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Delamination of filler-incorporated automotive epoxy adhesives from different steel substrates upon exposure to distilled water and NaCl solutions under applied bending stresses

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Delamination of four filler-incorporated automotive epoxy adhesives from five different steel substrates was studied using a three-point bending device. The bent specimens were exposed to distilled water and NaCl solutions with different concentrations from 1–5 weeks. It was found that the degree of adhesive delamination increased with the concentration of the NaCl solution, and with the magnitude of the applied bending stresses. The harder the adhesives, or the higher the content of the fillers in the adhesives, the lower was the degree of the adhesive delamination. In addition, the rank of the steel substrates in terms of their bonding resistance against adhesive delamination was determined. It is believed that the adhesion between the adhesives and the steel substrates is governed by the surface roughness of the steel substrates.

1. Introduction

Upon exposure to corrosive environments, adhesives can deteriorate, and a loss of adhesion between the adhesives and the metal adherends can occur. The durability and strength of the structural adhesive/metal bonding are critically dependent on the interaction between the adhesive and the metal substrate. Poorly durable adhesive-bonded joints are often a direct result of poor interfacial adherent properties [1, 2]. A sound structural adhesive-bonded joint needs excellent bonding between the cured adhesive and the adherend to resist the maximum applied stresses existing in the actual service environment. Regardless of the exposure time and the aggressiveness of the environment, a good structural adhesive/adherent bonding must be maintained throughout the service life. To understand the effect of corrosive environments on the durability of adhesive-bonded joints, attention should be focused on the interfacial areas of the adhesive-bonded joints.

There are two principal mechanisms of adhesion in structural adhesive bonding reported by Clearfield *et al.* [3]. The first mechanism assumes that adhesion is formed by the mechanical interlocking system between the adhesive and the microscopically rough adherend surface. The second mechanism assumes that adhesion results in chemical bonding (covalent or van der Waals bonds) of the adhesive molecules with the adherend oxide. Clearfield *et al.* [3] have claimed that the magnitude and the significance of both of these adhesion mechanisms depend greatly on the nature of the adherend surface, and on the rheology and chemistry of the adhesive. They have discussed the adherend morphology and surface chemistry of aluminium, titanium and steel pretreated with different surface preparations. The performance of these pretreated adherends has been reported in bond strength and durability tests performed in hot, humid environments under applied stresses.

In recent years, interest has increased in the adhesive bonding of stainless steel and galvanized steel surfaces. The effects of surface treatment of AISI-304 stainless steel on the interfacial properties of the alloy/epoxy joints have been investigated by Gaillard *et al.* [4] using X-ray emission spectroscopy. Ziane *et al.* [5] have studied the adhesive/metal interaction for galvanized steel sheet assemblies. Foister [6] and Foister and Schroeder [7] have investigated adhesive/adherend bonding using galvanized steel, and established important parameters that affect the adhesion between the adhesive and the adherend. They have discussed the galvanized steel adherend morphology, bond failure modes, loci of joint failure, oxide layer chemistry, bondline corrosion factors, lap shear strengths and environmental durability of adhesive-bonded joints. Foister [6] has presented evidence that the loci of interfacial failure of the adhesive-bonded joints consist of the galvanized oxide layer. He has also reported that hot-dip galvanized steel has a higher surface chemical heterogeneity and smoother surfaces when compared to electroplated galvanized steel. The higher the surface chemical heterogeneity and the smoother the galvanized adherend surface, the poorer the adhesion between the adhesive and the adherend. Foister and Schroeder [7] have concluded that the adhesion between an electroplated galvanized steel and a one-part epoxy adhesive is stronger than the adhesion of an electroplated galvanized steel bonded with a two-part epoxy adhesive. Breval and Rachlitz [8] have studied the surface structures of the as-received, painted and pretreated hot-dip galvanized steel. Paint adhesion to the different types of zinc coating has been investigated. They have quoted from a paper of Levingstone [9] that a superior adhesion between the hot-dip galvanized steel surface and the paint is obtained when the steel surface reacts with air, thus developing a protective cover layer of corrosion products prior to painting. The corrosion products are composed of oxides, hydroxides and carbonates. They have stated that the number of zinc/paint bonds increases with the surface roughness of the hot-dip galvanized steel surface. They have also given evidence that paint adheres better to a zinc–iron coating surface than to a pure zinc surface.

The topology of a metal oxide and a metallic coating has been studied by many researchers. Filbey and Wightman [10] have claimed that metallic oxides on a steel surface are either native (air-formed) or produced by surface pretreatments. Amore and Murphy [11] have observed a heavy oxide formation on a A606 mild steel surface under a phosphoric acid-etch treatment. A microporous topology of the iron oxide has been observed. Townsend [12] has reported the characteristics and the coating microstructures of four coated steel products used in the automotive industry, namely hot-dip zinc steel, hot-dip zinc iron steel, electroplated zinc steel, and electroplated zinc–iron steel. He has reported that the surface of hot-dip zinc-coated steel is relatively smooth and featureless. A thin, irregular intermetallic layer has been found between the uniform zinc layer and the steel substrate. A series of zinc–iron intermetallic compounds has been observed in hot-dip zinc–iron coating. The surface of hot-dip zinc–iron-coated steel is very porous and angular. The surface roughness of hot-dip zinc–iron steel provides a good mechanical interlocking relationship between the adhesive and the adherend, thereby enhancing the degree of adhesion. The single-phase coating surface of electroplated zinc steel is composed of crystallographic facets of hexagonal zinc crystals. The roughness and porosity of the electroplated zinc surface are intermediate between those of hot-dip zinc and the hot-dip zinc–iron steels. The electroplated zinc–iron alloy coating is composed of a series of fine alloy layers. The coating surface is characterized by irregular nodules. The roughness of the nodular surface of electroplated zinc–iron steel is less than that of a hot-dip zinc–iron steel surface. Townsend [12] has presented evidence that the zinc–iron alloy coatings, regardless of the coating processes, are more protective against cosmetic corrosion than the pure zinc coatings. Zinc–iron coatings are more protective because they are generally not as active as pure zinc coatings. Townsend [12] has also stated that the resistance of the coated steels against cosmetic corrosion increases with the coating thickness. Arnold [13] has studied the relationship between the adhesive joint durability and the corrosion resistance of galvanized steels against corrosive environments. He has reported that the joint durability of the galvanized steels is directly related to the corrosion resistance of the coating. The corrosion resistance of the galvanized steels has been found to increase linearly with the coating weight. He has also claimed that the thicker the protective galvanized coating, the longer it takes for corrosion to undermine the adhesive and degrade the interface. Leidheiser [14] has reported that the crystalline orientation of the zinc grains of a galvanized steel can affect the paint-adherence properties during severe bending. Damage of the thin zinc coating occurs by plastic deformation and by cracking. Cracking of the zinc coating occurs primarily in the directions parallel to the orientation of the zinc grains. During severe bending, the zinc grains with an orientation parallel to the coating surface, or perpendicular to the direction of the bending stresses tend to crack. As a result, corrosion occurs within the cracks underneath the coating during service in corrosive environments.

