Effect of fillers on the degradation of automotive epoxy adhesives in aqueous solutions

Part II The microhardness change and delamination of automotive epoxy adhesives in distilled water and NaCl solutions

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The effects of water and NaCl solutions on four different automotive epoxy adhesives bonded on electrodeposited zinc–iron steel substrate were investigated as a function of the degree of microhardness change in the adhesives under water and NaCl solution immersion tests. On the basis of the microhardness measurements, it was found that the soft and elastic adhesives were more susceptible to adhesive softening, swelling and microdamages than the hard and brittle adhesives upon exposure to the test solutions. The degree of microhardness decrease in the adhesives increased with the concentration of the NaCl solution. In the presence of sodium chloride, the same degree of microhardness decrease was obtained in the adhesives although less water was absorbed from the NaCl solution than from the distilled water. In addition, delamination of the adhesives from the steel substrate was observed after each microhardness measurement. Oxygen was found to play an important role in the process of adhesive delamination, although it had no effect on the change in the microhardness of the adhesives.

1. Introduction

Plasticization and microstructural damage in adhesive materials have been reported to be the detrimental consequences resulting from exposure to water, humidity, ionic contaminants, and atmospheric impurities [1–3]. Sorbed moisture acts as an adhesive plasticizer and a swelling agent that increases the matrix volume of the adhesive, thus decreasing the microhardness and enhancing the water absorption in the adhesive [3]. Microhardness measurements of an adhesive conducted before and after exposure to an aqueous environment can provide useful information about the effects of the environment on the changes in physical properties of the adhesive. Microhardness measurements on polymeric materials were conducted in several studies [4–6]. Lorenzo et al. [5, 6] measured the resistance of polyethylene samples to plastic deformation that was produced by the impact of a microhardness indentor. A series of commercial polyethylene samples with different densities was studied without exposure to moisture. Lorenzo et al. [5, 6] reported that longer diagonal lengths of indentation were obtained from the polyethylene samples having lower densities. They claimed that the higher the

density, the molecular weight and the crystallinity level of the polymer, the higher were the microhardness values of the polymers. Because the yield stress, Y, and the elastic modulus, E, of polymers are governed by the degree of crystallinity [7], microhardness values provide useful information for predicting the mechanical properties of polymers. Breval and Rachlitz [4] measured the microhardness of six different painted systems, and investigated the relationship between their microhardness values and adhesion to zinc coating before and after exposure to 100% relative humidity for 300 h. The microhardness values of the painted systems exposed to moisture for 300 h showed that a good adhesion of paint on the zinc coating resulted when high microhardness values of paints were retained.

The objective of this work was to evaluate the effects of distilled water and NaCl solutions on the properties of different automotive epoxy adhesives using microhardness measurements. The same four epoxy adhesives were used as those described in Part I [8]. Correlations between the water uptake and the microhardness change of different adhesives were determined. Observations of adhesive delamination and

corrosion on the steel adherends were made. In addition, adhesive delamination was studied in the presence and absence of oxygen.

2. Materials and experimental procedures

Microhardness measurements were made on four different adhesives, A, B, C, and D, before and after exposure to five different aerated test solutions at various time intervals over 6 weeks. The solutions used were: (i) distilled water; (ii) 100 p.p.m. NaCl solution; (iii) 1000 p.p.m. NaCl solution; (iv) 0.5 M NaCl solution; and (v) 1 M NaCl solution. Each of the adhesives investigated in this task was bonded on an electrodeposited zinc–iron steel substrate. Dimensions of the test specimens were 1.5 cm × 3.0 cm. The bondline thickness of the adhesive in each specimen was 0.1 cm. Fig. 1 shows a schematic diagram of a test specimen. Microhardness measurements were first conducted on the dry test specimens before they were immersed in the different test solutions. Microhardness measurements were conducted using a Vickers indentor which was attached to a Buehler Micromet II digital microhardness tester. A loading cycle of 10 s and a load of 100 g were used for all measurements. These values were selected to obtain indentations with measurable diagonal lengths under microscopical measurements. On each test specimen, 30 microhardness measurements were conducted. An average microhardness value was calculated for each particular adhesive specimen.

