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Degradation of Different Types of Polyethylene Using for Lining System Exposed to Hydrochloric Acid Solution

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Abstract

This paper focuses on degradation behavior of a maleic anhydride modified and another new modified polyethylene used for lining system as anti-corrosion agent when exposed to hydrochloric acid solution environment. Different concentrations of HCl solution : 0, 10, and 20 mass % at temperatures of 40, 60, and 80 °C were set to investigate the degradation behavior of the two types of modified polyethylene. Virgin PE was also subjected to the same conditions for comparison. Weight change, chloride element penetration, and changes in chemical structure were measured. The immersion test result showed that the diffusion of water and the HCl solution into the neat PE obeyed Fickian diffusion model while those into both modified PE obeyed Fickian mode at low temperatures only. Two-saturation stages were observed for the samples immersed in HCl solutions at 80 °C. The modified PE samples were degraded by the HCl solutions while there was no change of chemical structure for the case of the PE resin. The high temperature enhanced the order of degradation. IR spectra showed structural changes, which maybe attributed to the modifier components in the polymers. Chloride mapping analysis by EDS showed the penetration mode of chloride element into the polymers.

Key-words : *Modified Polyethylene, Lining, Corrosion, Diffusivity, Chemical Degradation*

1. Introduction

Polymeric coatings/linings are widely employed to protect steel/metal structures from corrosion. The main function of a coating/lining layer is to provide a barrier or sheath between the surface of structures and the corrosive environment. Parameters to be considered in the performance of coatings/linings are, therefore, (i) high adhesion strength to substrate and (ii) low permeability to corrosive species of service environment. Selection of a polymeric coating/lining material should be based on the type of protective structure, property of service environment, and expected forms of corrosion.

Polyethylene is well appreciated as an anticorrosion

coating/lining material for metal materials due to its physical and chemical properties, processability, and low cost¹⁾. However, because of its typical non-polar characteristic, which leads to poor adhesion onto steel substrate, the polyethylene used for lining needs to be modified in order to improve the adhesion strength. Chemical modification is one solution for adhering polyethylene onto substrate surface by introducing a polar group onto the polymer main chain as pendant units or as short chain-branches²⁾. This modification can be done by copolymerization of new monomers³⁾.

Grafting is a common way of modification for polyethylenes. It involves covalent bonding among the modified species and the polymer chain back bones. Grafting active sites are generated either by mechanical process, by chemical initiation, by photochemical activation, or by high energy radiation process. Recently, several other techniques have been developed to control the grafting length, such as atom transfer radical polymerization^{4,5)} or living radical polymerization^{6,7)}.

In spite of an improvement of adhesive performance

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to the substrate, the above methods may result in a change of molecular structure that may lead to an influence on the bulk properties of polyethylene. S. K. Singh and coworkers⁸⁾ reported that low density polyethylene grafted by maleic anhydride was changed in molecular structure by the existence of the carbonyl groups. They also pointed out that its crystallization behavior noticeably changed, as well as having high acid value and low melt flow index. A study on thermal expansion of maleic anhydride and ethylene-propylene-diene ter-polymer modified mid-density polyethylene (MDPE) showed that there is no significant change in thermal expansion for the MDPE blended with a small additional amount of the additives in comparison with the originals⁹⁾. Gaylord *et al.*¹⁰⁻¹²⁾ reported that single oligomeric grafts formed during the grafting of maleic anhydride onto polyolefins. Adhesion and compatibilization of maleic anhydride grafted polymers can be expected to depend on the chemical nature and microstructure of the graft¹³⁾.

Lined/coated polyethylene steel piping system is popularly applied in the industry. The working solution environment usually is water, under ground water, sea water, and in certain cases, hydrochloric acid solution. During exposure to service environment, the lifetime of coating/lining system is governed by the permeation/diffusion behavior of the environmental components. The environmental components may diffuse into coating/lining layer then reach substrate surface. These components may deteriorate the coating/lining materials or may react with the modifiers. Corrosion may occur when corrosive species accumulate at the interface of the coated/lined layer and the substrate. Disbondment is considered to result from this interface corrosion.

