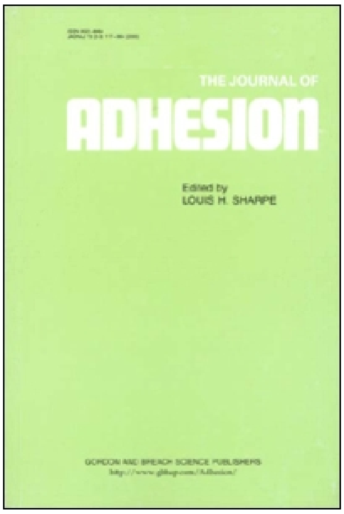

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Durability of Adhesive Bonds to Zinc-Coated Steels: Effects of Corrosive Environments on Lap Shear Strength

J. W. Holubka[a]; W. Chun[a]; R. A. Dickie[a]
[a] Research Staff, Ford Motor Company, Dearborn, MI, U.S.A.

To cite this Article Holubka, J. W. , Chun, W. and Dickie, R. A.(1989) 'Durability of Adhesive Bonds to Zinc-Coated Steels: Effects of Corrosive Environments on Lap Shear Strength', The Journal of Adhesion, 30: 1, 173 — 183

To link to this Article: DOI: 10.1080/00218468908048204

URL: http://dx.doi.org/10.1080/00218468908048204

J. Adhesion, 1989, Vol. 30, pp. 173–183
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

Durability of Adhesive Bonds to Zinc-Coated Steels: Effects of Corrosive Environments on Lap Shear Strength†

J. W. HOLUBKA, W. CHUN and R. A. DICKIE

Research Staff, Ford Motor Company, P.O. Box 2053, Dearborn, MI 48121, U.S.A.

(Received July 21, 1988; in final form November 11, 1988)

The effects of corrosive environments on adhesive bonds to electro-galvanized, zinc/aluminum alloy coated, coated electro-galvanized, and cold-rolled steels have been investigated. Bonds prepared using a rubber-modified dicyandiamide-cured epoxy adhesive, an epoxy-modified poly(vinyl chloride)-based adhesive, an acrylic-modified poly(vinyl chloride)-based adhesive a one-part urethane adhesive, and a two-component epoxy-modified acrylic adhesive were exposed under no-load conditions to constant high humidity or cyclic corrosion exposure for 50 days or 50 cycles (10 weeks) respectively.

Over the course of this study, exposure to constant high humidity had little effect on lap shear strength for any of the systems studied. Bond failures were initially cohesive, and with few exceptions remained so.

Bond strength retention under the cyclic corrosion exposure conditions employed was strongly dependent on adhesive composition and on substrate type. On galvanized substrates, lap shear strengths for the poly(vinyl chloride)-based adhesives were reduced by 90–100% during the course of the corrosion exposure, and a change in the mode of bond failure (from cohesive to interfacial) was observed. On the coated electro-galvanized steel substrate, the poly(vinyl chloride)-based adhesives showed about 50% retention in lap shear strength and a cohesive failure throughout most of the corrosion test. The dicyandiamide-cured epoxy adhesive used in this study generally showed the best lap shear strength retention to zinc-coated substrates; bonds to cold-rolled steel were severely degraded by corrosion exposure. The performance of the acrylic and urethane adhesives were intermediate to the dicyandiamide-cured epoxy and poly(vinyl chloride)-based adhesives in strength retention.

KEY WORDS Galvanized steel; bond strength retention; epoxy-dicyandiamide adhesive; poly(vinyl chloride) adhesive; urethane adhesive; acrylic adhesive.

INTRODUCTION

Durability of adhesive bonds is one of the key issues in establishing technical feasibility of structural bonding in automotive applications. Adhesive bond

---

† Presented at the 35th Sagamore Army Materials Research Conference, Manchester, New Hampshire, U.S.A., June 26–30, 1988.

durability has been the subject of intensive research within the aerospace and adhesive industries,[1–7] but there has been relatively little reported on bond durability to galvanized steel. Adhesive bond durability has been related to adhesive chemistry and properties.[1] Extensive reviews have appeared that relate mechanics, mechanisms of bond failure and interfacial chemistry to bond durability.[2–3] The effects of moisture on the durability of epoxy and urethane adhesives have also been reported.[4–7]