Three pieces of each particular adhesive-bonded specimen were immersed in an aerated test solution at room temperature. At various time intervals, test specimens were removed from the test solution, dried, and microhardness measurements were made. Before test specimens were immersed in the test solutions, adherence of the adhesives to the steel substrate was examined visually. After exposure to the different test solutions for 6 weeks, adherence between the adhesive and the steel substrate of each test specimen was observed carefully under an optical microscope.

Another set of adhesive-bonded specimens was immersed in five different deaerated test solutions. Each of the adhesives exposed to the deaerated solutions was also bonded on an electrodeposited zinc–iron steel substrate. Argon gas was charged into the test solutions in which test specimens were immersed.
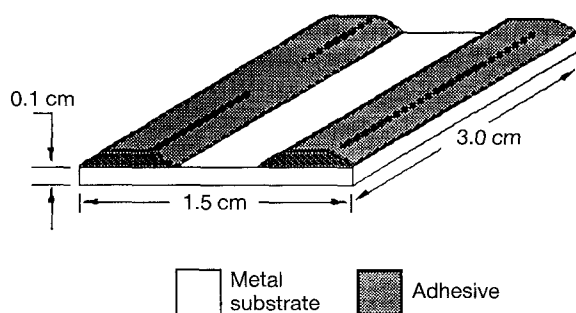

Figure 1 Schematic diagram of a specimen prepared for the microhardness measurement.

Microhardness measurements were conducted on each specimen after 6 weeks immersion, and the adherence between the adhesive and the steel substrate was observed under an optical microscope.

3. Results

Tables I–IV show the results obtained from the microhardness measurements for adhesives A, B, C, and D, respectively. It was found that adhesive A has the highest microhardness prior to exposure to the different test solutions, followed by adhesive B, D, and C. Adhesives A and B were found to be hard and brittle in the dry state, whereas adhesives C and D were found to be relatively elastic and soft. The percentage of microhardness decrease for adhesives A, B, C, and D exposed to the different solutions was plotted as a function of time (Figs 2–5). For the adhesives tested, regardless of the different test solutions used, an initial linear microhardness decrease was obtained during the first 3–4 days. After the first 3–4 days exposure, a gradual decrease in microhardness of the adhesives occurred. In all cases, a steady state of microhardness decrease of the adhesives was obtained after 30 days. The microhardness decrease of adhesives between the fifth and the sixth week was less than 5%. It can be assumed that all the adhesives were saturated with water after 30 days immersion in the different aerated test solutions. Moreover, the microhardness decrease of the adhesives that were immersed in distilled water was always higher than that of the adhesives upon exposure to different concentrations of NaCl solutions. The higher the concentration of the NaCl solu-

TABLE I Microhardness values of adhesive A (H_V)

Time	H_V				
	Distilled water	100 p.p.m. NaCl	1000 p.p.m. NaCl	0.5 M NaCl	1.0 M NaCl
0 day	21.50	21.50	21.50	21.50	21.50
3 day	12.68	12.78	12.88	13.33	13.69
1 wk	11.61	11.96	12.35	12.44	13.30
2 wk	9.10	9.23	9.31	9.55	10.48
3 wk	8.94	9.14	9.25	9.51	10.45
4 wk	8.10	9.09	9.19	9.46	9.71
5 wk	8.00	8.63	8.70	9.25	9.34
6 wk	7.85	8.49	8.68	9.01	9.29

TABLE II Microhardness values of adhesive B (H_V)

Time	H_V				
	Distilled water	100 p.p.m. NaCl	1000 p.p.m. NaCl	0.5 M NaCl	1.0 M NaCl
0 day	13.58	13.58	13.58	13.58	13.58
3 day	11.57	11.64	12.05	12.19	12.95
1 wk	11.25	11.63	11.90	11.94	12.58
2 wk	10.76	11.31	11.79	11.90	12.20
3 wk	10.75	11.12	11.70	11.79	11.88
4 wk	10.64	11.06	11.35	11.75	11.80
5 wk	10.61	10.76	11.30	11.42	11.64
6 wk	10.29	10.46	10.92	10.99	11.29

TABLE III Microhardness values of adhesive C (H_V)