Minford [15] has reported that differences in the modulus of the elasticity and the coefficient of thermal expansion between the adhesive and the adherend can induce unrecognized cracking in the interfacial areas under severe weathering conditions. He has stated that interfacial imperfections, for example, trapped air bubbles, can be produced when an adhesive with high viscosity fails to fill all the voids on a rough adherend surface. As a result of water absorption, such bondline imperfections can become vulnerable sites subjected to the high localized stresses that are produced during adhesive swelling. In addition, Minford [15] has reported that adhesive/metal bonds are dependent on the thickness, strength, adherence, and chemical resistance of the metal oxide layer. Metals with loosely adhering oxide layers are prone to sudden interfacial failures in service when stress, high impact, and severe weathering conditions are present. Furthermore, various interactions between the surface oxides and environmental factors such as water, temperature, and atmospheric chemicals have been discussed [15].

Leidheiser [14] and Minford [15] have claimed that the air-formed native oxide on most metals is non-uniform in thickness and does not form a stable protective layer for structural bonding. As a result, a chemical or mechanical deoxidizing process in removing the native or air-formed oxide is recommended for adhesive joints that require a long service life. During cutting and deforming processes, a steel surface can reoxidize instantly after the removal of the inactive native oxide or hydroxide layers. The freshly formed oxide is beneficial to adhesion due to its higher microroughness and chemical reactivity with an adhesive. The high surface roughness and chemical reactivity of the fresh oxide can lead to a superior durability of the adhesive/oxide bonding in corrosive environments [15].

Many studies have been performed to attempt to understand the mechanism and kinetics of adhesive joint failures on steel substrates upon water and corrosive environmental exposures. Laird [16] has investigated polymer/glass bond failure by water intrusion, and reported that water can penetrate along the polymer/glass interface 450 times faster than by diffusing through the polymer matrix. Working with mild steel/epoxy joints in the presence of water, Kinloch and co-workers [17–19] have shown evidence of the displacement of the adhesive on a ferric oxide surface. They have claimed that a similar type of bonding failure can be expected for other epoxy-to-metal oxide joints. Kinloch and Gledhill [17] have reported that losses in adhesive/metal joint strength during water immersion normally result from a water invasion at the interface, rather than from degradation of the properties of the adhesive. Three discrete steps for the debonding process related to the metal oxide surface have been proposed [18, 19].

1. Water diffusion through the adhesive to the interface initiates the displacement of the adhesive from the metal oxide. The rate of water diffusion governs this displacement step.
2. Owing to the subtle changes in the nature of the metal oxide under water invasion, a loss in strength occurs in the metal oxide. Eventually, an oxide layer failure results.
3. After the failure of the metal oxide, a severe joint debondment results due to the gross corrosion of the metal adherend.

Ritter and Kruger [20] and Leidheiser [14, 21] have claimed that adhesive delamination occurs when the native oxide film is corroded by corrosive solutions. Ritter and Kruger [20] used the ellipsometric–electrochemical technique to study the corrosion and delamination mechanisms beneath several organic coatings. They presented evidence that an organic coating delamination involves the following events: (i) corrosive solution (NaCl) diffuses through the organic coating and penetrates along the interface; (ii) pitting of the native oxide film between the organic coating and the metal substrate occurs; (iii) oxygen reduction reaction produces OH^- ions, and forms a high pH environment beneath the organic coating; (iv) a new oxide film growth and surface roughening occurs; and (v) a breakthrough arises between the separated anodic and cathodic sites underneath the organic coating. They have concluded that coating delamination is caused by oxide dissolution and reduction in density of the coating/oxide bonds. Similarly, Leidheiser [14, 21] has claimed that delamination of an organic coating on metal substrates is caused by the oxygen reduction reaction occurring underneath the coating. Leidheiser [14] has stated that the coating delamination phenomenon on a metal substrate is intimately related to the fact that the metal substrate is cathodically polarized. Leidheiser [21] reported that the highly alkaline environment resulting from the oxygen reduction reaction dissolves the oxide layer at the coating/metal interface, thus producing a cathodic coating delamination. In addition, he has stated that the rough oxide surface provides a superior mechanical interlocking system between the adhesive and the metal substrate, thus retaining the adhesive in close proximity to the metal substrate [21].

