

Research Article

Effect of High Temperature Sodium Hydroxide Immersion on Fusion Bond Epoxy Coating

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Fusion Bond Epoxy (FBE) coating system was exposed to 5% sodium hydroxide at elevated temperature for 30 days. The result of exposure showed formation of adhere deposit layer, a discolored zone underneath and remaining un-affected bulk of the coating. The deterioration of the coating was characterized using analytical techniques like scanning electron microscopy (SEM), energy-dispersive X-ray (EDAX) spectroscopy, attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), differential scanning calorimetry (DSC), pull-off adhesion, and electrochemical impedance spectroscopy (EIS). Results obtained indicated chemical deterioration of the coating in the discolored zone and leaching of low molecular weight coating component forming deposit layer. Although the adhesion strength and barrier property were not affected, the polymer matrix in the affected zone undergoes severe changes in its surface microstructure, primary chemical structure, and glass transition temperature. This may inflict serious impairment of the coating functional properties and premature failure of the coating in long term exposure.

1. Introduction

Polymeric coating employed on a steel surface is one of the most effective way to combat corrosion. FBE coating in particular is well appreciated as an anticorrosive coating system in coating industry [1]. With the continuous changes in new exposure conditions involving high operating temperatures, the demand for FBE coating that can resist the hostile environments like corrosive chemicals and reagents is growing. It is well known that coatings are susceptible to chemical degradation especially in immersion condition at the elevated temperature. Chemical degradation of the coating in service may affect both the barrier property and mechanical strength of the coating material. The degradation of polymer materials can be classified as physical degradation (e.g., swelling), chemical degradation (e.g., hydrolysis and oxidation), or both [2]. Depending upon the type of degradation a possible failure mechanism can be evaluated. Therefore, knowledge of degradation mechanism of these coating systems in harsh chemical environment is the immediate need of time, in order to predict their life expectancy and to improve the design techniques of industrial equipment and their components.

Many studies have been carried out on the degradation of FBE coating immersed in different media. For instance, electrochemical impedance spectroscopy study of the FBE coating immersed in 1.5 mol/L NaCl showed severe degradation of the coating [3]. In another study, EIS was used to monitor the degradations of a series of carbon black loading in FBE coatings which were exposed to a 3% NaCl solution at room temperature. The result indicated that the protective performance of the FBE coating was significantly improved when the carbon black loading exceeded the threshold concentration [4]. Study on FBE coated rebars exposed to 3.5% NaCl, chloride-contaminated simulated concrete pore solution, and solid-cast concrete mortars showed that the coating was more prone to the absorption of moisture and chloride in contact with alkaline solution but was very resistant to their diffusion in neutral solution [5]. Similarly, FBE coated rebars when exposed to simulated marine environment did not provide total protection to the steel reinforcement in cracked concrete [6]. A case study on the field performance of FBE mainline and field joint coatings applied on X100 steel for the transportation of high pressure gas under wet ground conditions revealed that the water soak and cathodic disbondment

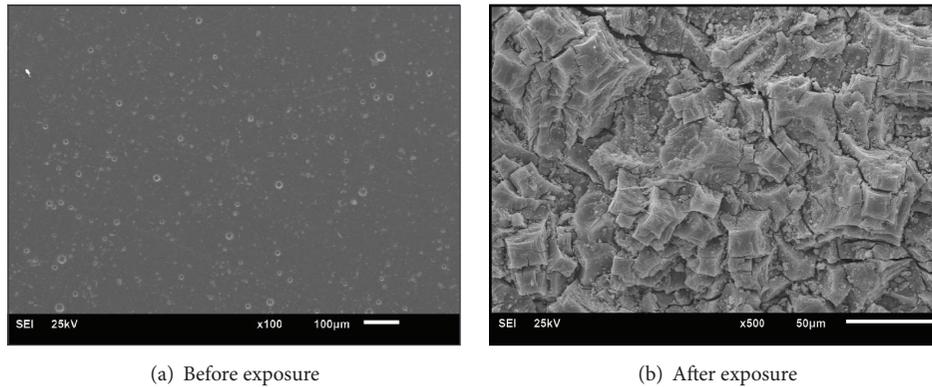


FIGURE 1: SEM surface morphology of Fusion Bond Epoxy coating: (a) before and (b) after exposure to 5% NaOH solution for 30 days at 93°C/200°F.