We have previously reported on the effects of adhesive composition on the durability of bonds exposed to salt spray and water immersion tests.[8] In these studies, adhesive bonds were not subjected to the variable environmental conditions characteristic of automotive applications, or to the cyclic exposure conditions that have been used for evaluation of sheet metal corrosion resistance.[9] Lap shear strength has been examined for a range of galvanized steels bonded with epoxy adhesives and exposed to a cyclic corrosion environment; adhesion was found to be specific to the galvanized steel type.[10,11] In the present study, the effect of adhesive composition on bond durability has been examined for representative electrogalvanized substrates: zinc/aluminum alloy substrates, a duplex galvanized/zinc-rich coated steel substrate and cold rolled steel. The effects of constant high humidity and cyclic corrosion exposure on lap shear strength are reported. Subsequent papers will discuss the interfacial chemistry of bond failure for several of these systems.

EXPERIMENTAL

Materials

The adhesives used in this study were chosen to be representative of resin types currently proposed for use in structural and semi-structural applications. All were applied and cured according to supplier recommendations. The adhesives chosen were:

Epoxy (EP): a rubber-modified, dicyandiamide-cured epoxy adhesive supplied by American Cyanamid (Cybond 5501) was used. The adhesive was cured at 170°C for 30 minutes.

Vinyl/epoxy (VE): an expoxy-modified poly(vinyl chloride)-based plastisol adhesive supplied by Uniseal (AP116HY) was used. The adhesive was cured at 170°C for 30 minutes.

Vinyl/acrylic (VA): an acrylic modified poly(vinyl chloride)-based plastisol adhesive supplied by Mortell (SS107G) was used. The adhesive was cured at 170°C for 30 minutes.

Urethane (UR): a one-part urethane adhesive supplied by Fuller (UR1100) was used. The adhesive was cured at 127°C for 30 minutes.

Acrylic: a two-part acrylic adhesive supplied by Lord (4750-64 A/B) was used. The adhesive was cured at room temperature for 16 hours, then post cured at 300°C for 30 minutes.

The steel substrates included:

Cold Rolled Steel (CRS): standard paint test panels of 0.95 mm thickness supplied by Parker Chemical Co.

Electro-galvanized Steel (EGS): one-side 60G electrogalvanized steel, thickness 0.7 mm, supplied by National Steel Company.

Coated Electrogalvanized Steel (GEG): one-side 60G electrogalvanized steel, coated with a zinc-rich coating, steel thickness 0.82 mm, supplied by Akzo Coatings America.

Zinc-aluminum Coated Steel (ZAL): zinc-aluminum alloy coated steel, AKDQ GF-60, skin rolled and NCT Oiled, metal thickness 0.91 mm, supplied by Weirton Steel Company.

Adhesive bonding technique

Conventional procedures for preparing adhesive bond specimens were used. Adhesive was applied to the "as received" steel. Shipping oils applied at the steel mills were not removed. Cut coupons 25 mm × 100 mm were bonded with a 12.5 mm overlap. Bond thickness was defined at 0.025 cm using wire of the appropriate thickness. Bonded samples were clamped during cure to maintain specimen alignment and bond thickness.

Adhesive testing and evaluation.

The humidity test used in adhesive evaluation involved exposing bonds to 40°C at 90% relative humidity for periods up to 10 weeks. In a typical study, 50 bonds were exposed to the environment; 5 bonded samples were removed from humidity at appropriate intervals and tested for bond strength.

The cyclic corrosion test that was used for this study was based on one developed for evaluation of the perforation resistance of painted steel; the test development and procedures have been reported elswhere.[9,12] A schematic outline of the test is given in Figure 1. The lap shear strength was determined for five specimens every five cycles (five days + weekend) through 50 cycles of this test.

All bond strength determinations were made using an Instron Model 1125 mechanical testing machine operating at a cross-head speed of 1 mm/min. Most bond strengths were within 10% of the reported mean values; bond strength variability tended to increase with decreasing retained bond strength during exposure.

RESULTS AND DISCUSSION

Effects of adhesive composition of bond strength retention

The effects of adhesive composition on bond durability were determined for the five adhesives applied to two substrates, cold rolled steel and electrogalvanized steel. Initial lap shear strengths varied from about 9 to 13 MPa.