The objectives of this work were: (i) to study the degree of delamination of four filler-incorporated automotive epoxy adhesives from five steel substrates under three-point bending in the presence of distilled water or different concentrations of NaCl solution, (ii) to evaluate the effect of applied bending stresses on adhesive delamination in the presence of a corrosive environment, (iii) to evaluate the resistance against delamination of different adhesive/steel combinations, and (iv) to determine the factors affecting the degree of adhesive delamination.

2. Experimental procedure

Four different epoxy adhesives, A, B, C, and D, were investigated. They were formulated and produced by several adhesive companies. Table I lists the composition of the adhesives. Five different steel substrates used in this investigation were as follows: (1) cold-rolled steel, (2) electrodeposited zinc steel, (3) electrodeposited zinc–iron steel, (4) hot-dip zinc steel, and (5) hot-dip zinc–iron steel. Table II shows the typical sheet and coating thicknesses of the steel substrates. The adhesive-bonded specimens, which are composed of the above adhesives and steel substrates, were bonded and provided by Chrysler Motors Corporation. One particular adhesive was bonded to one steel substrate in each combination. The adhesive-bonded

TABLE I Composition (wt%) of the adhesives investigated

Adhesive	Composition
A (one part epoxy)	Epoxy > 80% Fillers: <16%–17% silica (SiO_2) and calcium carbonate ($CaCO_3$) < 3%–4% acrylic epoxy as reinforcing filler
B (one part epoxy)	Epoxy 40% Fillers: 57.6%–59.4% magnesium aluminium silicate ($MgAlSiO_4$), and 0.6%–2.4% cabasal silica (porous type)
C (two parts epoxy)	Epoxy 50%–55% Fillers: 15%–20% calcium carbonate ($CaCO_3$), 5%–10% calcium oxide (CaO), 5%–10% silicon dioxide (SiO_2), and talc clay
D (one part epoxy)	Epoxy 60% Fillers: 35% silicon dioxide (SiO_2), and 5% calcium carbonate ($CaCO_3$), calcium silicate ($CaSiO_4$)

TABLE II Sheet and coating thicknesses of the steel substrates investigated

Steel substrate	Sheet thickness (mm)	Coating thickness (μm) [8]
Cold-rolled	0.81	0
Hot-dip zinc	0.83	6–20
Hot-dip zinc–iron	0.83	6–11
Electrodeposited Zn	0.84	4–14
Electrodeposited Zn–Fe (15%–25% iron)	0.84	≅7

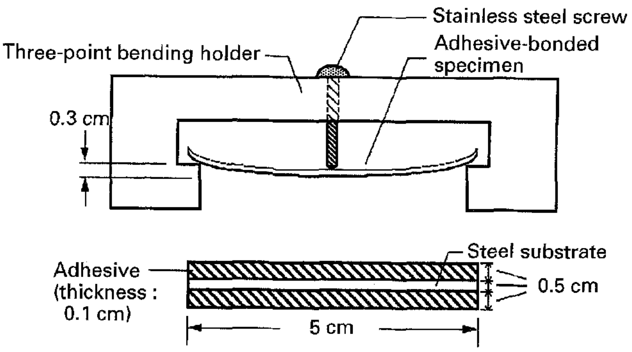

Figure 1 The cross-section of an assembled three-point bending device, and the dimensions of an adhesive-bonded specimen.

specimens were produced with two adhesive strips bonded on one side of the steel substrate surface. The bondline thickness of adhesive in all specimens was 0.1 cm.

The five test solutions used in this investigation were (1) distilled or deionized water, (2) 100 p.p.m. sodium chloride solution, (3) 1000 p.p.m. sodium chloride solution, (4) 0.5 M sodium chloride solution, and (5) 1.0 M sodium chloride solution.

Three-point bending devices made of transparent acrylic plastic sheets were used to evaluate the effect of applied bending stresses on adhesive delamination in the presence of corrosive environments. The specimens of different adhesive/substrate combinations were assembled and stressed as shown in Fig. 1. A group of four different adhesive-bonded test specimens (one steel substrate type and four different adhesives) with the adhesive-bonded side facing downward was assembled in a three-point bending device. The centre of each test specimen was pressed 0.3 cm down by a stainless steel screw. This value was chosen to provide sufficient bending stresses on the test specimen without causing the down-facing adhesive to crack. After assembling in a three-point bending holder, the adhesive-bonded surface of the specimen was subjected to a tensile stress, whereas the other side of the specimen was subjected to a compressive stress. Maximum stresses existed at the central area of the bent specimen. Assemblies were then immersed into the five different test solutions for 1–5 weeks. Each stressed specimen composed of one adhesive/metal system was exposed to one particular test solution for a specific time interval.

After different time intervals, the specimens were removed from the solution, released from the three-point bending holder, dried, and examined visually. A small surgery knife was then used to remove the delaminated adhesives from the steel substrate. The area percentage of the adhesive delaminated from the metal substrate was estimated by counting the number of squares on a transparent scale paper, which was placed over the delaminated areas of the steel substrate surface.

3. Results

A general corrosion on all the unbonded steel substrate surfaces was observed after 1 week exposure to different solutions. When adhesive delamination occurred, the delaminated adhesive could be easily removed from the steel substrate. A typical delaminated adhesive-bonded specimen is depicted in Fig. 2. It was found in all cases that severe adhesive delamination occurred at the central area of the specimen where a maximum tensile stress existed, and that the area of delamination increased with the magnitude of the applied tensile stress. The further the distance away from the centre of the specimen, the lower was the tensile stress applied on the adhesive, thus a smaller area of delamination was obtained. No crevice corrosion was observed on the steel substrates underneath the delaminated adhesives. It was found that, in all cases, the degree of corrosion on the unbonded steel substrate surfaces was higher than that on the steel substrate surfaces from which the delaminated adhesives were removed after 5 weeks of the experiment.