resistance of the field joint coatings were far inferior to those of the mainline coating [7]. When exposed to NaCl solution at 60°C under flowing and static immersion conditions, the results showed that flowing condition aggravated the deterioration of the FBE coatings [8]. Likewise in another study the corrosion-erosion behavior of some FBE coatings under simulated water transmission line conditions showed leaching of coatings under the test conditions [9]. Study on erosion resistance of FBE powder coating in emery sand slurry containing 1 wt.% NaCl using modified rotating disk rig concluded that the coating was suitable for the relative mild conditions of liquid-particle two-phase flow such as low flow velocity and small particles [10]. FBE coating on immersion in saturated calcium hydroxide aqueous solution (pH = 12.5) containing 0.6 moles/liter NaCl maintained at either 35°C or 50°C showed loss of adhesion and corrosion induced delamination [11, 12]. Also, use of FBE coatings above their T_g resulted in more water uptake and low barrier property [13]. All these studies were conducted on FBE coating under the experimental conditions similar to the industrial operation conditions; the material may experience during the actual service.

This study is an attempt to understand the effect of hot sodium hydroxide (NaOH) solution on the performance of FBE coating system. The study focuses on the changes in its microstructure, glass transition temperature, surface morphology, adhesion strength, barrier properties, type of deposit layer formed, and extent of deterioration within coating. The data generated will help in understanding the degradation mechanism and life expectancy of the coating in hot alkaline environment.

2. Experimental Procedure

2.1. Materials and Methods. In this study, Fusion Bond Epoxy (FBE) coated carbon steel samples (4" × 4") were exposed to 5% NaOH solution using attached cell method. A double jacketed glass cell was centered and attached to the coated samples using heat resistant sealant. The cell was filled with 5% NaOH (400 mL) and secured on a thermostatically controlled hot plate with a steel tray containing sand and maintained at 140°C/284°F (substrate temperature) for 30

days. The solution temperature recorded was 93°C/200°F (electrolyte temperature). The cell was fitted with condenser to prevent evaporation of the test medium.

After exposure, the coating system was characterized for the morphological changes and extent of coating deterioration using analytical techniques like scanning electron microscopy (SEM). Presence of heterogeneities was mapped using energy-dispersive X-ray (EDAX) spectroscopy. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) and differential scanning calorimetry (DSC) were used to determine the changes in chemical structure and glass transition temperature before and after exposure, respectively. Changes in adhesion strength of the coating were determined by pull-off adhesion strength method (ASTM D4541-09e1) and corrosion resistance property of the coating was investigated by electrochemical impedance spectroscopy.

3. Results and Discussion

3.1. SEM/EDAX Analysis. Figure 1 shows the SEM micrographs of FBE coated sample before and after 30 days of exposure to 5% NaOH solution at 93°C. Before exposure, the coating was uniform and consists of surface micropores that might have resulted from coating application (Figure 1(a)). After chemical exposure a marked change in morphology of the exposed sample was observed (Figure 1(b)). The distinctive crystalline features evident on the surface were attributed to the low molecular weight salt deposits and pigments/fillers, indicating coating degradation. The deposit layer formed was dense and well adhered but contains a network of interconnected microcracks. This indicates that the deposit layer was not protective against electrolyte diffusion and instead retards the diffusion of the electrolyte through the coating.