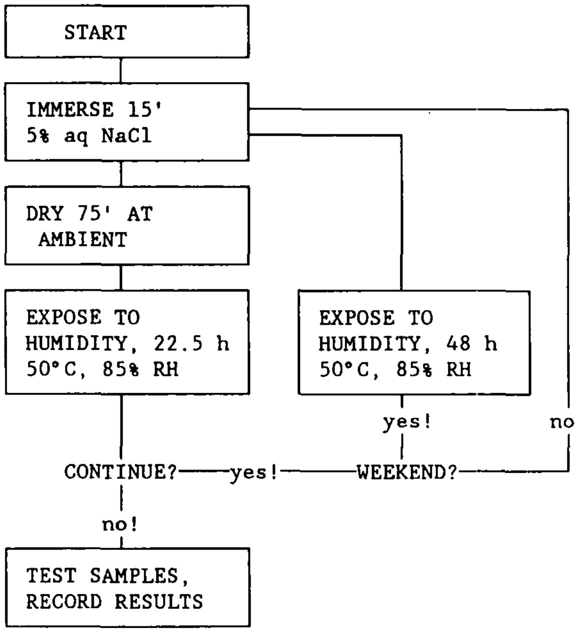

FIGURE 1 Cyclic corrosion test.

Durability of bonds to EG steel in humidity Figure 2 illustrates the effects of adhesive composition on bond durbility to EG steel during exposure to static humidity. About 75 to 85% of the initial bond strength was retained after 50 days in humidity. The locus of bond failure remained consistently cohesive in the adhesive throughout the duration of the experiment.

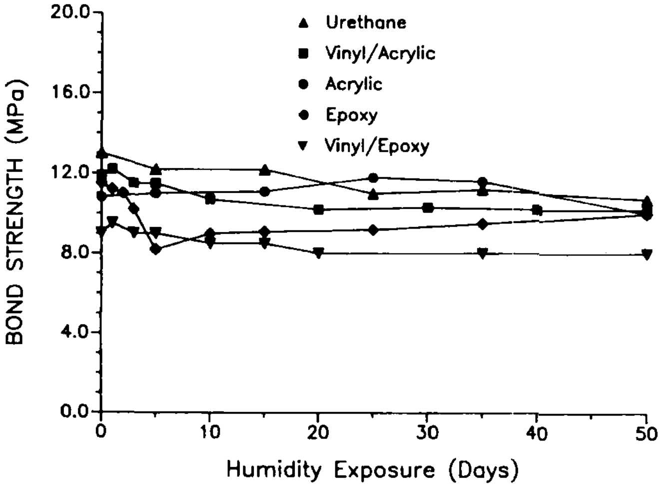

FIGURE 2 Effect of adhesive composition on lap shear strength to electrogalvanized steel in humidity.

Bond strength was found to decline gradually with time of humidity exposure for all except the epoxy adhesive. The gradual decline in bond strength and the consistent cohesive bond failure suggest that the effect of humidity exposure may be primarily related to diffusion of water into the adhesive and a gradual change in the mechanical properties of the adhesive. In the case of the epoxy, an initial drop in lap shear strength was observed followed by an apparent approach to equilibrium. The initial decline in lap shear strength of the epoxy may be associated with moisture-induced crack formation at the edge of the bond.

Durability of bonds to EG steel in cyclic corrosion Figure 3 shows the effects of adhesive composition on lap shear strength in cyclic corrosion for bonds to EG steel. Bond strength retention was strongly dependent on adhesive composition. Best overall performance was observed with the epoxy adhesive. As in humidity exposure, bonds prepared with the epoxy adhesive showed a significant initial drop in bond strength in the first few cycles of the test, but remained at about 60% of the initial bond strength through the remainder of the test exposure. The locus of bond failure for the epoxy adhesive remained cohesive in the adhesive throughout most of the cyclic corrosion test (0 to 35 cycles) with little or no reduction in bonded area. Partial adhesion (interfacial) failure to the substrate was observed for the epoxy adhesive at 50 cycles. Subsequent surface analytical work has shown that the long term adhesion failure of the epoxy adhesive is associated with dissolution of the substrate (anodic undercutting) rather than a degradation of either the interface *per se* or the adhesive.[13]

