

Study on Degradation Behavior of a Modified Polyethylene (sPE)-Lined Blasted Steel Substrate Exposed to Hydrochloric Acid Solution Environment

C. Van Dinh,^{†*} M. Kubouchi,^{*} K. Tsuda,^{*} T. Sakai,^{*} and R. Kobayashi^{**}

ABSTRACT

Polyethylene is well known as a good chemical-resistant material and is widely utilized in practice. In lining applications, some types of modified polyethylene are developed and used as a lining for the purpose of substrate protection from corrosive environments. In this paper, the degradation behavior of a new modified polyethylene (sPE) lined on a steel substrate exposed to hydrochloric acid (HCl) solution environment was investigated. Diffusion behavior of the HCl solution, adhesion strength, and blister formation with time dependence were considered as key parameters of the degradation behavior. Influences of elevated temperature (80°C to 15°C and 40°C to 15°C, corresponding to the inner and outer sides of the lining system) and the concentrations of the HCl solution (0, 5, 10, 15, and 20% in mass) on the key parameters were studied. Diffusion of the solutions into the polymer was strongly affected by its concentration and temperature. Chloride element was found in the interface of the polymer and substrate by the use of energy-dispersive x-ray spectrometry (EDS). No blister was observed after 2,800 h exposure time. The adhesion strength data obtained from the peeling test showed the significant influences of temperature elevation and concentration of HCl solution on delamination.

KEY WORDS: adhesion strength, diffusion, polyethylene lining

INTRODUCTION

Polyethylene is well known as a good material for steel corrosion protection from corrosive environments because of its properties such as excellent mechanical properties, good barrier against moisture and water, chemical and biological resistance, electrical insulation, convenient processability, and low cost.¹ However, due to its nonpolar characteristic, polyethylene used for lining needs a modification to enhance its adhesion ability on the steel substrate. This modification may affect the bulk properties of the polymer, resulting in a change on the service life of the lining system.²

When exposed to corrosive environments, the lining service life depends upon the permeation/diffusion behavior of the environments into the polymer lining. Chemical degradation of the lining layer, delamination, blister formation, and corrosion of substrate are phenomena related to the diffusion process. The environment penetration into a polymer depends on the polymer characteristics such as density and the order of pore, defects or contamination, and the polymer-environment affinity.³⁻⁶ In the studies of molecular transport of liquids into a polymer membrane, diffusion has been classified as Case 1 (Fickian type), Case 2 (relaxation-controlled), and non-Fickian (anomalous).⁷⁻¹¹ Penetrant molecules diffuse into the membrane until the concentration is equal over the whole of the membrane (saturation state). When Fickian diffusion is assumed, the time-dependent relative concentration of the liquids into the polymer membrane can be expressed by the following equation:¹²

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[†] Corresponding author. E-mail: chau@chemeng.titech.ac.jp.

^{*} Department of Chemical Engineering, Graduate School of Science and Engineering, Tokyo Institute of Technology, Japan.

^{**} Technical Division, Dai-ichi High Frequency Co., Ltd., 1-6-2, Nihonbashibakuro-cho, Chuo-ku, Tokyo, Japan.

$$1 - \frac{C_{(t,x)}}{C_{\infty}} = \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \exp\left[-\frac{D(2m+1)^2 \pi^2 t}{l^2}\right] \sin\left[\frac{(2m+1)\pi x}{h}\right] \quad (1)$$

in which $C_{(t,x)}$ and C_{∞} are the concentrations of the liquid inside the membrane at time t , position x , and saturate state; D is diffusivity, which depends on the nature of liquid-polymer interactions; and h is the thickness of the membrane.

In the initial stage, the diffusion coefficient, D , of the polymer-solvent systems has been calculated by:¹³

$$\frac{M_t}{M_{\infty}} = \frac{4}{h} \left(\frac{Dt}{\pi}\right)^{0.5} \quad (2)$$

where M_t and M_{∞} are the mass uptake at time t and saturation state, respectively. The diffusivity can be calculated from the initial slope of the curve generated from Equation (2).

Occurrence of penetration of the corrosive environment into the polymer lining layer may result in a degradation and, therefore, may affect the environment diffusion resistance of the polymer. Once the corrosive environment reaches the interface between the polymer and metal substrate, corrosion (anodic reaction) may take place. The disbondment or delamination that occurs at surrounding anodic reaction sites is caused by a cathodic process and is known as cathodic disbondment.

