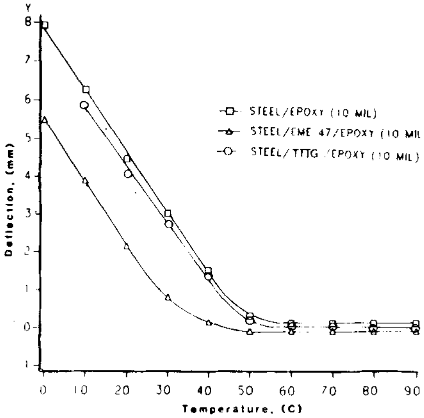

FIGURE 7 Deflection of steel/epoxy, steel/EME/epoxy and steel/TTTG/epoxy beams from horizontal upon cooling at −1°C/min from 90°C.

TABLE IV
Surface tensions and fractional polarities of EME copolymer and epoxy surfaces

Polymer	γ^{p}*	γ^{s}*	X^{p}**
Epoxy (1001/V115)	9.9	40.8	0.24
EME (23)	3.0	37.2	0.08
EME (47)	8.4	43.1	0.19
EME (90)	14.8	46.2	0.32

* Surface energy in dynes/cm
** $X^{p} = \gamma^{p}/\gamma^{s}$

Surface energy

When an EME copolymer coupling agent is applied to a metal surface before bonding it greatly reduces the surface energy of the metal substrate. How well an epoxy adhesive wets the substrate will be governed by the surface energetics of the two contacting phases. The surface energy of the EME copolymers have been determined using contact angle measurements and the harmonic-mean equation.[17,20] Table IV lists the calculated values of the polar components (γ^{p}) and total (γ^{s}) surface energies along with the resulting fractional polarities ($X^{p}:X^{p} = \gamma^{p}/\gamma^{s}$) of these polymers. It is apparent that the concentration of polar reactive groups on the EME coupling agents has a significant effect on the fractional polarity and hence the wettability of the adherend surface.

DISCUSSION

The polymeric nature of the EME coupling agents should provide significant advantages over the more common low molecular weight coupling agents. Unlike low molecular weight compounds, polymers are capable of bearing a load, which should make the effectiveness of the coupling agents much less sensitive to the thickness of this layer. In addition, low molecular weight coupling agents are normally quite water permeable. Therefore, their presence can actually promote the infiltration of destructive water molecules into the interfacial region. Since the EME copolymers consist of reactive hydrophilic groups on a hydrophobic hydrocarbon backbone, their use should reduce the water permeability of the interphase.

Unlike the low molecular weight compounds, the viscoelastic properties of the polymeric coupling agents should enable them to help relieve internal stresses in metal/thermoset adhesion systems. This is advantageous since significant stresses can develop during the post-cure cooling of the thermoset, primarily due to the thermal expansion coefficient mismatch between the metal and the polymer.[19,21–23] The crosslinked structure and the elevated glass transition temperatures of most thermosets limit their stress relaxation ability. Epoxy resins have thermal expansion coefficients which exceed that of steel by an order of magnitude.[19] Hence, a large degree of stress can develop. Interfacial stress has been cited as the cause of failure in a number of adhesion systems.[19,21,24,25]

Table I shows that the initial adhesion strength was enhanced by almost an order of magnitude over the controls by employing the EME 90 coupling agent. On the other hand, the more hydrophobic EME 23 coupling agent was the most successful at protecting the steel adherend from corrosion reactions. Corrosion protection was extended over a period three times as long as that achieved in the control systems.

The peel strength results in Table I indicate that maximum initial (dry) adhesion is obtained by incorporating a large concentration of polar reactive moieties along the polymer coupling agent backbone. However, such practice is not without its consequences. The increased hydrophilicity associated with an increase in polar group concentration reduces the ability of the coupling agent/resin system to protect the steel adherend from corrosion. The presence of an electrolyte at the steel surface is required to initiate the corrosion reactions. Apparently water molecules can reach the steel surface, in sufficient concentration to provide the necessary electrolyte, more readily when a coupling agent that is less resistant to water permeation is present in the interphase.

The results suggest that the properties required of the interfacial region for maximum dry adhesion strength differ from those required for maximum wet adhesion durability and corrosion protection. Consequently, the optimum coupling agent/resin adhesion system for a structural joint will most likely differ from that for a protective coating. Often too much emphasis is placed on initial adhesion strength. The polar groups that are generally incorporated into adhesion systems to improve dry strength can actually be detrimental to adhesion durability. These factors should be considered when designing an adhesion system.

