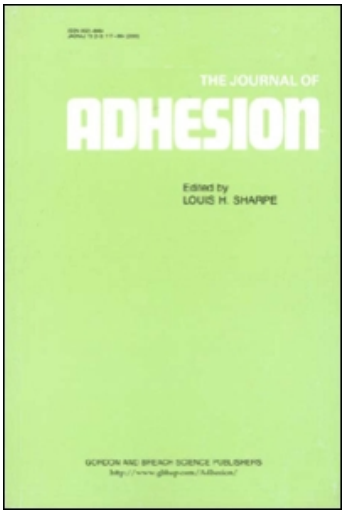

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Investigation of Steel/Epoxy Adhesion Durability Using Polymeric Coupling Agents III. Influence of Coupling Agent Layer Thickness

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Steel/epoxy peel specimens were prepared using ethylene-mercaptoester (EME) copolymer coupling agents (90 wt% mercaptoester units) applied in thickness ranging from 25 to 350 Å. An optimum thickness of approximately 140 Å, which corresponded to an over 200% increase in peel strength when compared to 50 Å thick samples, was determined from ellipsometry and 90° peel strength measurements. The corrosion protection obtained was essentially independent of coupling agent thickness.

KEY WORDS Steel/epoxy bonding; adhesion durability; corrosion protection; coupling agents; coupling agent thickness; interfacial bonding.

INTRODUCTION

All adhesion scientists will agree that water is a very destructive environment for metal/polymer adhesion systems. Several reviews 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 have met some success, but further improvements are desirable.

In Part I of this series,[12] it was reported that ethylene mercaptoester (EME) copolymers with various mercaptoester unit concentrations (23–90 wt%) have been synthesized and employed as coupling agents in steel/epoxy thick film adhesion systems. These copolymers exhibit good thermal stability. In addition, they have been shown to interact chemically with epoxide rings of epoxy resins

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and with free iron ions.[13] Part II showed[14] that the EME coupling agents can significantly improve initial adhesion strength and corrosion protection over that of controls in steel/epoxy peel adhesion systems. Failure was found to occur within the epoxy resin or at the epoxy-coupling agent interfacial region in all cases. Also, using a bending beam apparatus, the EME copolymers have exhibited the ability to relieve a portion of the interfacial stress that develops in these systems due to the large thermal expansion coefficient mismatch between the steel substrate and the epoxy resin.

In the present study the effect of the polymer coupling agent thickness on adhesion properties was analyzed in steel/EME/epoxy peel systems.

EXPERIMENTAL

Materials: The EME copolymers used in this study were synthesized from ethylene-vinyl acetate copolymers as reported previously,[12,15] first by hydrolysis of acetate groups to the alcohol, followed by esterification with mercaptoacetic acid yielding 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 Minnesota Mining and Manufacturing Co.

Ellipsometry: Approximately 2000 Å smooth 1010 low carbon steel films were sputter coated onto one inch diameter silicon wafers. The wafers were dip coated in various weight concentration EME/xylenes solutions at 60°C under nitrogen and allowed to air dry horizontally. The thicknesses of the resulting EME films were measured using a Gaertner Scientific Variable-Angle Laser Ellipsometer. The light source was a Helium-neon laser with a wavelength of 6328 Å, positioned to provide an incidence angle of 70°. The thickness was measured at eight random locations on each sample. The values reported are the averages of the measurements from at least two separate samples.

The refractive index of the solid EME copolymers were determined using a Leitz light microscope in conjunction with standard refractive index oils (Cargille Laboratories).

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 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 were designed to provide a fresh, thin, oxide layer for bonding. XPS spectra suggest that the outermost layer is primarily composed of ferric oxide. The absence of high binding energy *C* 1 s photoelectrons in the spectra indicate that the rinse steps were successful at removing residual citric acid and complexes. The XPS procedures used have been described previously.[14] The EME coupling agents were applied to the steel plates from solution (0.01–0.4 wt% in xylenes) at 60°C under nitrogen and allowed to air dry horizontally. Epon 1001/Versamid 115 (five-mil dry thickness) films were applied to the pretreated samples 45 minutes 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. The back and sides of the samples were masked with polyethylene tape prior to 57°C distilled water bath exposures.