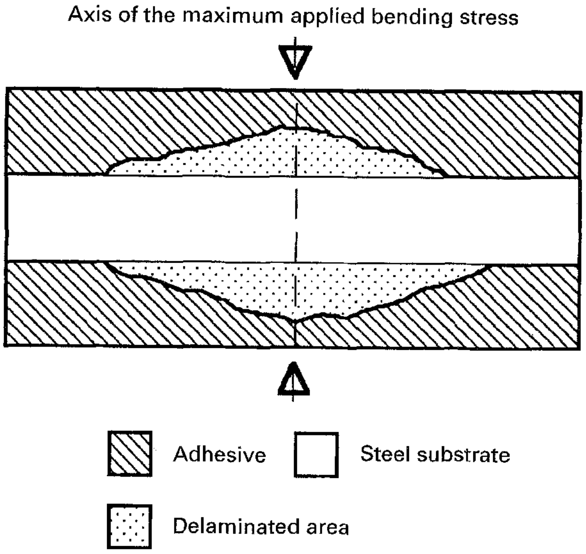

Figure 2 A typical delaminated adhesive-bonded specimen.

Adhesive cracking was found at the central part of the specimens that were bonded with adhesive A or B after 1 week exposure to a test solution. Cracking of these adhesives was found to occur primarily in the direction perpendicular to that of the applied tensile stress. For the specimens that were bonded with adhesive C or D, no adhesive cracking was observed at any time during the 5 weeks immersion in any of the solutions. However, a change in colour (from dark grey to light grey) at the central part of these adhesives was observed after 1 week exposure to a test solution. It is presumed that the colour change at the central part of these adhesives was due to water absorption, and displacement of the adhesive matrix produced by the applied tensile stress.

The percentage of the area delaminated was plotted as a function of time (Figs 3–6). Regardless of the test solutions and metal substrates used, the specimens that were bonded with adhesive C had the largest average value of delaminated areas, followed by specimens bonded with adhesive D, B and A. A relatively lower degree of adhesive delamination was found in the cases where the adhesives were bonded on the

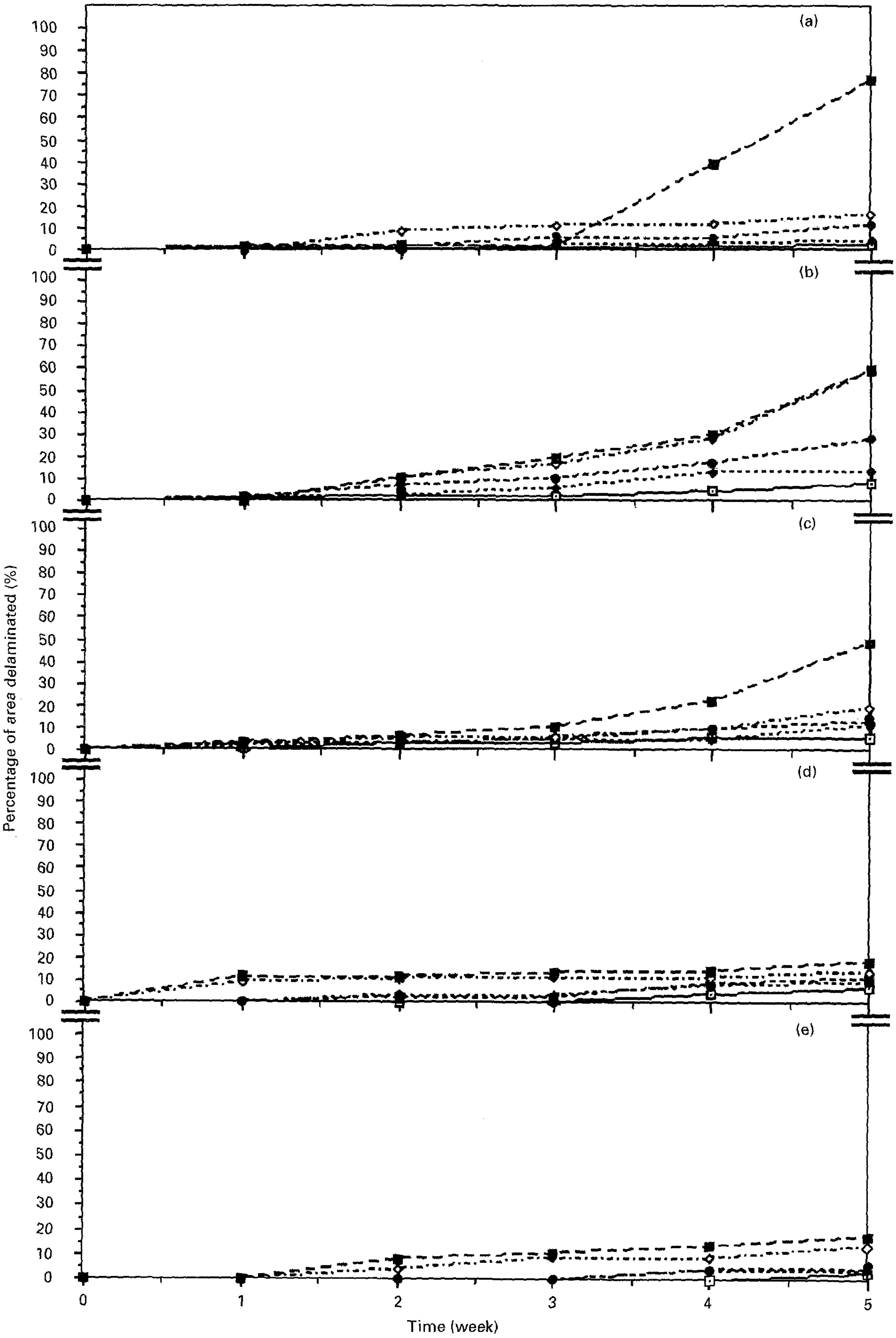

Figure 3 Plots of percentage of area delaminated versus time for the bent specimens bonded by adhesive A and the different steel substrates upon exposure to different solutions. (a) 1.0 M NaCl solution, (b) 0.5 M NaCl solution, (c) 1000 p.p.m. NaCl solution, (d) 100 p.p.m. NaCl solution, (e) distilled water. (□) Cold-rolled steel, (◆) hot-dip Zn–Fe, (●) electrodeposited Zn–Fe, (◇) electrodeposited Zn, (■) hot-dip Zn.