Most notable by their poor performance were the two poly(vinyl chloride)-based adhesives. These materials showed a rapid drop in bond strength as well as nearly complete loss of bond strength after 50 cycles of testing. The rapid and eventually complete loss in lap shear strength noted for these adhesives was

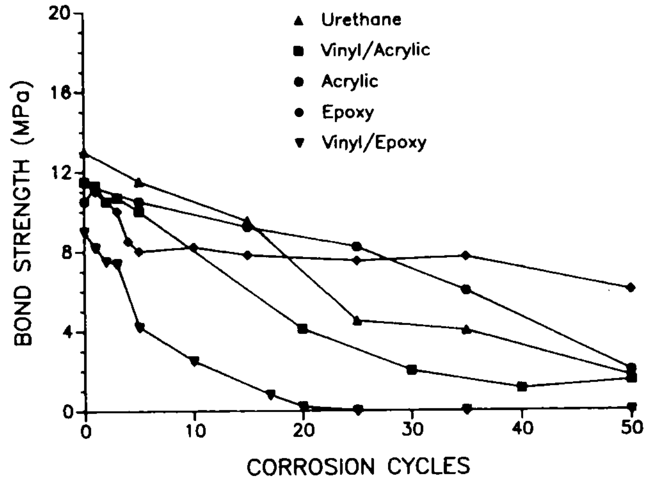

FIGURE 3 Effect of adhesive composition on lap shear strength to electrogalvanized steel in cyclic corrosion.

accompanied by a change in failure locus during the test. Both poly(vinyl chloride)-based adhesives showed cohesive failure for bonds that were unexposed and in early cycles of cyclic corrosion (i.e., 1–15 cycles). Longer exposure to cyclic corrosion conditions resulted in rapid and progressive interfacial adhesion loss. Subsequent work[14,15] has shown that poly(vinyl chloride) reacts with galvanized surfaces during cure; an ionic chloride species is formed. It is likely that the presence of ionic species at the interface at the start of the corrosion exposure promotes corrosion of the substrate, lowering bond durability. The interfacial corrosion process itself has been shown to be dominated by dissolution of the substrate.[16,17]

For the urethane and acrylic adhesives, reduction in bond strength occurred gradually throughout the corrosion test. The urethane adhesive failed adhesively throughout the entire cyclic corrosion test. Corrosion under the adhesive appeared gradually, indicating an encroachment of corrosion processes under the adhesive bond. The acrylic adhesive failed mainly cohesively through 35 cycles of testing.

Bond strength to CRS in humidity Figure 4 illustrates the effects of adhesive composition on bond strength to CRS in humidity. The bond strengths ranged from about 13 to 18.5 MPa. The bonds to CRS are generally somewhat stronger initially than the corresponding bonds to EG, but these differences in initial bond strengths are likely due to differences in mechanical properties of the steels. About 75% to 95% retention in bond strength to cold rolled steel after 50 days of humidity was observed for all adhesives except the acrylic-modified poly(vinyl chloride)-based adhesive. This material showed only 36% retention in bond strength. Again with the exception of the acrylic-modified poly(vinyl chloride)-based adhesive, the relative ordering of performance was identical for bonds to EG and CRS.

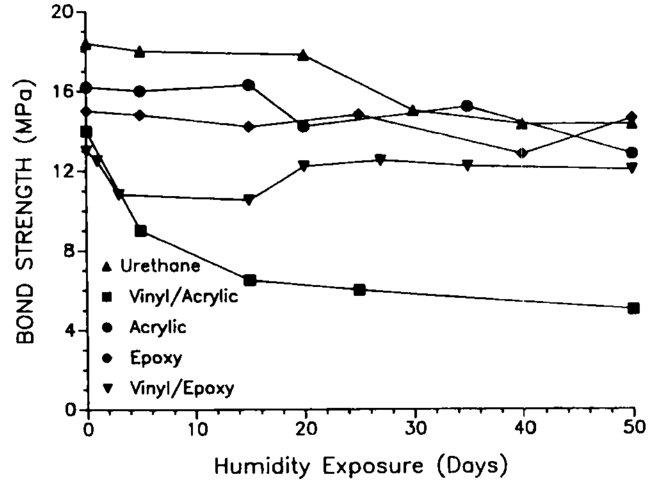

FIGURE 4 Effects of adhesive composition on lap shear strength to cold-rolled steel in humidity.