The present paper discusses the diffusion behavior of HCl solutions at different temperatures into a new developed polyethylene grade (sPE) used for lining on steel in comparison with that of a maleic anhydride modified polyethylene and virgin polyethylene. The chemical degradation of these polymers caused by the environment solution is also discussed.

2. Experiments

2.1 Specimens and materials

A grade of linear-low-density polyethylene resin having a density in the range of 0.925 g/cm³ to 0.930 g/cm³ was used to form test pieces in this study. The resin was chemically modified both by maleic anhydride and another chemical compound to form MAPE and sPE polyethylene blend, respectively. Due to limitations on information sharing, further details of the modification process and the use of the modified agent for sPE are not released. From these polyethylene blends (MAPE, sPE) and the original resin (PE), rectangular sample sheets with a thickness of 1.0 mm were made by hot compression molding method. MAPE, sPE and PE test pieces having dimensions of 60 × 25 mm were cut out from the prepared sample sheets, then were dried up at 50 °C for 72 hours to ensure that the remaining moisture was removed before the immersion test was carried out. Table 1 shows details of the test pieces.

2.2 Immersion studies

An immersion test was carried out by simply immersing the test pieces in the environmental solutions under the given conditions (see Table 1). The test pieces were fixed in a polytetrafluoroethylene holder to avoid surface contact with each other, and immersed in separable flash bottles filled with the test solution, connecting to a condensing system. Temperatures of the environmental solution were constantly set at 40, 60, and 80 °C.

At regular intervals of time, the specimens were taken out, wiped by filter paper to remove attached solution on their surfaces and weighed by a balance with 0.1 mg accuracy. A change in mass was measured related to the initial mass.

To characterize the degradation mechanism, the penetration pattern of the chloride (Cl) element into the specimens was observed by using energy dispersive X-ray spectroscopy (EDS) on the cross section of the sample. Change of the chemical structure was monitored by using infrared spectroscopy (FT-IR).

Table 1 Specimens and experimental conditions.

Resin	Density [g/cm ³]	Modified chemical and its percentage [mass%]	Exposure Environment	Environmental temperature [°C]
Virgin PE	0.925–0.930	none	De-ionised water, HCl 10 mass%, HCl 20 mass%	40 ; 60 ; 80
MAPE	0.925–0.930	Maleic anhydride—5%	De-ionised water, HCl 10 mass%, HCl 20 mass%	40 ; 60 ; 80
sPE	0.925–0.930	Modifier—5%	De-ionised water, HCl 10 mass%, HCl 20 mass%	40 ; 60 ; 80

The samples, converted into thin films by hot pressing at 160 °C, were directly mounted on the frame of the spectrophotometer.

3. Results and discussion

3.1 Diffusion behavior of the experimental environment into the resins

The environmental diffusion isotherms for the virgin PE were gravimetrically investigated over the temperature range of 40 ~ 80 °C and are shown in Fig. 1. It can be seen that the concentration of HCl, temperature of the environmental solutions, and nature of the polymers play an important role on the diffusion. The Fickian diffusion assumption requires that the weight change curve with respect to the square root of immersion time is linear at the initial duration and, thus, the diffusivity of the material can be determined by the slope of the linear curve based on the following equation¹⁴⁻²¹⁾:

$$\frac{W_t}{W_\infty} = \frac{4}{L\sqrt{\pi}} \sqrt{Dt} \quad (1)$$

in which, W_t and W_∞ is weight change at time t and infinite time, respectively ; L is the thickness of the specimen, and D is the diffusion coefficient. As seen in the figure, the diffusion isotherms of the PE were reasonably well-fitted to a Fickian diffusion model.