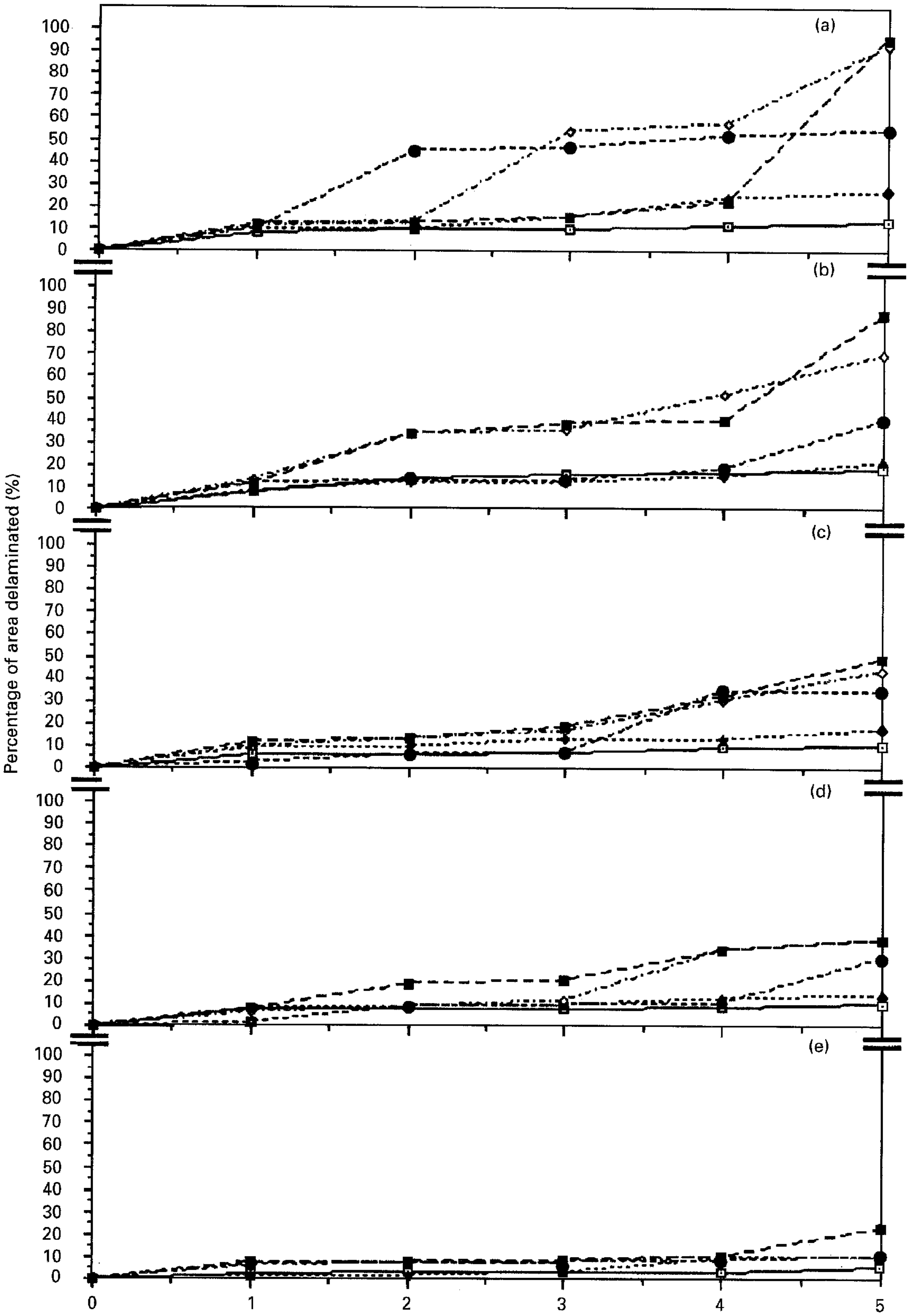

Figure 4 Plots of percentage of area delaminated versus time for the bent specimens bonded by adhesive B and the different steel substrates upon exposure to different solutions. (a)–(e) as in Fig. 3. For key, also see Fig. 3.

cold-rolled steel substrates. These results reveal that the adhesive bonding on a cold-rolled steel substrate exhibits the strongest adhesive bonding of all the other steel substrates tested. The adhesive bonding on a hot-dip zinc–iron steel substrate was found to be the second strongest, followed by the adhesive bonding on an electrodeposited zinc–iron steel, an electrodeposited zinc steel, and a hot-dip zinc steel. Of all the adhesive bonded specimens tested, the adhesive bonding between adhesive C and a hot-dip zinc steel substrate was found to be the weakest. In contrast, the strongest bonding was found in the combination of adhesive A and a cold-rolled steel substrate. Moreover, it was found that the area of adhesive delamination increased with the exposure time, and with the concentration of the NaCl solutions. It was found that