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 and a TM–S Instron ® tensile tester as described previously.[12] The peel rate for all tests was 0.4 in/min. 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 those reported here. Each reported value is the mean from at least four samples.

RESULTS

EME 90(90 wt% mercaptoester groups) solutions of various concentrations in xylenes were dip coated at 60°C onto smooth steel substrates and allowed to air dry horizontally. The thicknesses of the resulting films were determined by ellipsometry. Figure 1 shows that for concentrations ranging from 0 to 0.4 wt% an essentially linear relationship exists between EME 90 concentration and film thickness.

Using Figure 1 as a calibration curve, steel/EME 90/epoxy peel specimens with five different coupling agent thicknesses were prepared and tested under dry conditions. The epoxy thickness was held constant at 5 mils. The average peel strengths are plotted in Figure 2. These data indicate that the peel strengths are quite strongly dependent on coupling agent thickness, with the maximum strength of 4.9 lb/in occurring at an EME 90 thickness of approximately 140 Å (average coefficient of variation 13%).

Peel test specimens were prepared with EME 23, 47 and 90 coupling agents using solution concentrations of 0.06 wt% EME in xylenes to yield approximately 140 Å EME film thickness. EME 23 and EME 47 solutions were found to exhibit

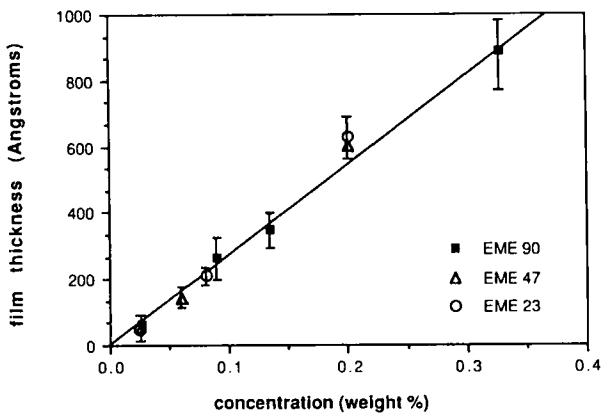

FIGURE 1 Effect of EME solution concentration on the resulting coupling agent layer thickness.

concentration *vs.* thickness behavior which was very similar to that of the EME 90 solutions up to concentrations of 0.1% (Figure 1). Table 1 lists 90° peel adhesion values for the wet and redried samples following exposure to 57°C water for the times indicated. Table 1 also lists the average amount of time the coupling agent/epoxy resin systems protected the steel adherends from corrosion under these conditions. The appearance of an average of three or more pits per sample was used as the criterion for the presence of significant corrosion. Peel strengths for the samples prepared with only a citric acid pretreatment are also listed.

Previously,[12,14] a similar set of results were reported on samples that were prepared with EME film thickness of approximately 50 Å. As before, a significant increase in both the initial and redried adhesion strengths was observed with an increase in coupling agent functionality. However, as Figure 3 indicates, the use

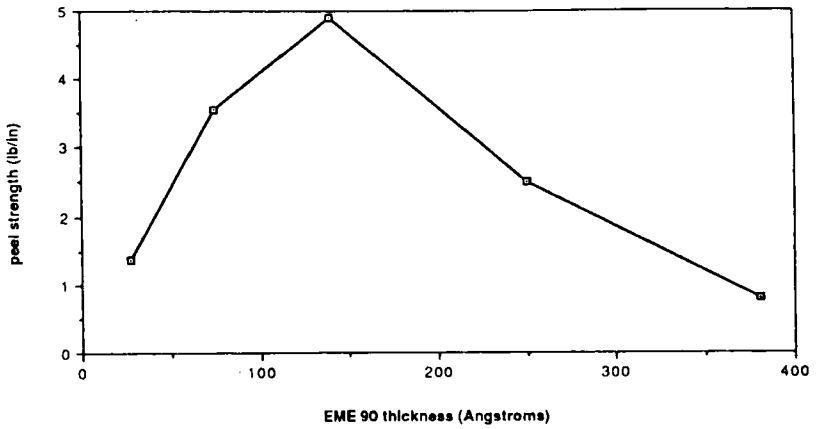

FIGURE 2 Effect of EME 90 thickness of peel strength (dry).