In this paper, the degradation behavior of a modified polyethylene (sPE)-blasted steel substrate system exposed to hydrochloric acid (HCl) solution environment was studied and discussed to evaluate the polymer applicability for lining purposes.

EXPERIMENTAL PROCEDURES

Materials

Specimens for Immersion Experiment — The modified polyethylene (sPE) sheet samples with an average of 1 mm in thickness, made of linear-low-density polyethylene (LLDPE), and having a density of 0.925 g/cm³ to 0.930 g/cm³ were prepared by the compression molding method. Before being used for the immersion experiments, these specimens were dried at 50°C for 72 h to ensure any remaining moisture was removed.

Specimens for Lining Panel Exposure — Blasted steel panels having a dimension of 85 mm by 85 mm by 5 mm were prepared with the hot powder spray method. The average thickness of the sPE lining layer was 2 mm.

Experiments

Immersion Test — This experiment was conducted to study the diffusion behavior of the environment into the polymer. Rectangular sPE sheet specimens

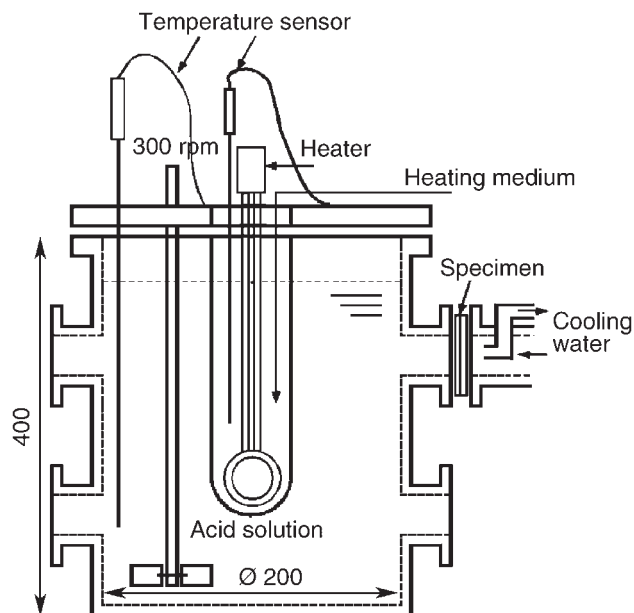


FIGURE 1. Schematic of the lining test apparatus.

having the length of 60 mm and breadth of 25 mm cut from the given sheet were used for studying the diffusion behavior of environments into the polymers. These specimens were immersed in water and 5, 10, 20 mass% of HCl solutions were contained in stopper glass bottles that were connected to a condensing system. The corrosive environmental temperature was set constant at 40, 60, and 80°C.

Lining Test — This test was conducted to measure changes in the adhesion strength of the sPE lining specimens when they were exposed to the corrosive environment. The lining side of panel specimens was exposed to water and 5, 10, 15, 20 mass% of HCl solutions contained in a vessel cell at one open end. This solution was stirred and kept constant at 40°C and 80°C. The metal side of the panel specimens was in contact with cycling cooling water whose temperature was set constant at 15°C (Figure 1).

Measurement Methods

Environmental Uptake — At regular time intervals, the specimens were taken out, wiped with filter paper to remove any attached solution on their surfaces and weighed by using a balance with a 0.1-mg resolution. Solution uptake was measured relative to initial mass.

Adhesion Test — Cathodic disbondment and adhesion loss due to exposure were measured using a 180° peeling test under wet conditions. The data were recorded and converted into N/mm. All adhesion tests were conducted at room temperature and at a peeling rate of 50 mm per minute.

Energy-Dispersive Spectroscopy (EDS) Analysis — The chloride (Cl) element in the interface of the lining and substrate was monitored using scanning electron microscopy (SEM) combined with x-ray analysis.

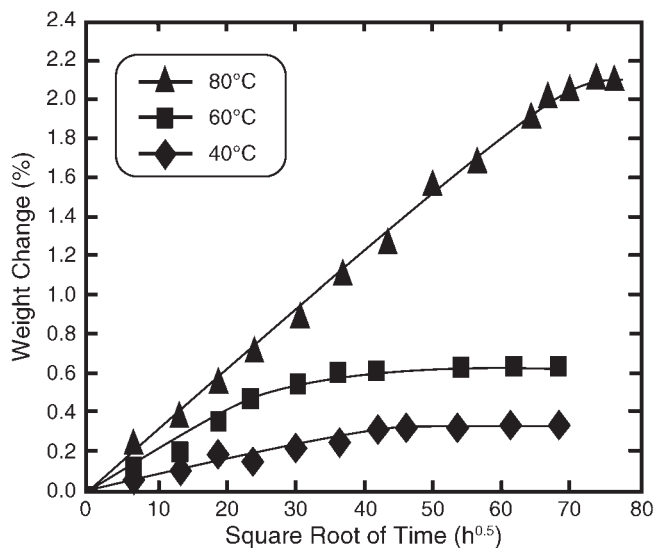


FIGURE 2. Diffusion behavior in water.