Time	H_V				
	Distilled water	100 p.p.m. NaCl	1000 p.p.m. NaCl	0.5 M NaCl	1.0 M NaCl
0 day	1.07	1.07	1.07	1.07	1.07
3 day	0.33	0.36	0.35	0.40	0.45
1 wk	0.30	0.30	0.33	0.35	0.43
2 wk	0.30	0.28	0.29	0.30	0.31
3 wk	0.35	0.31	0.36	*0.38*	*0.38*
4 wk	*0.36*	*0.38*	*0.38*	*0.39*	*0.39*
5 wk	*0.35*	*0.36*	*0.38*	*0.38*	*0.39*
6 wk	*0.35*	*0.36*	*0.38*	*0.38*	*0.39*

TABLE IV Microhardness values of adhesive D (H_V)

Time	H_V				
	Distilled water	100 p.p.m. NaCl	1000 p.p.m. NaCl	0.5 M NaCl	1.0 M NaCl
0 day	6.75	6.75	6.75	6.75	6.75
3 day	2.19	1.65	1.83	2.35	2.60
1 wk	1.40	1.65	1.28	2.25	2.34
2 wk	1.79	1.88	1.71	2.09	2.34
3 wk	0.63	0.68	0.69	*0.86*	*0.91*
4 wk	*0.63*	*0.66*	*0.66*	*0.86*	*0.91*
5 wk	*0.31*	*0.36*	*0.36*	*0.45*	*0.74*
6 wk	*0.28*	*0.29*	*0.31*	*0.44*	*0.50*

Figure 3 The plot of percentage of microhardness decrease versus time for adhesive B exposed to different solutions.

Figure 4 The plot of percentage of microhardness decrease versus time for adhesive C exposed to different solutions.

Figure 2 The plot of percentage of microhardness decrease versus time for adhesive A exposed to different solutions.
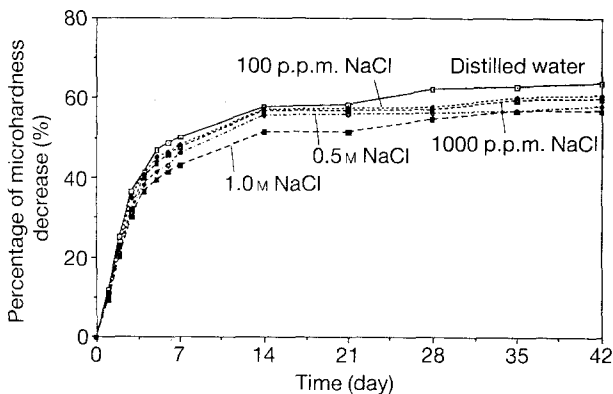

Figure 5 The plot of percentage of microhardness decrease versus time for adhesive D exposed to different solutions.

tion in which the adhesives were immersed, the lower was the microhardness decrease of the adhesives. After 6 weeks of the experiment, adhesive D was found to have the highest microhardness decrease, followed by adhesives C, A and B.