TABLE I
Wet and (redried) 90 degree peel strengths

Treatment	Peel strength (g/in) immersion time (hrs 57°C water)						Corrosion protection, hours
	0	1	3	5	11	24	
Control[b]	78	69	17	9	4	2	14
		(57)	(30)	(24)	(16)	(5)	
EME-23[a]	44	51	30	27	23	18	45
		(31)	(31)	(32)	(23)	(20)	
EME-47[a]	1165	1400	255	36	26	13	21
		(1565)	(680)	(390)	(150)	(41)	
EME-90[a]	2465	2880	715	102	28	11	22
		(2960)	(1620)	(187)	(180)	(48)	
Citric acid	1675	344	67	28	13	3	11
		(1022)	(650)	(590)	(20)	(5)	

( ) Samples dried 1 hour under vacuum at 50°C
[a] 140 Å coupling agent layer thickness
[b] Acetone degreasing only. Average coefficient of variation: 13%

of the thicker (140 Å) coupling agent layers resulted in superior strengths for the EME 47 and EME 90 treated specimens.

It was previously reported that the ability of thin coupling agent films to protect the steel substrates from corrosion decreased with an increase in coupling agent functionality. Figure 4 reveals that the thicker coupling agent layers exhibited very similar behavior except for the EME 47 samples which showed reduced corrosion protection. As was observed with the thin coupling agent samples, within 11 to 24 hours exposure to the 57°C water the wet strengths of all the thick coupling agent samples dropped essentially to equal values.

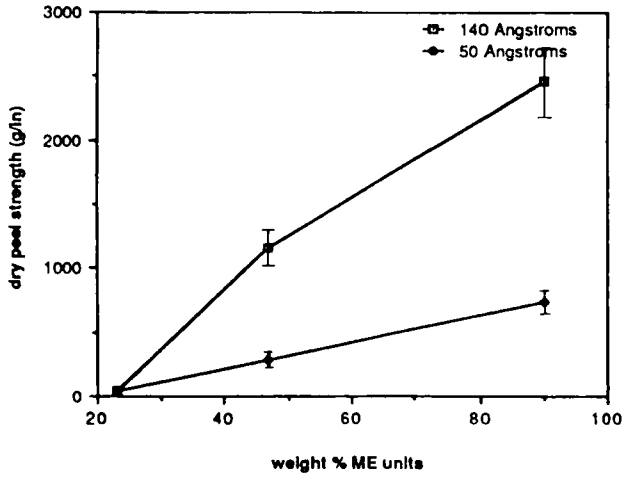

FIGURE 3 Steel/EME/epoxy peel strengths for EME thicknesses of 50 and 140 Å

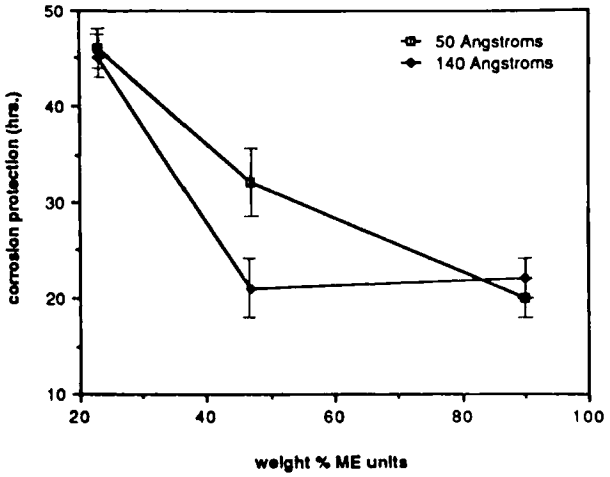

FIGURE 4 Corrosion protection observed with 50 and 140 Å EME coupling agent thicknesses.

DISCUSSION

It was originally proposed that the effectiveness of polymer coupling agents should be less dependent on their thickness than low molecular weight coupling agents.[12] This was based on the fact that unlike most organic low molecular weight materials, the EME polymers are capable of bearing a load. Therefore, regardless of thickness, the polymer coupling agents should provide a tough coupling interlayer in the steel/epoxy adhesion system. Actually, most successful low molecular weight coupling agents (such as silanes[5]) have the ability to form a polymeric network *in situ*.