To determine the extent of coating degradation along the coating front, a cross section analysis of before exposure and exposed coating was carried out as shown in Figure 2. Comparison of cross section analysis of the before exposure coating with the exposed coating showed extent of coating degradation and unaffected coating zone. Cross section analysis of the exposed coating revealed that the coating thickness has changed from initial average thickness

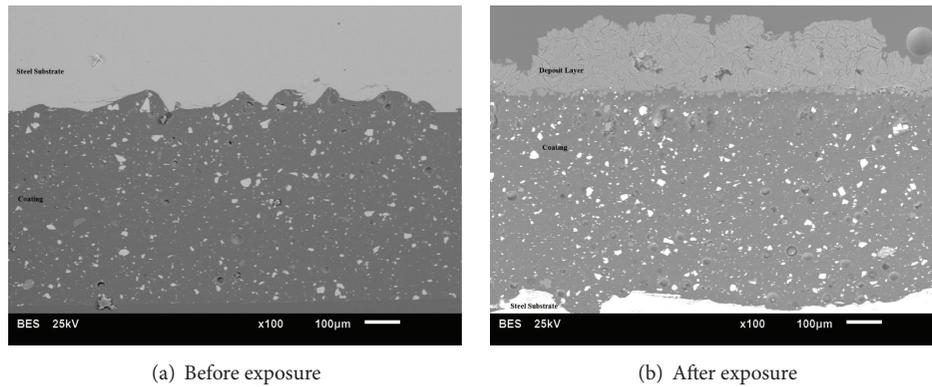


FIGURE 2: SEM cross section analysis of Fusion Bond Epoxy coating: (a) before and (b) after exposure to 5% NaOH solution for 30 days at 93°C/200°F.

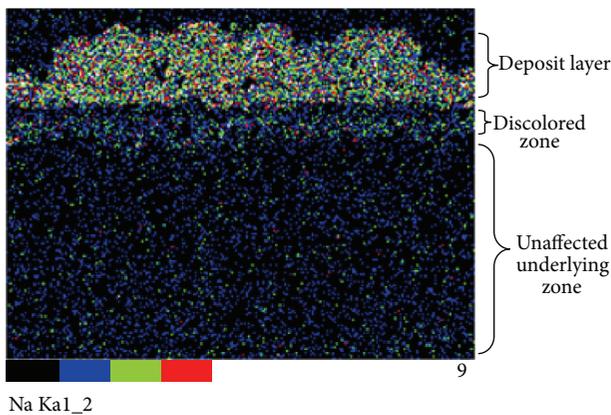


FIGURE 3: EDAX (Na element mapping) analysis of Fusion bond Epoxy coating exposed to 5% NaOH solution for 30 days at 93°C/200°F.

of 23.0 mils to 30.0 mils due to formation of adhering deposit on the surface, indicating chemical degradation of the coating [2]. The thickness of deposit was about 3.0–4.0 mils, that of discolored zone was 4.0–5.0 mils, and the unaffected zone was 18.0–22.0 mils as determined by SEM. Interaction of alkali with coating was investigated by mapping the distribution of sodium (Na) element from the solution into the coating as shown in Figure 3. Elemental mapping of the exposed coating showed variation in the distribution of Na element at the degraded area and unaffected zone. A high concentration of Na element from the solution was detected in a deposit layer and a uniform distribution in a discolored zone was observed. The unaffected zone detected relatively low distribution of Na element.

SEM/EDAX analysis showing a formation of adhering deposit layer and a uniform discolored zone underneath is evidence of diffusion of electrolyte through the coating and the degradation of the FBE. It indicates that the coating exposed to hot caustic environment degrade forming a deposit layer as a result of hydrolysis reaction of polymers and leaching of pigments [2, 14–16]. This type of chemical degradation phenomenon is supported by ATR-FTIR analysis.

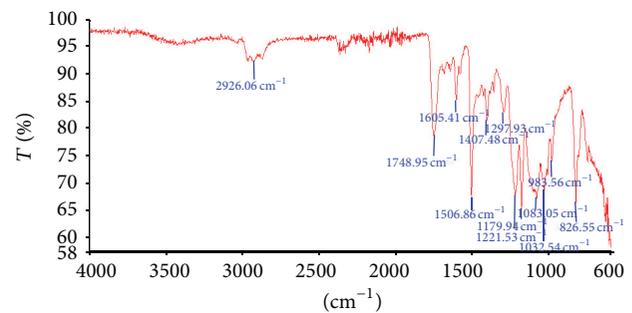


FIGURE 4: ATR-FTIR spectrum of the coating system before exposure.