The diffusion behavior of the virgin PE sample is detailed in Fig. 1. The saturation value changed from 0.08 % to 0.24 % for the water, from 0.16 % to 0.42 % for the 10 mass % HCl solution, and from 0.39 % to 0.98 % for the 20 mass % HCl, apparently increasing

with increasing temperature. Note that at the same temperature of the solution, the higher the HCl concentration gets, the higher the saturation value is obtained. The diffusion coefficients are listed in Table 2. The increase of diffusivity with increasing temperature may indicate that the polymer chains would be more mobile at higher temperature, making the environmental molecules easy to penetrate into, resulting in an increase of the diffusion coefficient. The HCl concentration also influences on the diffusivity. The diffusion coefficient reduced with increasing HCl concentration. This influence can be considered by the difference in penetration speed between water and the hydrochloric component into the polymer. The water molecules penetrated much more rapidly than those of the HCl molecules ; therefore, the diffusivity tends to be lower in higher HCl concentration.

Fig. 2, which shows the IR spectra result of the 3900 hours immersed virgin PE, points out that there was no noticeable change in the chemical structure of the sample. Therefore, the higher saturation value

Table 2 Diffusion coefficient of the environments into the virgin PE.

Environment	Diffusion coefficient, [$10^{-14} \text{ m}^2/\text{s}$]		
	40°C	60°C	80°C
Water	6.72	7.51	10.22
HCl 10 mass %	3.99	5.75	8.98
HCl 20 mass %	2.73	3.68	7.09

Fig. 1 Solution diffusion isotherms for virgin PE at various temperatures (a)- water, (b)- HCl 10 mass %, and (c)- HCl 20 mass %.

in the higher HCl concentration solution may have contributed to physical change in the specimen (ex. ; swelling).

3.2 Degradation of the MAPE in the water and HCl solution environment

The test specimens were immersed in the 0, 10 and 20 mass% HCl solutions at 40, 60, and 80 °C. Fig. 3 shows diffusion behavior of the solutions into the MAPE. It was seen that the weight change profile was reasonably fitted well with the Fickian model for test pieces immersed in the 40 and 60 °C HCl solutions, while the two-stage saturation diffusion behavior was observed for those in the 80 °C HCl solution. In the water, only the Fickian diffusion mode was observed at

Fig. 2 IR spectra of the PE immersed in various solutions at 80 °C.

all examined temperatures. The influence of temperature and HCl concentration on the saturation value for MAPE had a similar tendency as those for the pure PE resin. However, this effect was more significant for the MAPE than the corresponding PE resin, resulting in higher saturation value. The higher saturation value may be attributed to the incorporated modifiers.

In the 20 mass% HCl solution at 80 °C, the higher saturation values of the first diffusion stage (2.5 %), in comparison with those of the PE resin in the corresponding solutions, may indicate that beside the part of the PE resin component, the maleic anhydride component also played a part in this diffusion stage. Results of EDS chloride mapping described in Fig. 4 serves as evidence for this consideration. As seen in this figure, qualitatively, the penetration of chloride element was higher in the second stage than those in the first stage and in the saturation at 40 and 60 °C. This suggested that the second stage may be governed by diffusion of the HCl component while the others are controlled by diffusion of the water component.

Fig. 5 shows the FTIR spectra of the MAPE immersed in 20 mass% HCl solution. Two peaks (812 and 1259 cm^{-1}) are obtained when test pieces are immersed in the solution at 80 °C while another (3389 cm^{-1}) is observed at all temperatures. The peak of 812 cm^{-1} may be considered for the dichloride hydrocarbon group ($-\text{CCl}_2-$), while the peaks of 1259 cm^{-1} and 3398 cm^{-1} maybe attributed to the presence of $-\text{C}-\text{O}-\text{C}-$ in three-member rings and of hydroxyl group, respectively.

Fig. 3 Solution diffusion isotherms for the MAPE at various temperatures (a)- water, (b)- HCl 10 mass%, and (c)- HCl 20 mass%.

Fig. 4 EDS chloride mapping of the MAPE immersed in HCl 20 mass % solution at 80 °C for : (a) - 216 hrs ; (b) - 721 hrs, (c) - 2225 hrs ; (d) - at 40 °C for 2225 h and (e) - at 60 °C for 2225 h. (巻頭カラー写真参照)

Fig. 5 IR spectra of the MAPE immersed in the 80 °C HCl 20 mass % for 2256 hrs.