Contrary to initial beliefs, Figure 2 shows that the thickness of EME 90 copolymer coupling agent has a strong influence on the dry adhesion strength. The strength increases as the coupling agent thickness increases up to approximately 120 to 160 Å, but then decreases steadily for greater thicknesses. No clear-cut explanations have been developed for this behavior. However, as the coupling agent layer becomes quite thick this region can become a weak link in the adhesion system, since its strength-related properties will be inferior to those of the epoxy resin. The development of a weak layer is believed to be the cause of the observed drop in peel strength at large coupling agent thickness.

A possible explanation for the initial increase in strength that is observed with an increase in EME thickness involves the chemical bonding mechanisms of the EME coupling agents. IR spectroscopy[12,13] work has shown that the thiol moiety of the mercaptoester group is very much involved in the bonding mechanisms both to the iron oxide surface and to the epoxide rings of the epoxy resin. The coupling agents are applied directly to the steel surface as a final pretreatment step. If a very thin coupling agent layer is applied (<50 Å approximates a

monolayer), most of the thiol groups may be used in bonding to the steel surface, leaving relatively few reactive groups available for bonding to the epoxy resin. Increasing the coupling agent thickness could alleviate this potential problem and result in increased peel strengths.

It has been shown[12,14] that the surface energies of the EME 47 and EME 90 are much more favorable than EME 23 for promoting the development of intimate contact with the epoxy resin. The data in Figure 3 show that increasing the coupling agent thickness from 50 to 140 Å significantly improves the EME 90 peel strengths while having little influence on the EME 23 samples. Since the wetting between the epoxy resin and the EME 23 surface is believed to be poor, it is doubtful that substantial chemical bonding occurs across the interface. Therefore, increasing the thickness of the coupling agent appears only to be beneficial when good wetting conditions exist between the EME copolymer and the epoxy resin.

Previously it was shown[14] using XPS that for 50 Å thick coupling agent samples, failure occurred within the epoxy resin, but very near the epoxy/EME interface. Similar trends in the water durability results of the 50 Å and 140 Å samples suggest the same failure region occurs in the 140 Å samples. The increase in peel force that is observed by increasing both the thickness and the mercaptoester concentration of the EME coupling agents is most likely due to a strengthening of this region. Whether this can be attributed to an increase in the number of successful bonds formed with the resin or an increase in interpenetration between the two phases is not yet known.

Figure 4 indicates that corrosion protection achieved by the epoxy/EME systems generally decreases with increased coupling agent functionality. Only EME 47 samples deviated from this trend by exhibiting a significant decrease in corrosion protection when thicker coupling agent films were employed.

It was previously proposed[14] that the corrosion protection observed was controlled by the permeability of the coupling agent used. However, the observation that coupling agent thickness has very little influence on corrosion protection (Figure 4) contradicts this earlier belief. More likely the equilibrium water content of the interfacial region and/or the stability of the EME/steel interface in the presence of water govern the degree of corrosion protection in these systems.

As indicated in Table I, citric acid alone can be used as a pretreatment for steel to obtain good initial adhesion strengths with epoxy resins. However, the peel strength drops quite drastically in the presence of hot water and the corrosion protection observed was poor (11 hours).

CONCLUSIONS

A series of steel/EME 90/epoxy peel adhesion samples was prepared with EME 90 thicknesses ranging from 25 to 350 Å. As the coupling agent thickness was increased, the dry adhesion strength exhibited a maximum at an EME 90 thickness of approximately 140 Å. The maximum corresponded to an improve-

ment of over 200% when compared with the strength of specimens prepared with an EME 90 thickness of 50 Å. Explanations for this behavior based on weak boundary layer and chemical bonding theories were proposed.

Employing 140 Å thick coupling agent layers, steel/EME/epoxy peel specimens were prepared with EME copolymers containing 23–90 wt% mercaptoester units. As previously observed with 50 Å thick samples, the dry adhesion strengths increased and the corrosion protection decreased with an increase in coupling agent functionality. The dry strengths of the EME 47 and EME 90 samples were enhanced from 284 to 1165 g/in and 729 to 2465 g/in, respectively, by increasing the thickness of the coupling agent layer from 50 to 140 Å. On the other hand, the degree of corrosion protection obtained did not appear to be strongly dependent on the thickness of the coupling agent used.

Acknowledgements

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