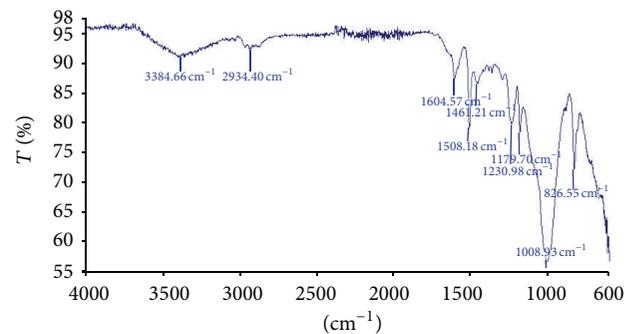


FIGURE 5: ATR-FTIR spectrum of the discolored zone of the coating system after exposure.

3.2. ATR-FTIR Analysis. Figures 4–6 show the ATR-FTIR spectrum of the FBE coating system, before exposure, discolored zone, and underlying unaffected zone. Before exposure, the ATR-FTIR spectrum of the FBE coating system showed strong narrow peak at 827 cm⁻¹ was attributed to C-H absorption of para-disubstituted benzene rings. The medium strong and broad absorption bands in the range of 1033–1083 cm⁻¹ were assigned to the stretch vibrations of the aliphatic functional groups C-O. Absorptions observed at 1181 cm⁻¹ and 1221 cm⁻¹ were caused by the stretching vibration of aromatic ether C-O, in-plane deformation of C-O of

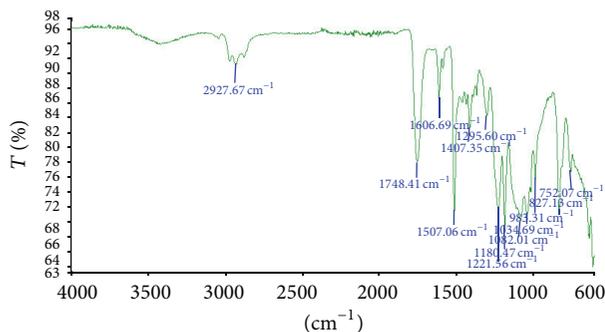


FIGURE 6: ATR-FTIR spectrum of the underlying layer of the unaffected zone.

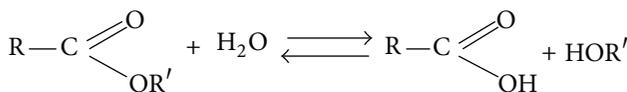


FIGURE 7

phenolic groups and at 1507 cm^{-1} and 1605 cm^{-1} by C=C of benzene rings. The strong absorption at 1749 cm^{-1} was due to carbonyl C=O stretching vibration.

After exposure to sodium hydroxide solution several distinctive changes were observed as indicated by appearance of a new peak at 3385 cm^{-1} associated with hydroxy group (-OH) indicating diffusion of electrolyte through the coating [17]. Also, the peak at 1749 cm^{-1} completely disappears and the peak at 1508 cm^{-1} decreases and at 1460 cm^{-1} increases in intensity. Similar changes in the chemical structure of epoxy resin cured with acid anhydride type curing agent after immersion in NaOH solution at high temperature are reported by Hojo et al. [2, 18]. According to the study, these changes are due to the hydrolysis of the ester groups and the subsequent leaching of the low molecular mass in the caustic environment. The hydrolysis of epoxy coating under chemical attack by alkali results into scission of polymeric chain. The hydrolytic reaction by alkali is expressed as follows [15, 19].

The carboxyl group results from the hydrolysis of the ester linkages as shown in Figure 7 and can further react with NaOH to yield carboxylate anion as shown in Figure 8.

No appreciable changes in ATR-FTIR characteristic of underlying un-affected zone were observed, except for increase in the intensity of peak at 1456 cm^{-1} , when compared with the spectra of the coating before exposure. However, no sign of hydrolysis or formation of carboxylate salt (Figure 8) was observed, as evident by absence of Na element evaluated by EDAX analysis.