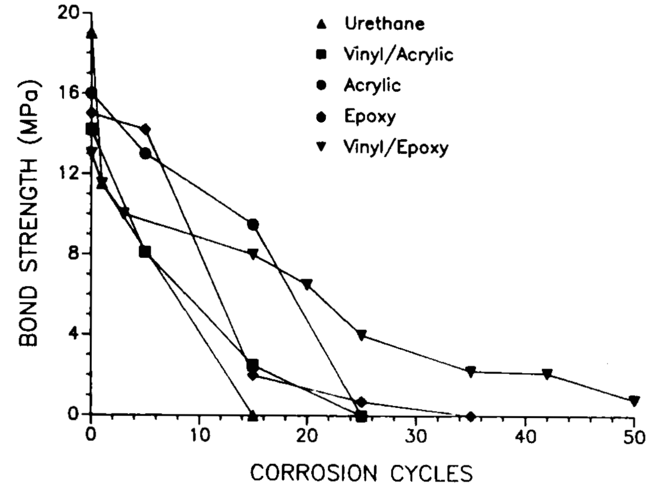

FIGURE 5 Effect of adhesive composition on lap shear strength to cold-rolled steel in cyclic corrosion.

Durability of bonds to CRS In cyclic corrosion Figure 5 shows the effects of adhesive composition on bond strength retention in cyclic corrosion. All of the adhesives tested show a significant and rapid loss of strength to cold rolled steel. The loci of failure for the unexposed bonds were cohesive, but were interfacial throughout the exposure sequence.

Effects of substrate on bond durability

The effect of substrate on bond durability was assessed by comparing the performance of the dicyandiamide-crosslinked epoxy adhesive and the epoxy-modified poly(vinyl chloride)-based adhesive on four substrates: cold rolled steel (CRS), electro-galvanized steel (EGS), coated electro-galvanized steel (CEG) and a zinc-aluminum alloy coated steel (Zn/Al). The order of initial bond strengths was found to be CRS > Zn/Al > CEG > EGS for both adhesives. All bond failures for unexposed bonds were cohesive within the adhesive. The differences in initial bond strength are attributed to differences in the mechanical properties of the steel rather than differences in adhesive.

Effect of steel substrate on bond durability in humidity Figure 6 and 7 illustrate the effect of steel substrate on lap shear strength retention in humidity. Humidity exposure caused minimal loss of bond strength. The initial drop in adhesion noted previously for the dicyandiamide-cross-linked epoxy adhesive on EGS is observed also on the Zn/Al steel, but not on the other two substrates.

Effect of steel substrate on epoxy bond durability in cyclic corrosion Figure 8 illustrates the effect of steel substrate on bond durability of the dicyandiamide-

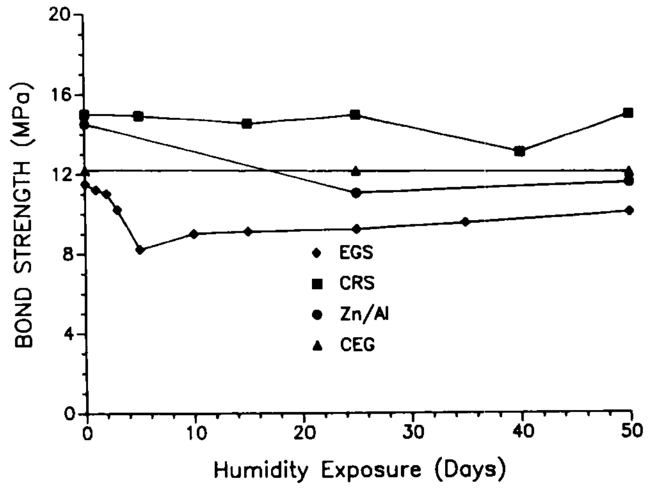

FIGURE 6 Effect of substrate on lap shear strength of a dicyandiamide-cross-linked epoxy adhesive in humidity.

crosslinked epoxy adhesive in cyclic corrosion. The results show a large range in performance. The best bond-strength retention is observed for the coated electro-galvanized steel (75% retention in bond strength). Bonds prepared on this substrate failed cohesively throughtout the entire cyclic corrosion test. Delamination of the precoating was noted at long test times.