After 4 weeks immersion in the different solutions in the presence of atmospheric air, a total or partial adhesive delamination was found on all specimens that were bonded by either adhesive C or D. When adhesive delamination was detected, the delaminated adhesives could easily be removed from the electrodeposited zinc–iron steel substrate using a fingernail. In contrast, no adhesive delamination was observed on specimens that were bonded by adhesive A or B during the 6 weeks of the experiment. After 6 weeks immersion in different aerated solutions, adhes-
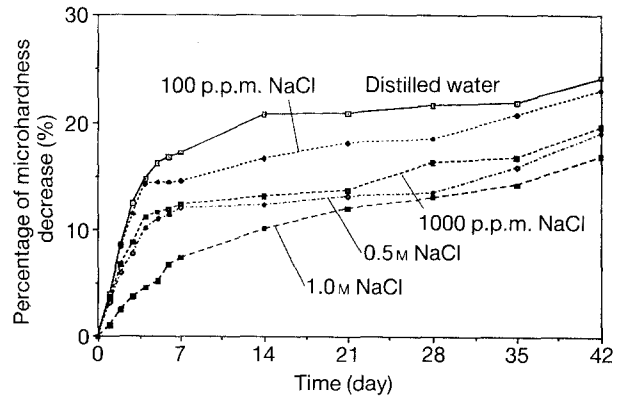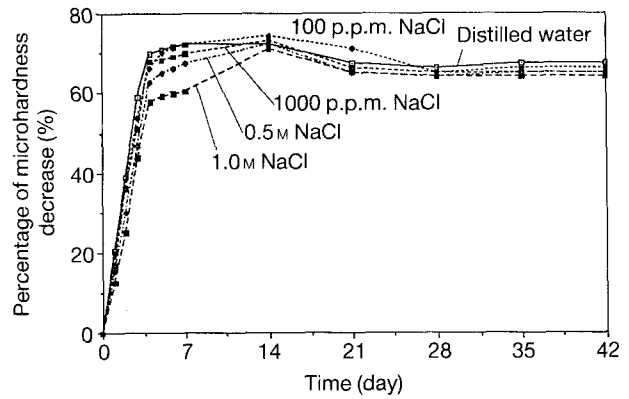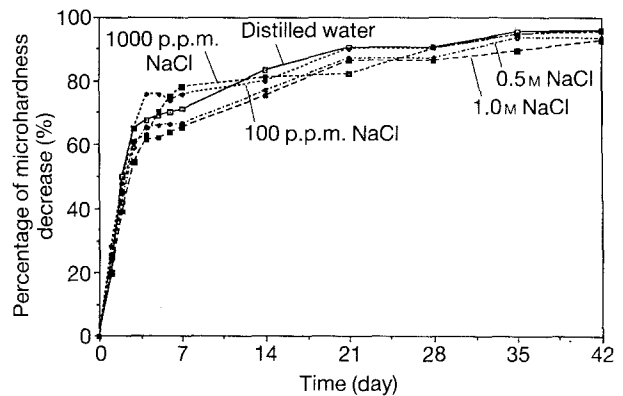
ives A and B were found tightly bonded with the steel substrate, and were still very hard. The italic entries in Table III and IV show the occurrence of adhesive delamination during the 6 weeks exposure of the adhesives to the different aerated solutions. Fig. 6 shows the cross-section of a specimen (adhesive C bonded with an electrodeposited zinc–iron steel substrate) that was immersed in an aerated 1.0 M NaCl solution for 6 weeks. Partial adhesive delamination was observed in this specimen. No corrosion was observed underneath the adhesive for the specimens having an adhesive delamination. For all of the specimens tested during the 6 weeks, general corrosion was
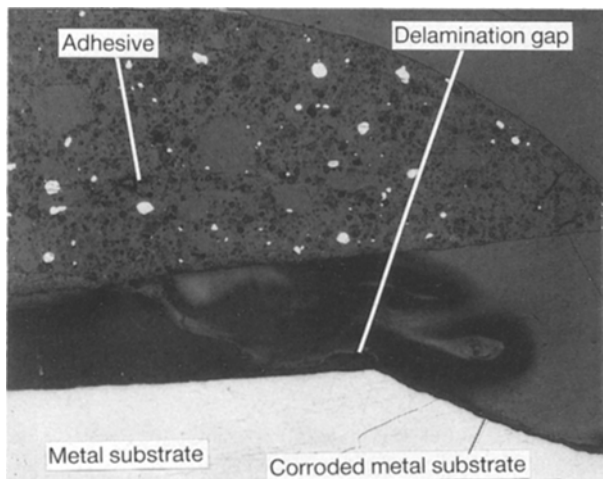
Figure 6 Adhesive delamination on a specimen (adhesive C bonded with electrodeposited zinc–iron steel substrate) that was immersed in aerated 1.0 M NaCl solution for 6 weeks (× 17.5).

found on the steel surfaces which were not covered by the adhesive.

No adhesive delamination was found in the adhesive-bonded specimens that were immersed in deaerated test solutions during the 6 weeks. A very strong adherence between the adhesives and the steel substrates was found in all cases. Detachment of the adhesives from the steel substrates was impossible using either a fingernail or a small surgery knife. However, the microhardness values of the adhesives immersed in the two different environments were very close to each other. These results show that the presence of oxygen in test solutions plays an important role in adhesive delamination, but has no effect on the change in the microhardness of the adhesives.