3.3. DSC Analysis. Figure 9 shows the DSC scans of the FBE coating system, before exposure, discolored zone, and underlying unaffected zone. The glass transition temperature (T_g) of the coating before exposure was 157°C (Figure 9(a)). After exposure, T_g of the discolored zone decreased substantially to 129°C (Figure 9(b)), indicating that at high temperature

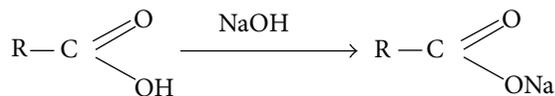


FIGURE 8

exposure the chemically influencing media modified the property of the polymer irreversibly [20]. The reason for this distinct change in the T_g is attributed to hydrolysis and subsequent leaching of low molecular weight hydrolyzed fragments [21].

T_g of underlying unaffected zone of the coating after the immersion test referred to as a “wet T_g ” was about 141°C (Figure 9(c)), a relatively small change when compared with T_g of 157°C for the untested one. This reduction in T_g of 16°C of underlying unaffected zone was due to absorption of water molecule in a polymer matrix as a result of capillary uptake by existing pores in the coating system [21, 22]. This observation was supported by similar change in T_g value of 141°C after saturation of the FBE coating in distilled water for 30 days at $93^\circ\text{C}/200^\circ\text{F}$ as shown in Figure 10.

3.4. Pull-Off Adhesion Strength. Figure 11 shows the average pull-off adhesion strength of the FBE coating before and after exposure to 5% NaOH for 30 days at $93^\circ\text{C}/200^\circ\text{F}$ determined on triplicate samples. Before exposure, the coating showed the adhesion strength of 23.8 MPa and did not fracture within itself or disbond from the substrate indicating that the coating possesses good adhesion strength. After exposure, the pull-off adhesion strength of the coating without removal of the deposit layer was 10.8 MPa and fractured cohesively within the deposit layer. The pull-off adhesion strength after removal of the deposit layer was 17.8 MPa and did not fracture within itself or from the substrate. The result indicated that the bulk adhesion strength of the coating was not affected after exposure to the alkaline environment [23].

3.5. Electrochemical Impedance Spectroscopy (EIS). Figure 12 shows the Bode plot of the coating before and after exposure to 5% NaOH for 30 days at $93^\circ\text{C}/200^\circ\text{F}$, determined using EIS. The high frequency region of the Bode plot provides information about coating characteristics; the low frequency region provides information about processes occurring near the metal surfaces. Generally, the coatings with resistance over $10^8\ \Omega\text{cm}^2$ provide good corrosion protection, while those with resistance under $10^6\ \Omega\text{cm}^2$ provide poor corrosion protection [24, 25]. Analysis of the low frequency region at 0.1 Hz of the Bode plot indicates that the coating system has effective barrier properties. Initially before exposure, the Bode plot of the coating shows a straight line of slope -1 with high impedance value of $1.21 \times 10^{11}\ \text{ohm}\cdot\text{cm}^2$ at low frequency, indicating that the coating system behaved like a pure capacitor. After 30 days of exposure to NaOH solution, the coating maintained high impedance characteristics and showed the impedance value of $1.49 \times 10^{10}\ \text{ohm}\cdot\text{cm}^2$, indicating retention of the barrier property. The high impedance