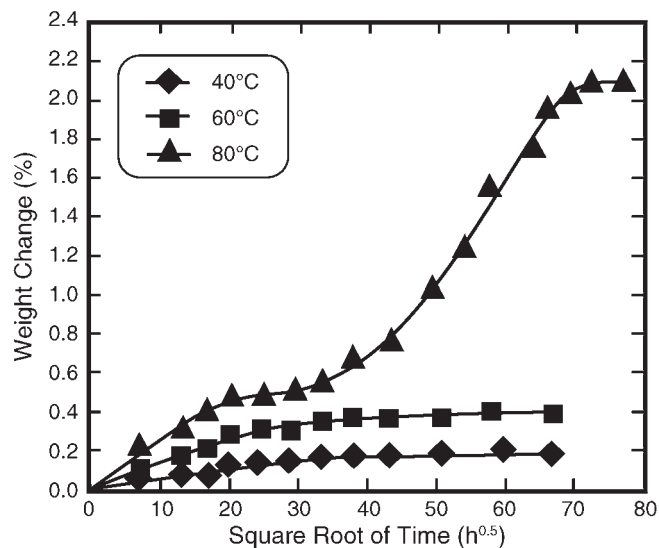


FIGURE 3. Diffusion behavior in 5% HCl solution.

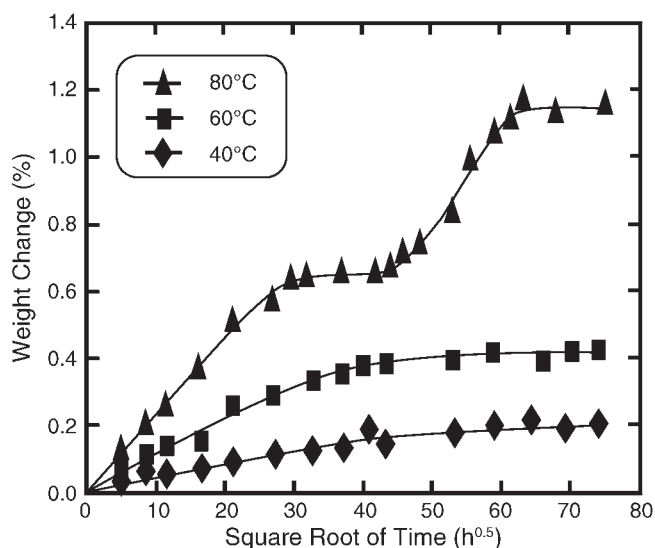


FIGURE 4. Diffusion behavior in 10% HCl solution.

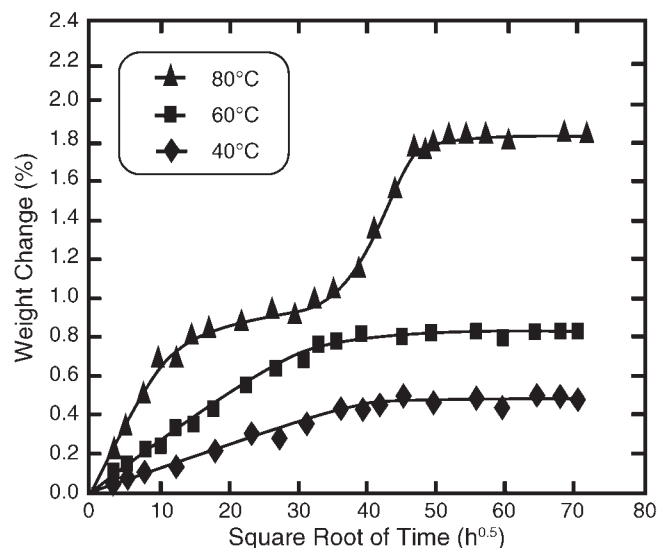


FIGURE 5. Diffusion behavior in 20% HCl solution.