Bonds to the Zn/Al and EG steels show 25 and 52% retention of bond strength, respectively, after 50 corrosion cycles. Significant interfacial adhesion loss was observed on Zn/Al steel even at 25 cycles of testing. Epoxy bonds to the electrogalvanized steel show cohesive failure further into the corrosion test. The

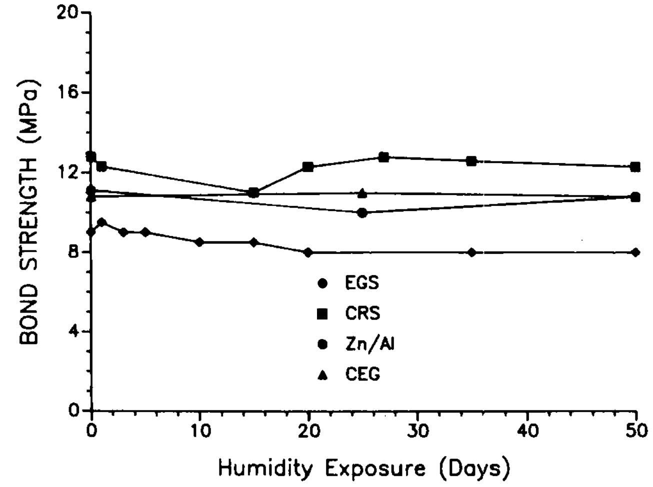

FIGURE 7 Effects of substrate on lap shear strength of a poly(vinyl chloride)-based ashesive in humidity.

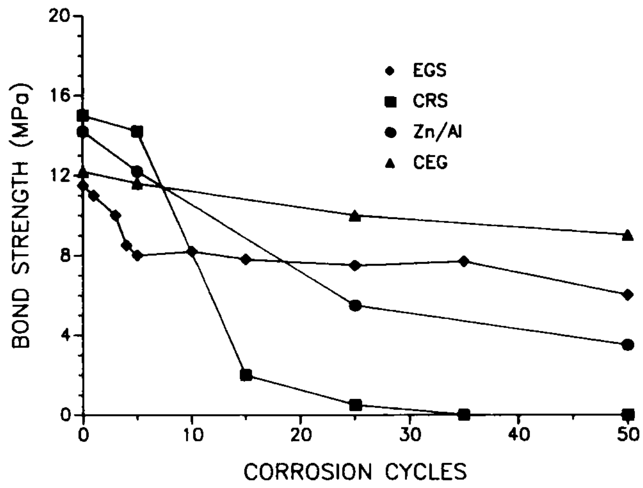

FIGURE 8 Effects of substrate on lap shear strength of a dicyandiamide-cross-linked epoxy adhesive in cyclic corrosion.

difference in performance of the two galvanized substrates may be due to the presence of aluminum oxide on the surface of the zinc aluminum alloy coated steel: bond strengths to hot dipped galvanized steel have been shown to be adversely affected by the presence of surface aluminum oxide.[11,18]

Most striking is the poor performance of epoxy bonds to cold-rolled steel (CRS). These results have been discussed earlier.

Effect of steel substrate on poly(vinyl chloride)-based adhesive bond durability in cyclic corrosion Figure 9 illustrates the effect of steel substrate on bond

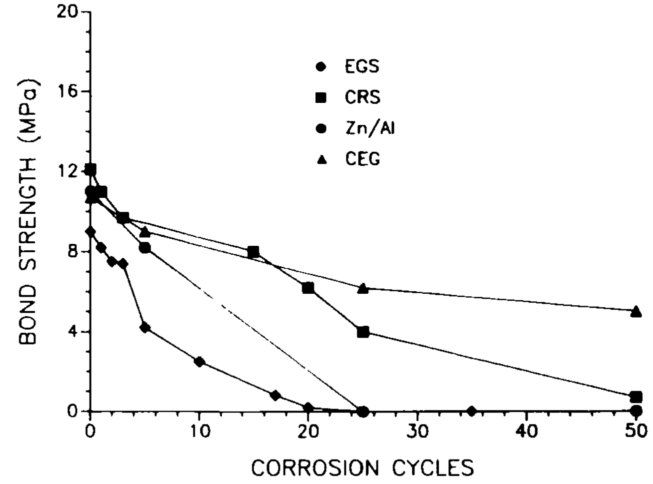

FIGURE 9 Effects of substrate on lap shear strength of poly(vinyl chloride)-based adhesive in cyclic corrosion.