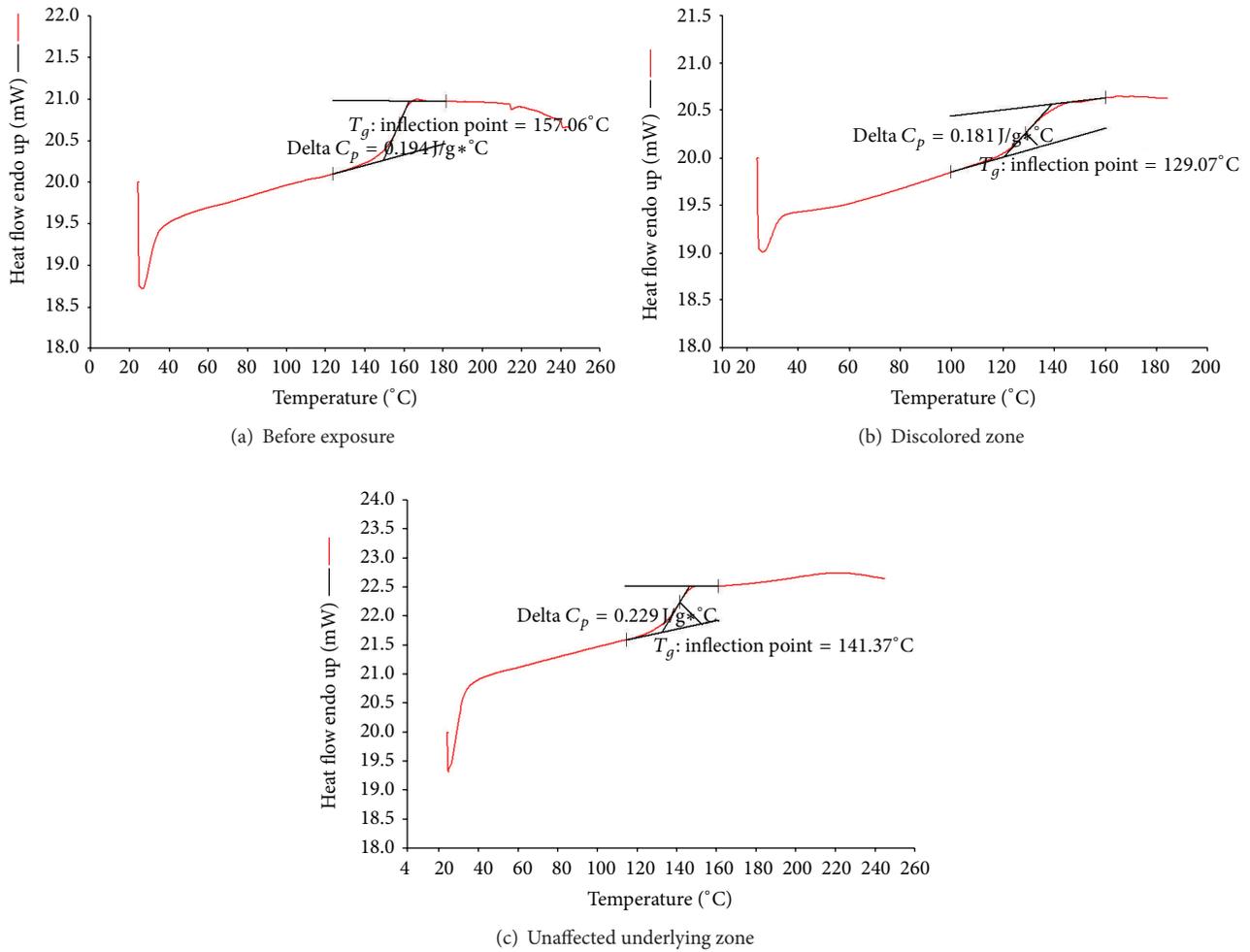


FIGURE 9: DSC scans of FBE coating system: (a) before exposure and after exposure to 5% NaOH solution for 30 days at 93°C/200°F (b) discolored zone, and (c) unaffected underlying zone.

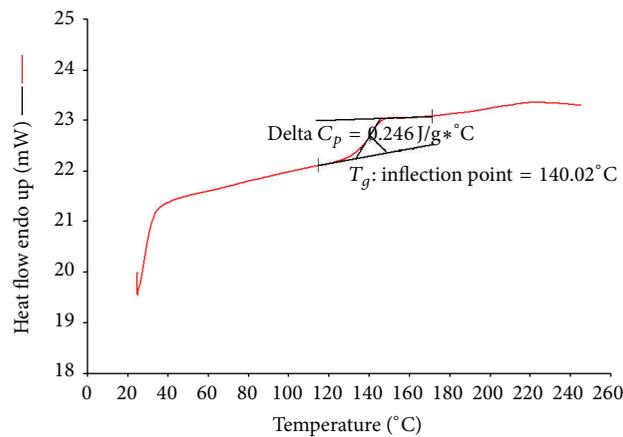


FIGURE 10: DSC scan of FBE coating system after immersion in distilled water for 30 days at 93°C/200°F.

value of the coating on exposure to 5% NaOH solution at high temperature may be attributed to the formation of the deposit layer that retards the diffusion of electrolyte through the coating.