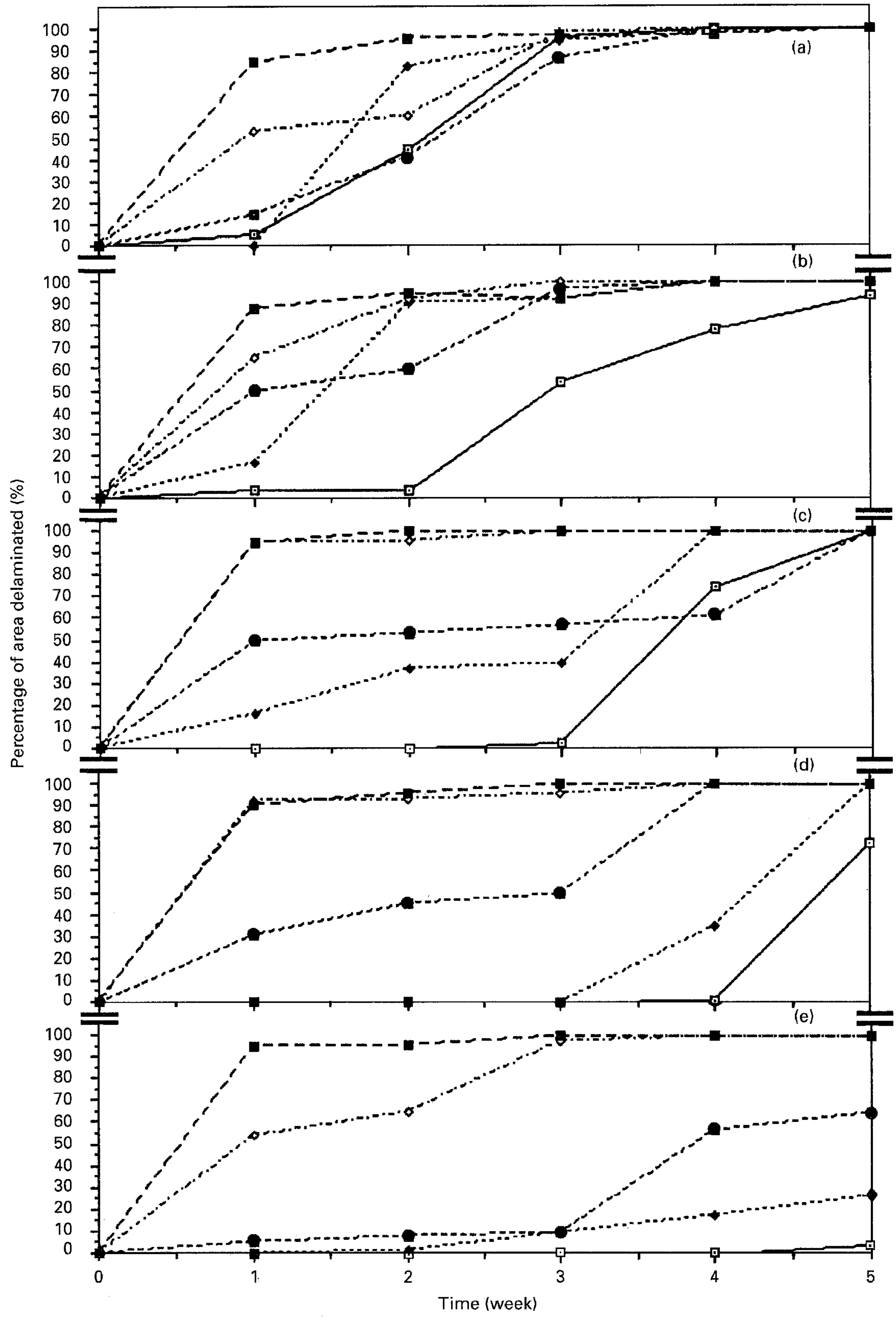

Figure 5 Plots of percentage of area delaminated versus time for the bent specimens bonded by adhesive C and the different steel substrates upon exposure to different solutions. (a)–(e) as in Fig. 3. For key, also see Fig. 3.

adhesive delamination occurred more rapidly when tensile stress was applied on the specimens when compared to the rate of adhesive delamination that occurred on the unstressed specimens. Upon exposure to a 1000 p.p.m. NaCl solution for 4 weeks, adhesive delamination was first found on an unstressed electrodeposited zinc–iron steel specimen that was bonded with adhesive C [22]. However, upon exposure to an NaCl solution with the same concentration for 1 week, 50% of the total bonded adhesive area was found to be delaminated on a bent specimen that was bonded by the same adhesive and the same steel substrate (Fig. 5).