4. Discussion

It was found that adhesive A has the highest microhardness prior to exposure to different test solutions, followed by adhesives B, D, and C. Adhesives A and B were found to be hard and brittle in their dry states, whereas adhesives C and D were found to be relatively elastic and soft in texture. It is believed that the microhardness value of a dry, cured adhesive is governed by the composition, and the types of fillers incorporated in the adhesive matrix. Because fillers are many times more rigid than epoxy resins, they can increase the modulus (shear, Young's, or bulk) of epoxy resins significantly, especially when fine, wide size-range fillers with high packing fractions are used. In addition, the hardness of the adhesive depends on the degree of filler dispersion, interfacial bonding between fillers and resin, and the shear degradation of the adhesive during filler incorporation [9]. Although adhesive A contains only about 20% fillers, it is incorporated with about 3%–4% reinforcing acrylic epoxy filler (Table I of [8]). The high microhardness values of adhesive A are primarily governed by the high moduli (shear, Young's, and bulk) of this reinforcing filler. Adhesive B has the second highest microhardness values in its dry state. The high microhardness values of this adhesive are attributed to the extremely high content of fillers

(57.6%–59.4% of the total adhesive composition) incorporated inside the adhesive matrix. Adhesives C and D are relatively softer and more elastic due to their relatively low filler contents. Adhesive D contains 35% silica or silicon dioxide, and 5% calcium carbonate and calcium silicate. It is considered that the higher silica content in adhesive D produces a higher microhardness value in comparison to that of adhesive C (5%–10% silica, 10%–20% talc clay, and 15%–20% calcium carbonate). Silica or silicon dioxide is a hard and tough filler material that has good abrasive resistance. On Moh's scale of hardness [9], diamond has a hardness of 10, silica has a hardness of 7–7.5, calcium carbonate has a hardness of 3, and talc has a standard hardness of 1.

After the adhesives were immersed in different solutions for the 6 weeks, adhesive D was found to have the highest microhardness decrease, followed by adhesives C, A and B. The microhardness decrease in the adhesive indicates the degradation and plasticization of the adhesive matrix. When water is absorbed into the adhesive, adhesive degradation results from the dissolution of the water soluble fillers (calcium carbonate, and calcium silicate). Plasticization (swelling) of the adhesive occurs as a result of the generation of osmotic pressure inside the microcracks or microcavities. The results of microhardness measurements reveal that the resistance to a microhardness decrease of the softer and more elastic adhesives, namely C and D, is lower than that of the stronger and harder adhesives A and B upon exposure to distilled water and different concentrations of NaCl solutions. Degradation in the adhesives may involve the following events: (i) water is absorbed into the adhesive matrix by diffusion and by capillary action through cracks and micropores; (ii) water-soluble inorganic fillers, namely calcium carbonate, and calcium silicate, in the adhesive dissolve in water, thus producing microcavities that enhance water accumulation in the adhesive matrix; (iii) water from the bulk solution intrudes into the adhesive matrix and dilutes the electrolyte produced by the dissolution of the water soluble fillers; (iv) water intrusion into the adhesive matrix sets up osmotic pressures that are high enough to produce adhesive swelling, and microdamage; (v) the rate of water transport into the adhesive matrix increases with the density of the microcavities, and with the degree of adhesive swelling; (vi) microhardness of the adhesive decreases as the density of the microcavities, and the degree of adhesive swelling increase. It is worth mentioning that a lower osmotic pressure is required to cause adhesive swelling in soft and elastic adhesives than in hard and brittle adhesives. Therefore, soft and elastic adhesives (C and D) are more susceptible to adhesive swelling and microdamage than the hard and brittle adhesives (A and B) upon exposure to corrosive solutions.