RESULTS AND DISCUSSION

Diffusion Behavior

The mass uptake of the sPE samples immersed in water and HCl solutions are shown in Figures 2 through 5. It can be seen that the uptake amount increased with increasing temperature, indicating the entry of more environmental molecules into the free volume spaces of the matrix polymer. However, as shown in the figures, the mode of diffusion is distinguished by the temperature and nature of the environment. For instance, the Fickian mode (Case 1) was observed for the cases of the HCl solution, at 40°C and 60°C, and the water environment. The two-stage diffusion occurred for the case of HCl solution at

80°C, due to the interaction of the chemical degradation and thermal relaxation effects.¹⁴

The uptake is also influenced by the concentration of the exposed environment. As shown in these figures, the rate and equilibrium of the uptakes are fastest and highest for the samples exposed to 20 mass% HCl solution, then to water, 5 mass% HCl, and slowest and lowest in 10 mass% HCl solution. The diffusivities calculated by Equation (2) are shown in Table 1. These may be attributed to the influence of the nature of the environments to the bulk properties of the samples during immersion.

Analysis of EDS data shows that the Cl element transported through possible micropores that act as channels for conducting the corrosive element from

TABLE 1
Meant Diffusion Coefficients (D , 10^{-14} m^2/s)

Environment	40°C	60°C	80°C	
Water	2.69	5.32	1.052	
5 mass% HCl	4.72	5.33	1st stage, 9.47	2nd stage, slope = $4.63 \times 10^{-4} s^{-0.5}$
10 mass% HCl	1.87	2.82	1st stage, 8.07	2nd stage, slope = $8.33 \times 10^{-4} s^{-0.5}$
20 mass% HCl	2.37	3.78	1st stage, 21.30	2nd stage, slope = $11.90 \times 10^{-4} s^{-0.5}$

environments into the polymer. Cl elements penetrated easily into these regions, and diffused then to adjacent regions by a molecular diffusion mechanism.¹⁴

Adhesion Strength Loss

Wet adhesion strength results for the lining samples are shown in Figures 6 and 7. It can be seen that the adhesion strength decreases with increasing exposure time. The results show significant influences of the elevated temperature and the nature of the environmental solution on the adhesion loss.

For instance, under the 40°C to 15°C condition, the adhesion strength reduces early for the samples exposed to water, then to 5 mass%, then to 10 mass% HCl solution, and slowest when exposed to 15 mass% HCl solution (Figure 6). However, the rate of adhesion loss is highest for the samples exposed to 20 mass% HCl solution, lower for 15, then 10, and then to 5 mass%, and lowest for those exposed to water. For the samples conducted under the 80°C to 15°C condition, the adhesion strength reduced quickly at high HCl concentrations. The rate of adhesion loss is highest at 15 mass% HCl solution, lower for 10 mass% and 5 mass% HCl solutions, and lowest for water (Figure 7). An explanation for this adhesion loss tendency would be the effect of HCl concentration on the rate of environmental diffusion process into the lining layer, as shown in Table 1. This proves that the Cl element concentration plays an important role in the adhesion loss of these samples.

By comparing the results obtained from the two temperature conditions, it can be seen that the temperature elevation significantly influences the adhesion loss. The adhesion loss starts within 24 h of exposure for all samples under 80°C to 15°C, while the earliest for the samples under 40°C to 15°C is after about 144 h of water exposure. The influence of the elevated temperature may be considered in two aspects: (1) the rate of the environmental diffusion and (2) the rate of corrosive reaction taking place within the lining/metal substrate interface. It can also be noticed that no blister can be observed for all samples.

Mechanism of Adhesion Loss

As mentioned above, the diffusion of the environments into the polymers obey a logarithmic of time expression. The penetrant reached and accumulated in the interface is attributed to be the critical factor