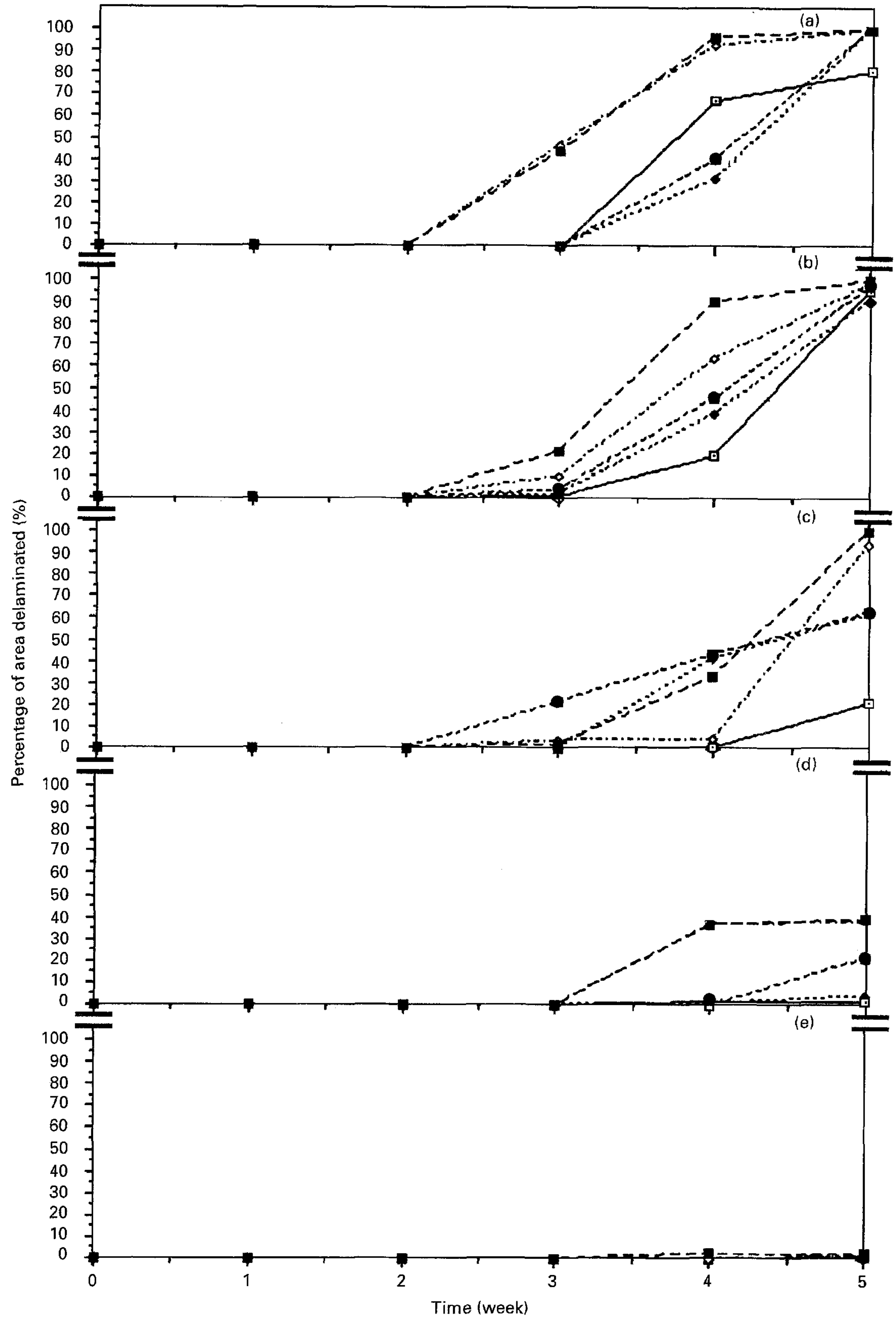

Figure 6 Plots of percentage of area delaminated versus time for the bent specimens bonded by adhesive D and the different steel substrates upon exposure to different solutions. (a)–(e) as in Fig. 3. For key, also see Fig. 3.

4. Discussion

Using the above results of adhesive delamination, together with the results obtained from the water absorption measurements [23] and microhardness measurements [22], three factors influencing adhesive delamination were determined. They are: (1) the adhesive/substrate system, (2) the corrosive environments, and (3) the applied stresses.

4.1. The adhesive/substrate system

Regardless of the test solutions and the metal substrates used, the bent specimens that were bonded with adhesive C had the largest average value of delaminated areas upon exposure to different test solutions, followed by the specimens bonded by adhesives D, B and A. It is recalled that the average values of microhardness for the dry adhesives were ranked in ascending order as C, D, B and A [22]. These results reveal that the harder the adhesive, or the higher the concentration of the fillers incorporated in the adhesive, the stronger the bonding between the adhesive and the metal substrate produced to resist adhesive delamination. It is worth mentioning that the hardness of the adhesives is governed by the composition and the type of fillers incorporated in the adhesive matrix. It is believed that a strong adhesive/metal bonding is produced by the mechanical interlocking mechanism between the strong adhesive and the metal substrate. Table III shows a summary of the results obtained from the water-absorption measurements, the microhardness measurements, and the three-point bending experiment for the four adhesives A, B, C, and D. No correlation was found between the area percentage of the adhesive delaminated and (i) the percentage of water absorbed in the adhesives, and (ii) the percentage of microhardness decrease in the adhesives. These results reveal that adhesive delamination is not governed by (i) the amount of water absorbed in the adhesive, and (ii) the degree of degradation of the adhesive matrix resulting from water intrusion. It is believed that adhesive delamination depends strongly on the bonding between the adhesive and the steel substrate, and that the degree of delamination is governed by the reactions occurring at the adhesive/substrate interface.

A relatively lower degree of adhesive delamination was found on the cold-rolled steel substrate than on the other steel substrates upon immersion in a test solution for the same period of time. It was found that the adhesive bonding on a cold-rolled steel substrate is the strongest of all the steel substrates tested. The adhesive bonding on a hot-dip zinc–iron steel substrate was found to be the second strongest, followed by the adhesive bonding on an electrodeposited zinc–iron steel, an electrodeposited zinc steel, and a hot-dip zinc steel. These results were compared with the surface roughness data of different steel substrates given in the literature [12]. A correlation between the surface roughness of the steel substrates and the degree of adhesive delamination was clearly found. It is seen that the rougher the steel substrate surface, the lower was the degree of adhesive delamination. These results confirm that the adhesion between the adhesive and the steel substrate occurs according to the mechanical interlocking mechanism, and that the degree of adhesive delamination depends strongly on the adhesive/substrate bonding of the specimen that is exposed to corrosive environments. A strong adhesive/substrate adhesion is obtained when the metal oxide surface of the substrate provides a significant degree of microscopic roughness for the substrate to interlock mechanically with the overlaying adhesive [3, 24, 25]. Of all the adhesive-bonded specimens tested, the adhesive bonding between adhesive C and a hot-dip zinc steel substrate was found to be the weakest. Note that adhesive C was the softest adhesive of the four adhesives investigated [22], and that the hot-dip zinc steel had the smoothest substrate surface of the five steel substrates tested [12]. In contrast, the strongest bonding found between the adhesive and the steel substrate was in the combination of adhesive A (the hardest adhesive) and a cold-rolled steel substrate (the roughest surface).