Figs 7–10 show the correlation between the percentage of the microhardness decrease and the percentage of the water uptake of different adhesives. The water-absorption data of the adhesives were taken from Part I [8]. A linear relationship between the percentage of the microhardness decrease and the
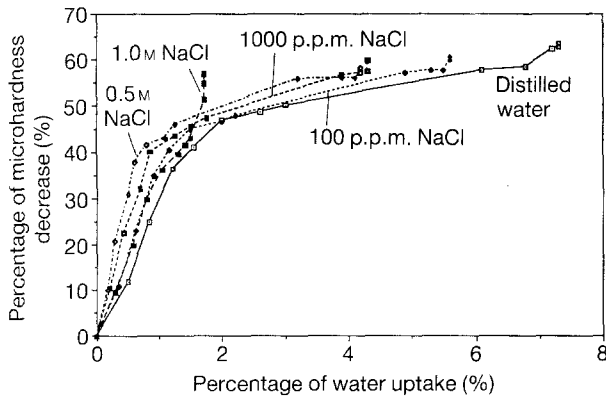
Figure 7 Correlation between the percentage of microhardness decrease and the percentage of water uptake of adhesive A.
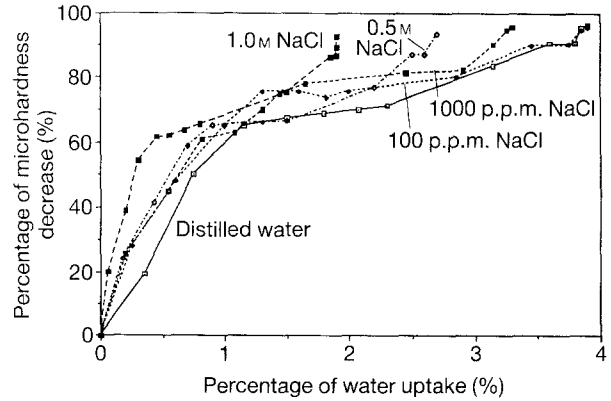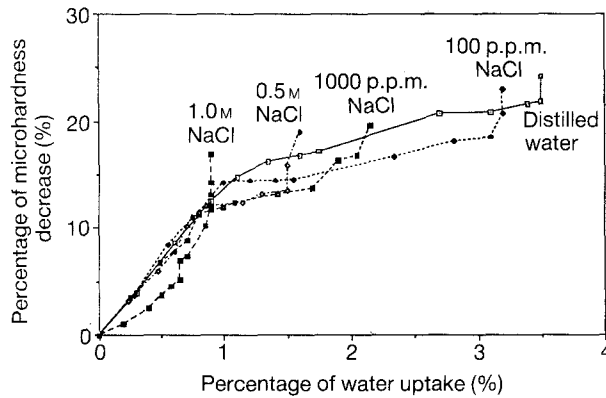

Figure 8 Correlation between the percentage of microhardness decrease and the percentage of water uptake of adhesive B.

Figure 9 Correlation between the percentage of microhardness decrease and the percentage of water uptake of adhesive C.

Figure 10 Correlation between the percentage of microhardness decrease and the percentage of water uptake of adhesive D.
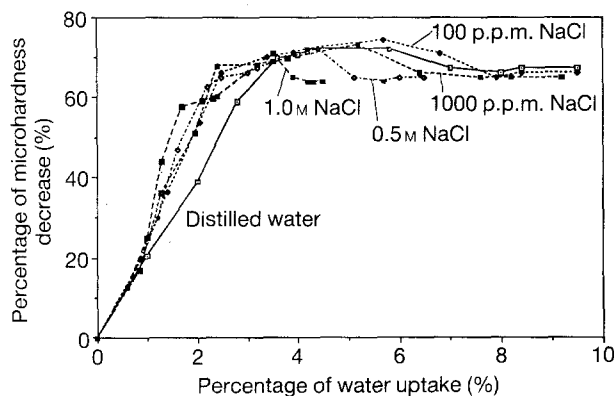
low as 1.8% of the water uptake in the adhesive from the bulk 1.0 M NaCl solution is required to decrease 55% of the microhardness of this adhesive, whereas 3.2% of the water from the 0.5 M NaCl solution, 3.8% of the water from the 1000 p.p.m. NaCl solution, 4% of the water from the 100 p.p.m. NaCl solution, and 4.8% of the distilled water are required to decrease the same percentage of the microhardness of adhesive A. As the concentration of the NaCl solution increases, less water uptake in the adhesives from the bulk solution is required to decrease the microhardness of the adhesives. This proves that the degree of adhesive degradation increases with a concentration of sodium chloride in the bulk solution. These results are in agreement with previous reports in the literature [10–15] that an NaCl solution enhances the formation of microcavities in adhesive materials, thereby increasing the rate of water intrusion, and the degree of swelling or adhesive degradation.