durability of a poly(vinyl chloride)-based adhesive in cyclic corrosion. In general, poly(vinyl chloride)-based adhesive bonds to galvanized substrates do not perform well in corrosion. The failure locus on the Zn/Al steel became partly interfacial after only 5 cycles. Similar interfacial failure was noted for poly(vinyl chloride)-based adhesive bonds to electrogalvanized steel at somewhat longer test times. Best durablity—about 50% retention of bond strength—was observed to coated electrogalvanized steel. With this substrate, cohesive bond failure was noted even after 50 cycles of corrosion testing.

CONCLUSIONS

For the range of structural adhesives and zinc-coated substrates included in this study, it has been found that cyclic corrosion exposure results in a more rapid differentiation of bond performance than does constant exposure to high humidity. The differences in performance can not be traced solely to differences in substrate composition or adhesive formulation: both factors are evidently important.

Under the no-load conditions employed, it was found that humidity exposure *per se* had little effect on bond strength or failure locus. For bonds to electrogalvanized steel exposed to a cyclic corrosion environment, bond strength retention ranged from 0 to 50% after 10 weeks of exposure; in order of improving performance, vinyl/epoxy < vinyl/acrylic < urethane < acrylic < epoxy. The locus of failure after corrosion exposure was mainly cohesive for the dicyandiamide-crosslinked epoxy and acrylic adhesives and mainly interfacial for the urethane and poly(vinyl chloride)-based adhesives. Substrate surface composition was found to play a major role in determining adhesive bond durability in corrosion. Dicyandiamide-crosslinked epoxy adhesive durability increased in the order cold rolled steel < zinc/aluminum alloy coated steel < electrogalvanized steel < precoated electrogalvanized steel. Poly(vinyl chloride)-based adhesive bonds to zinc-coated substrates other than coated electrogalvanized steel generally did not perform well in corrosion.

REFERENCES

1. A. V. Pocius, D. A. Wangness, C. J. Almer, and A. G. Mckown, in *Adhesive Chemistry*, Lieng-Huang Lee, Ed. (Plenum Publishing Corporation, New York, 1984).
2. A. J. Kinloch, *J. Mat. Sci.* **15,** 2141 (1980).
3. A. J. Kinloch, *ibid.* **17,** 617 (1982).
4. E. H. Andrews and A. Stevenson, *J. Adhesion* **11,** 17 (1980).
5. H. Dodiuk, L. Drori, and J. Miller, *ibid.* **17,** 33 (1984).
6. S. G. Abbot and N. Brumpton, *ibid.* **13,** 41 (1981).
7. A. J. Kinloch, *Durability of Structural Adhesive Joints* (Applied Science Publishers, New York, 1983).
8. J. W. Holubka, W. Chun, A. R. Krause, and J. Shyu, *Poly. Mat. Sci. and Eng.* **53,** 574 (1986).
9. V. Hospadaruk, J. Huff, R. W. Zurilla, and H. T. Greenwood, *Trans. SAE* **87,** 755 (1978).

10. R. T. Foister and K. J. Schroeder, *J. Adhesion* **24,** 259 (1987).
11. R. T. Foister, *ibid.* **24,** 279 (1987).
12. Ford Laboratory Test Method, BI-23-1, April 30, 1981.
13. R. A. Dickie, J. W. Holubka, and J. E. deVries, *J. Adhesion Sci. Technol.*, submitted.
14. J. E. deVries, J. W. Holubka, and R. A. Dickie, *J. Ahesion Sci. Technol.*, in press.
15. J. E. deVries, L. P. Haack, J. W. Holubka, and R. A. Dickie, *J. Adhesion Sci. Technol.*, in press.
16. R. A. Dickie, J. W. Holubka, and J. E. deVries, in *Adhesion Science Review, Vol. 2,* H. F. Brinson, J. P. Wightman, and T. C. Ward, Eds. (Virginia Polytechnic Institute and State University Center for Adhesion Science, Blacksburg, VA), in press.
17. J. W. Holubka, J. E. deVries, and R. A. Dickie, unpublished results.
18. R. F. Kiesel and B. M. Joshi, unpublished results.