4. Conclusions

FBE coating system exposed to 5% NaOH solution at elevated temperature for 30 days showed formation of adhering

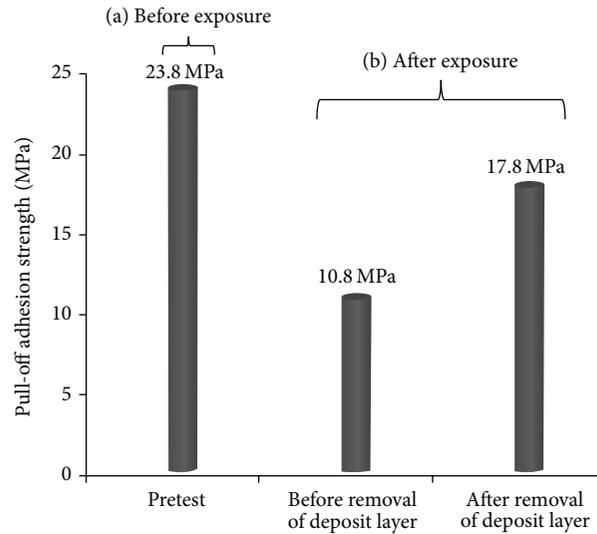


FIGURE 11: Pull-off adhesion strength of Fusion Bond Epoxy coating: (a) before and (b) after exposure to 5% NaOH solution for 30 days at 93°C/200°F.

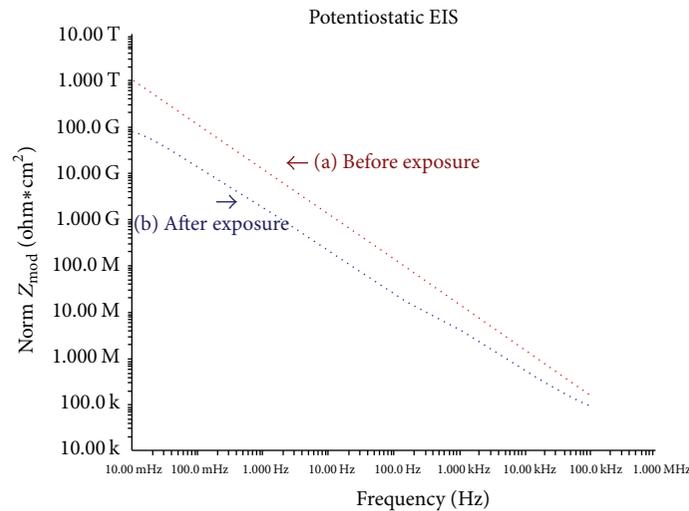


FIGURE 12: EIS Bode magnitude plots of the Fusion Bond Epoxy coating: (a) before and (b) after exposure to 5% NaOH solution for 30 days at 93°C/200°F.

deposit layer and chemical degradation of the coating. It was observed that the deposit layer formed was dense and comprises the low molecular weight hydrolyzed fragments as a result of leaching of pigments/filler components of the coating. The deposit layer was not protective and retards the diffusion of electrolyte along the coating front forming a discolored zone underneath and remaining unaffected bulk of the coating. The degradation of the coating in the discolored zone resulted in irreversible changes in chemical structure and significant decrease in glass transition temperature (T_g), while the unaffected zone showed no significant changes in its characteristics properties. The bulk adhesion strength and barrier property of the coating were not affected. However, exposure of the coating system for longer duration can provide further information about the rate of degradation that is extent of coating thickness forming discolored zone

along the coating front as a function of immersion time, from which life expectancy of the coating can be predicted.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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