4.2. The corrosive environments

It was found that the areas of adhesive delamination on the test specimens increased with the concentration of the NaCl solutions, and with the exposure time. These results indicate that water and sodium chloride penetrate into the adhesive/substrate interface and damage the bonding between the adhesive and the steel substrate electrochemically and mechanically. When water and sodium chloride are absorbed into the adhesive/metal interface, electrochemical reactions (anodic metal dissolution and cathodic oxygen reduction) occur at different sites underneath the adhesive. After the bonding between the adhesive and the steel substrate is damaged electrochemically, a delamination gap forms between the delaminated adhesive and the steel substrate. When the hydraulic pressure inside the delamination gap increases and becomes high enough to break the adhesive/substrate bonding at the tips of the gap, the degree of adhesive delamination is intensified mechanically. As a result, more corrosive solution can enter the delamination gap, and further intensify the degree of adhesive delamination electrochemically and mechanically. These postulates of adhesive delamination are in agreement with the mechanism of the disbondment of organic coatings in water proposed by Leidheiser and Funke [26].

TABLE III A summary of the results for the adhesives tested

Average amount of water absorbed:	C > A > D > B (highest) (lowest)
Average microhardness in dry state:	A > B > D > C (highest) (lowest)
Average percentage of microhardness decrease:	D > C > A > B (highest) (lowest)
Average percentage of area delaminated (upon bending):	C > D > B > A (highest) (lowest)

4.3. The applied stresses

It was found that in all the adhesive-bonded specimens tested, severe adhesive delamination occurred at the central area of the specimen where maximum tensile stress existed, and that the degree of delamination increased with the magnitude of the applied tensile stress. The further the distance from the centre of the specimen, the lower was the magnitude of the tensile stress applied on the adhesive, and thus smaller delaminated areas were found. Adhesive cracking was found at the central part of the specimens that were bonded with adhesive A or B after 1 week exposure to a test solution. Cracking of these hard and brittle adhesives was found to occur primarily in the direction perpendicular to that of the applied tensile stress. Because the largest magnitude of the tensile stress existed at the central part of the adhesive surface, localized adhesive cracking initiated preferably at these central surface areas. When the hard and brittle adhesives (A and B) were subjected to the tensile stress, microcavities or microvoids were produced in the adhesive matrix. Cracks initiated from the adhesive surface, and propagated through the microcavities inside the adhesive matrix in the direction perpendicular to that of the applied tensile stress. It can be presumed that cracking of the adhesive produced by the tensile stress enhanced the rate of water or NaCl solution transport into the adhesive/substrate interface. After the adhesive cracks propagated into the adhesive/substrate interface, water or sodium chloride solution could penetrate into the interface and could produce vulnerable sites on the oxide-covered metal substrate. When the air-formed metal oxide layer at the localized vulnerable sites dissolved in the surrounding solution, the bonding between the adhesive and the metal substrate broke, thus adhesive delamination occurred. As the corrosive solution entered the delamination gap through the adhesive cracks, and spread into the surrounding interfacial areas, the degree of adhesive delamination was intensified.

For the specimens that were bonded with the soft and elastic adhesives (C and D), no adhesive cracking was observed at any time during the 5 weeks of the experiment. However, a change in colour (from dark grey to light grey) at the central part of these adhesives was observed after 1 week exposure to a test solution. It is presumed that the colour change at the central part of these soft and elastic adhesives was due to water absorption and deformation of the adhesive matrix (adhesive plasticization) produced by the applied tensile stress. According to the data given by Fahmy *et al.* [27], the value of the water diffusion coefficient of an adhesive increases exponentially with the magnitude of the tensile stresses that exist inside the adhesive. Because the central part of the adhesive surface was subjected to the highest magnitude of the tensile stress, a significant amount of corrosive solution could penetrate through the deformed adhesive matrix, thus reaching the adhesive/substrate interface. Adhesive delamination occurred when the adhesive/substrate bonding was damaged by both the metal oxide dissolution and the high pH solution produced by oxygen reduction. Because the deformed adhesive areas found in adhesives C and D were much larger than the areas of localized cracking found in adhesives A and B, a larger vulnerable area on the metal substrate surface underneath adhesive C or D was produced. As a result, larger delaminated areas were observed on the specimens bonded with adhesives C and D than those found on the specimens bonded with adhesives A and B.

5. Conclusions

1. Ranking of the adhesives in the percentage of area delaminated under tensile stress when the specimens are exposed to the different test solutions (regardless of the steel substrates used) was found to be:

$$C > D > B > A$$

(highest) (lowest)

2. The degree of adhesive delamination increases with the concentration of the NaCl solutions, the magnitude of the applied tensile stress, and the exposure time.
3. The harder the adhesive in its dry state, or the higher the concentration of fillers in the adhesive, the lower was the degree of delamination in the three-point bending tests.
4. Ranking of the metal substrates against adhesive delamination was found to be:

cold-rolled steel (best) > hot-dip Zn–Fe steel > electrodeposited Zn–Fe steel > electrodeposited Zn steel > hot-dip Zn steel (worst)

5. The adhesion between an adhesive and a steel substrate is governed by the hardness of the adhesive and the surface roughness of the steel substrate. Strong adhesive/substrate bonding is obtained when a strong and hard adhesive is mechanically interlocked by a steel substrate having a very rough surface. In the three-point bending tests, regardless of the test solutions used, the strongest bonding was found in the adhesive A/cold-rolled steel specimens, whereas the weakest bonding was found in the adhesive C/hot-dip zinc specimens.
6. The factors affecting the degree of adhesive delamination were: (i) the adhesive/substrate system; (ii) the corrosive environments; and (iii) the applied stresses.

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