Table I indicates that, regardless of the coupling agent employed, all of the peel samples exhibited very poor adhesion strengths after 5–11 hours exposure to hot water. It was first thought that this may be attributable to the susceptibility of the ester functional group to hydrolysis. The hydrolysis stability results in Table II do indeed show that the EME coupling agents were somewhat susceptible to hydrolysis over a month's exposure to 57°C water. This suggests that hydrolysis of the coupling agent could contribute to the observed adhesion strength loss that occurred in the steel/EME/epoxy systems. In addition, the mercaptoacetic acid formed by hydrolysis of the EME could aid in the acceleration of both epoxy resin degradation and steel corrosion reactions. However, since the time frame of the wet peel adhesion experiment spanned only 24 hours, hydrolysis is not believed to be the primary cause of peel strength decline.

Both XPS and SEM analyses (Table III and Figure 3) indicate that the locus of failure in all samples tested (0 and 5 hour 57°C water immersion) occurred within the epoxy in a region very near the interface. This suggests that the observed strength losses were most likely controlled by the wet strength properties of the epoxy resin. Figure 6 shows that the epoxy resin system used in this study was quite water sensitive. A substantial decline in the bulk tensile properties was observed as water was absorbed. Realizing that the tensile properties in the thin interfacial boundary layer of the epoxy may very well be even more water sensitive than the bulk resin, it is reasonable to assume that the properties of the resin are the primary factors controlling the adhesion strength loss that occurs in the presence of hot water. In an attempt to gain more information about the ability of the EME coupling agents to promote improved adhesion durability, a more tightly crosslinked and thus less water sensitive epoxy resin system is currently being evaluated.

Unlike typical water absorption behavior, the curve in Figure 6 did not approach an equilibrium weight gain value asymptotically. A gas chromatography/mass spectrometry analysis of the water bath has shown that a small but significant amount of residual MIBK was extracted from the resin during water exposure. Therefore, the atypical water absorption curve has been attributed to the loss of weight of the epoxy resin by solvent extraction while water was absorbed. Since residual solvent serves as a plasticizer to the epoxy resin, its removal also influenced the resulting tensile properties.

Although XPS and SEM results indicate that the failure region for all samples appeared to be very similar, the initial strength varied quite drastically with change in coupling agent functionality. A complete explanation for this behavior has yet to be determined. However, it appears that the failure region is initially strengthened by increasing the concentration of coupling agent reactive groups present in the interphase. Whether this can be attributed to either an increase in the number of successful chemical bonds formed with the resin or an increase in interpenetration between the two phases due to an increase in coupling agent surface energy or both is not known. But, regardless of the strengthening mechanisms, immersion in 57°C water for 5–11 hours greatly reduces the effect of coupling agent functionality on adhesion strength in these systems.

Table I shows that adhesion tests were also completed on specimens treated with a low molecular weight multifunctional mercaptoester compound (TTTG). As reported previously,[12] the TTTG coupling agent contains a significantly higher concentration of mercaptoester groups by weight than EME 90. As shown in Table I, peel specimens constructed with TTTG exhibited a greater rate of strength loss and a lesser degree of corrosion protection in the presence of hot water than those prepared using EME 90. Based on the previous discussion this is not surprising since the TTTG interlayer is expected to be more water permeable than that of EME 90. On the other hand, the initial adhesion strength of the EME 90 samples exceeded that of the TTTG samples. This contradicts the previous observations indicating that a greater concentration of reactive groups leads to greater initial adhesion strength.

The bending beam results in Figure 7 indicate that the EME polymeric coupling agents have the ability to relieve, at least in part, the interfacial stresses present in steel/epoxy adhesion systems. Calculating (see Appendix) the interfacial stress in both of these systems showed that the stress at 25°C was reduced from approximately 400 psi to 175 psi by the presence of the polymeric coupling agent. On the other hand, samples prepared with the low molecular weight TTTG coupling agent were found to exhibit negligible stress reduction.