After each microhardness measurement on the adhesives at various time intervals, the adhesives were examined visually. General corrosion was found on the steel surfaces that were not covered by the adhesive. Adhesive delamination was found on specimens that were bonded by either adhesive C or D after 3 weeks immersion in 1000 p.p.m., 0.5 M and 1.0 M NaCl solutions. In these cases, the adhesive was found to be partially delaminated from the electrodeposited zinc–iron steel substrate. After 4 weeks immersion in different aerated solutions, a total or partial adhesive delamination was found on all specimens that were bonded by either adhesive C or D. In contrast, no adhesive delamination was observed on specimens that were bonded by adhesive A or B during the 6 weeks of the experiment. These results show that (i) bonding between an electrodeposited zinc–iron steel substrate and adhesive C or D has poor resistance against the attack of different concentrations of the NaCl solution; and (ii) the higher the concentration of the NaCl solution, the more severe the attack on the adhesive/metal bonding. When adhesive delamination occurs, the adhesive tends to move away from the metal substrate due to the effect of residual stresses in the adhesive that were produced during the curing process, and of the hydraulic pressure that exists between the delamination gap. When an adhesive is cooled from its curing temperature, significant

percentage of the water uptake is observed in the initial stage of these plots. A gradual change between the percentage of the microhardness decrease and the percentage of the water uptake is observed after the initial stage. At this stage, the microhardness of adhesives continued to decrease as water was absorbed into the adhesives. In the cases of adhesives A, B, and D, regardless of the test solutions used, the percentage of microhardness continued to decrease as these adhesives were saturated with absorbed water. It can be seen that the attack of NaCl solutions against the adhesives was more severe than the attack of the distilled water. In the case of adhesive A (Fig. 7), as

tensile residual stresses are produced in the adhesive by the great difference in thermal expansion coefficients between epoxy resins and fillers [16].

No adhesive delamination was found in the adhesive-bonded specimens that were immersed in deaerated test solutions during the 6 weeks. The microhardness values of the adhesives immersed in two different states (aerated and deaerated) were very close to each other. These results show that the presence of oxygen in test solutions plays a principal role in adhesive delamination, but has no effects on the change in the microhardness of the adhesives. It is believed that delamination of the adhesive-bonded specimens is primarily governed by the metal dissolution (anodic reaction) and the oxygen reduction (cathodic reaction) that occur at the adhesive/metal interface when the metal substrate is in contact with the absorbed water or electrolyte. The hydroxide ions produced by the oxygen reduction increases the pH value of the solution underneath the adhesive. When the pH value of the solution underneath the adhesive is high enough to break the adhesive/metal bonding, adhesive delamination occurs. These proposed events are in agreement with the mechanisms of organic-coating delamination given by Ritter and Kruger [17], Leidheiser [18, 19], Leidheiser and Kendig [20], Kendig et al. [21] and Scully [22].

5. Conclusions

1. Microhardness of adhesives is governed by the composition and nature of fillers incorporated in the adhesive matrix. Rank of the adhesives in the average microhardness in dry state is

$$A > B > D > C$$
(hardest)   (Softest)

2. Soft and elastic adhesives, namely C and D, are more susceptible to adhesive swelling and microdamage than the hard and brittle adhesives A and B upon exposure to corrosive solutions. Rank of the adhesives in the average percentage of microhardness decrease upon exposure to test solutions is

$$D > C > A > B$$
(highest)   (lowest)

3. No correlation exists between the rank of the percentage of hardness decrease and the rank of the percentage of water uptake of the adhesives tested.

4. In the presence of NaCl, less water from the bulk NaCl solution is absorbed to obtain the same degree of microhardness decrease of the adhesives compared to the amount of water absorbed from distilled water.

5. The degree of adhesive degradation increases with the concentration of the NaCl solution.

6. Adhesive delamination was observed only when the adhesive-bonded specimens were immersed in solutions in the presence of oxygen.

7. Upon exposure to a test solution, a higher degree of delamination was found on specimens bonded by the soft and elastic adhesives, namely, adhesives C and D.

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