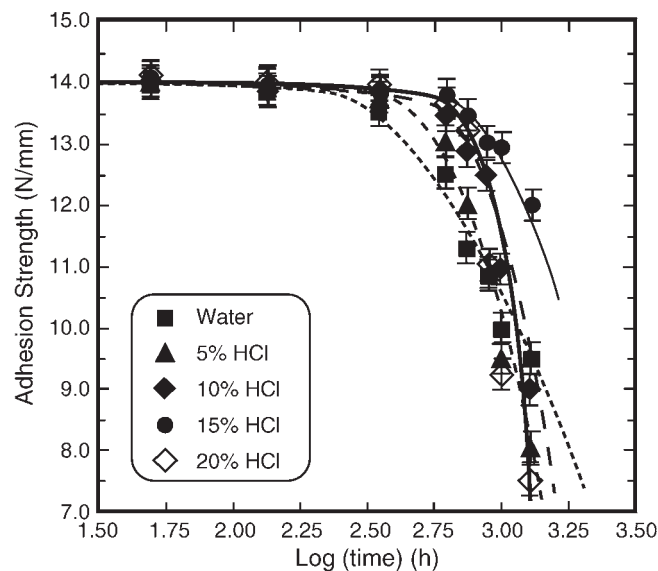


FIGURE 6. Adhesion strength under the 40°C to 15°C condition.

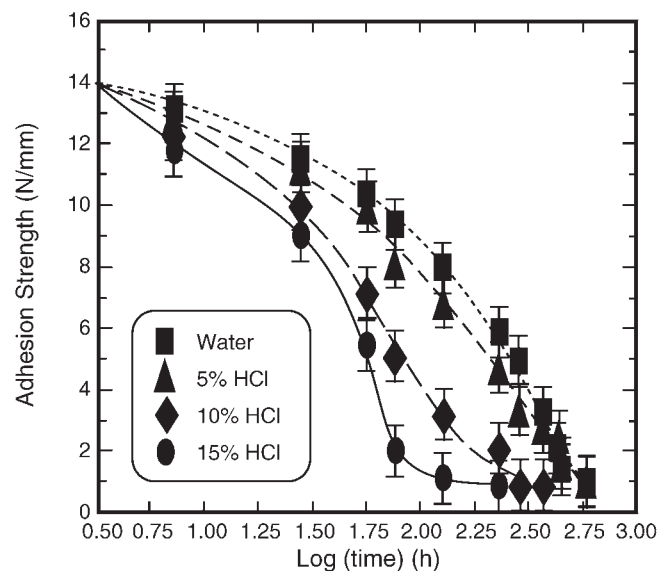


FIGURE 7. Adhesion strength under the 80°C to 15°C condition.

that reduces the adhesion of the lining layer on the substrate.¹⁵ In this study, Cl element accumulation in the interface was obtained from the EDS analysis of the experienced time specimens. Pieces of the peeled-off lining obtained after the peeling test were used to monitor the Cl and Fe elements at the interface. A

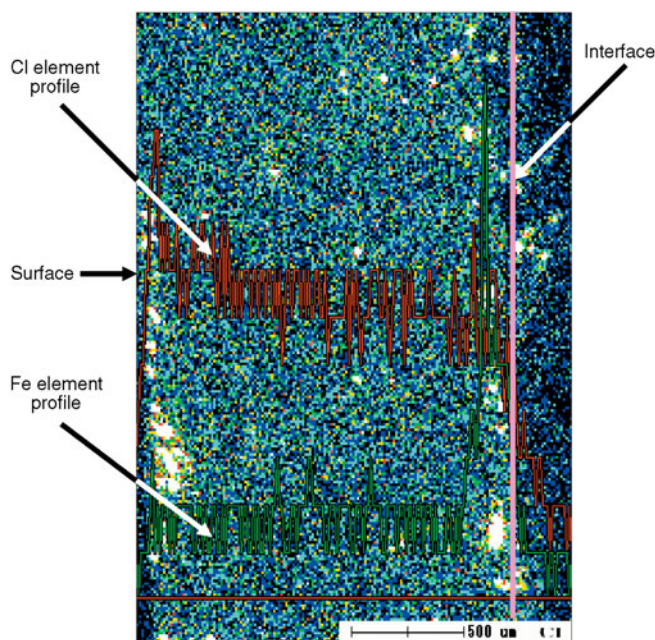
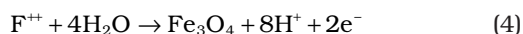
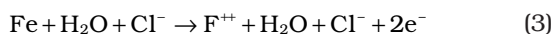


FIGURE 8. EDS image of Cl element inside the lining layer exposed to 5 mass% HCl solution after 2,000 h.