CONCLUSIONS

A series of EME copolymers containing 23–90 wt% mercaptoester units have been employed separately as coupling agents in steel/epoxy peel adhesion systems. As coupling agent functionality was increased the initial adhesion strength of the steel/EME/epoxy peel (90 degree) systems increased, approaching a ten-fold improvement over the controls. These results have been attributed to the increase in both the number of interfacial chemical bonds formed and the adherend surface energy with increase in EME functionality. The thermal stresses in the present case do not appear to be large enough to dominate the failure behavior (see Appendix).

All of the coupling agent samples exhibited an increase in corrosion protection beyond that of the controls. The best corrosion protection was obtained with the EME 23/epoxy resin system which protected the steel adherend for an average of 48 hours in 57°C water baths. The degree of protection decreased significantly with an increase in the concentration of EME mercaptoester units. This suggests that the corrosion protection obtained was governed by the hydrophobicity of the interfacial region.

Regardless of the coupling agent used, all of the peel specimens exhibited very poor adhesion after 5–11 hours exposure to hot water. Although hydrolysis stability experiments indicate that the EME copolymers were somewhat susceptible to hydrolysis over a long period of time (months), they appeared to be hydrolytically stable over the time frame of the peel specimen exposures (1 day).

Locus of failure analyses (XPS and SEM) show that failure of the peel specimens in all cases occurred cohesively within the epoxy resin very near the interface. In addition, the tensile properties of the epoxy resin used in this study (Epon 1001/V115) were found to decrease substantially with exposure to water. Consequently, the rapid wet adhesion strength loss exhibited by the peel specimens have been attributed to the water sensitivity of the epoxy resin. Additional specimens are currently being prepared and tested using an epoxy resin system which should be more resistant to water. It is believed that the use of such a resin system should enable more information regarding the influence of coupling agent functionality on adhesion durability to be obtained.

By using a bending beam apparatus it was shown that the EME copolymers have the ability to delay the onset of interfacial stress and hence reduce the degree of residual stress present in steel/epoxy adhesion systems. Most likely the thickness of the polymeric coupling agent layer will control the extent of stress relief that can be obtained. More work must be completed to fully understand the dependence of stress relief and adhesion results on this variable.

Acknowledgements

The Adhesive and Sealant Council is gratefully acknowledged for providing the funds for this research. The authors also wish to thank William Willis for collecting the XPS data and for generously helping with XPS sample preparation and data analysis.

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Appendix

Elastic modulus of cured resin at 25°C (double-coated beam) after Ref. 15:

$$E = 12(Wtr - (Wtr)_o)/b(H^3 - h_2^3)$$

W = weight attached to each side of beam (0.524 g),
t = length of beam between weight and nearest support (3.65 cm),
b = width of beam (0.79 cm),
H = total thickness of coated beam (0.065 cm),
h_2 = thickness of uncoated beam (0.0076 cm),
r = radius of curvature of coated beam under load $= L/8d$ (219.94 cm),
r_o = radius of curvature of uncoated beam under load $= L/8d_o$ (37.03 cm)
L = length of beam between supports (7.62 cm),
d = deflection of coated beam under load (0.033 cm),
d_o = deflection of uncoated beam under load (0.196 cm),

$$\begin{aligned} E &= 1.94 \times 10^7 \text{ g/cm}^2 \\ &= 2.75 \times 10^5 \text{ psi} \end{aligned}$$

Stresses in single-coated steel/epoxy and steel/EME/epoxy beams after Ref. 15: From deflection measurements, the stresses across the cross-section of the coated beams were calculated using Eq. (1) and the elastic modulus determined above;

$$E = 1.94 \times 10^7 \text{ g/cm}^2, \qquad E = 2.11 \times 10^9 \text{ g/cm}^2,$$

$$h = 0.0274 \text{ cm}, \qquad h_2 = 0.0076 \text{ cm}, \qquad H = 0.035 \text{ cm},$$

$n = 3.596$, $m = 9.2 \times 10^{-3}$, $b = 0.79$ cm,

$L = 7.62$ cm, $F = 6.906$

steel/epoxy	steel/EME/epoxy 25°C
$d = 0.0364$ cm	$d = 0.0157$ cm
$r = 19.94$ cm	$\mathrm{r} = 46.08$ cm
$P = 608.2$ g	$P = 263.2$ g
$S = 2.81 \times 10^4$ g/cm^2	$S = 1.22 \times 10^4$ g/cm^2
$= 399$ psi	$= 173$ psi