result of the EDS analysis is shown in Figure 8. As discussed regarding diffusion behavior, water and Cl elements diffuse into the lining polymer through the conductive pathways, which generated from polymer processing (contamination, nonuniformity of temperature, etc.) and during the exposure. The penetrant reached the interface at the particular points at which anodic reaction took place [Reactions [3] through [5]]. The products from the anodic reactions may be related to the blister formation caused by an osmotic pressure mechanism.¹⁶ Along with the establishment of these anodic sites, the cathodic regions are also established. They surround the anodic sites and then spread along the lining/metal interface. Another reason for the loss of adhesion is the presence of a water layer at the lining/iron oxide interface. At that water layer, which had stronger affinity to the polar, a high-energy iron oxide surface (40 kJ/mol to 60 kJ/mol) replaced the weaker secondary polymer/iron oxide bonds (<25 kJ/mol), thus causing the delamination.¹⁷⁻¹⁸



CONCLUSIONS

❖ The sPE sheet and sPE-lined blasted steel substrate were used to investigate its applicability in lining applications. Immersion tests for neat sPE showed that the diffusion behavior of water and 5, 10, and 20 mass% HCl solutions into the polymer is significantly influenced by the temperature and nature of the environments. Non-Fickian mode diffusion behavior can be observed at 80°C while Fickian mode diffusion behavior was observed at 40°C and 60°C. Diffusivity for these behaviors can also be calculated to predict the relationship between the diffusion process and the adhesion loss for the lining. Adhesion loss depends strongly on exposure time and elevated temperature. Under the 40°C to 15°C condition, the adhesion strength reduces more slowly than those under the 80°C to 15°C condition. The influence of the nature of the solution environment on adhesion loss behavior can also be observed. Chloride element monitored in the interface of the lining and the substrate is considered a factor that reduces the adhesion strength. Mechanisms for adhesion loss can explain these behaviors.

REFERENCES

1. B. Bar-on, H. Shigemoto, M. Matsumoto, W. Hinterbauer, "The Japanese Experience and a European Challenge Two-Layer Polyethylene Coating System for Steel Pipes," Proc. 12th Int. Conf. Pipeline Protection, held Nov. 4-6 (Paris, France: BR Group, 1997), p. 69.
2. N. Villareal, J.M. Covas, R. Perera, C. Rosales, J.C. Merino, *Macromol. Chem. Phys.* 203 (2002): p. 238.
3. T.C. Wong, L.J. Broutman, *Polym. Eng. Sci.* 25 (1995): p. 521.
4. Y. Diamant, G. Marom, L.J. Broutman, *J. Appl. Polym. Sci.* 26 (1981): p. 3,015.
5. M.J. Adamson, *J. Mater. Sci.* 15 (1980): p. 1,736.
6. P. Moy, F.E. Karasz, *Polym. Eng. Sci.* 20 (1980): p. 315.
7. N.L. Thomas, A.H. Windle, *Polymer* 21 (1980): p. 613.
8. H.L. Frisc, *Polym. Eng. Sci.* 20 (1980): p. 20.
9. A. Peterlin, *Polym. Eng. Sci.* 20 (1980): p. 238.
10. M.C. Hansen, *Polym. Eng. Sci.* 20 (1980): p. 252.
11. G. Astarita, G.C. Sarti, *Polym. Eng. Sci.* 18 (1978): p. 338.
12. J.M. Vergnaud, *Liquid Transport Process in Polymeric Materials: Modelling and Industrial Application* (Englewood Cliffs, NJ: Prentice-Hall, 1991).
13. J. Crank, *The Mathematics of Diffusion*, 2nd ed. (Oxford, U.K.: Clarendon Press, 1976).
14. C.V. Dinh, M. Kubouchi, T. Sakai, T. Tsuda, R. Kobayashi, "Study on Degradation of Different Types of Polyethylene Exposed to Hydrochloric Acid Solution," Proc. 54th Japan Conf. Materials and Environments, held Oct. (Hiroshima, Japan: Japan Society of Corrosion Engineering [JSCE], 2007), p. 65.
15. T. Nguyen, F.W. Martin, "Modes and Mechanisms of Degradation of Epoxy-Coated Reinforcing Steel in Marine Environment," in *Durability of Building Materials Components* 7, vol. 1, ed. C. Sjöström (London, U.K.: E&FN Spon, 1996), p. 491.
16. W. Funke, *Prog. Org. Coat.* 9 (1981): p. 29.
17. J.C. Bolger, A.S. Micheals, *Interface Conversion for Polymeric Coatings* (New York, NY: Elsevier, 1969), p. 3-60.
18. T. Nguyen, E. Byrd, D. Bentz, *J. Coat. Technol.* 66, 834 (1994): p. 39.