These may be derived from the reactions of functional groups of maleic anhydride with water and HCl. The same results are also obtained for samples immersed in 10 mass % HCl.

3.3 Degradation of the sPE in the HCl solution environment

The diffusion behavior of the environments into the sPE was described in the previous paper²²⁾. The diffusion of the environments into the sPE was similar to those of the MAPE. The two-stage diffusion was observed in the 80 °C HCl solution while the Fickian diffusion model was observed in the water and corrosive solution at low temperatures. The somewhat higher saturation value of the first stage for the sPE in the

80 °C HCl 10 mass % and 20 mass % (0.65 % and 1.0 %, respectively), in comparison with those of the corresponding solutions for PE resin (0.42 % and 0.98 % respectively) suggested that the first diffusion stage may be dominated by the PE resin component in the sPE. The second diffusion stage may be attributed to the reaction of the modifier with HCl in the solution.

Fig. 6 shows Cl element mapping for the sPE test specimens immersed in 20 mass % HCl at 80 °C for 505, 1224, 4000 hrs, at 60 °C for 4012 hrs, and at 40 °C for 4024 hrs. It can be seen that the chloride element distributed non-uniformly in the first saturation for the case of 80 °C (see Fig. 6 (b)) and in the saturation for the case of 40 and 60 °C, while it seems to fully occupy the sample in the second saturation. This suggests that the chloride element has penetrated initially into the polymer through so-called low Cl-resistant areas, then diffused to neighbouring regions. Water diffuses predominantly in the first stage while HCl does so in the second stage. The weak areas may result from defects generated during polymer processing or from the actions of the solution environment during immersion.

IR analysis shows that new peaks occur only when the samples immersed in HCl at 80 °C. Fig. 7 is an example of the IR results. It can be seen that the peaks of 812 and 1259 cm^{-1} occur in the second stage. These peaks are maybe attributed to the chemical bonds resulting from the reactions of HCl and functional groups of the modifier.

Table 3 shows the sorption capacity of polymers. The

Fig. 6 EDS chloride mapping of the sPE immersed in HCl 20 mass % solution at 80 °C for : (a) - 505 h ; (b) - 1224 h, (c) - 4000 h ; and (d) at 40 °C for 4024 h, (e) - at 60 °C for 4012 h. (巻頭カラー写真参照)

Fig. 7 IR spectra of the sPE immersed in the 80 °C HCl 20mass % after various durations.

Table 3 Sorption capacity of the virgin PE, MAPE, and sPE.

Polymer	Environment	Sorption capacity, [%]			
		40 °C	60 °C	80 °C	
				1 st stage	2 nd stage
virgin PE	Water	0.08	0.12	0.24	—
	HCl 10 mass %	0.16	0.33	0.42	—
	HCl 20 mass %	0.39	0.64	0.98	—
MAPE	Water	0.09	0.10	0.38	—
	HCl 10 mass %	0.35	0.69	1.25	1.87
	HCl 20 mass %	1.00	2.20	2.67	3.65
sPE	Water	0.28	0.63	—	—
	HCl 10 mass %	0.19	0.41	0.64	1.15
	HCl 20 mass %	0.49	0.83	1.00	1.83

Table 4 Diffusion coefficient of the environments into the MAPE and sPE.

Polymer	Environment	Diffusion coefficient, [$10^{-14} \text{ m}^2/\text{s}$]			
		40 °C	60 °C	80 °C	
				1 st stage	2 nd stage
MAPE	Water	4.75	7.09	10.22	—
	HCl 10 mass %	1.78	7.11	11.73	6.38
	HCl 20mass %	2.73	7.10	14.72	23.00
sPE	Water	3.40	5.75	—	—
	HCl 10 mass %	1.88	3.40	6.05	13.61
	HCl 20mass %	3.16	5.75	17.39	19.01

sorption capacity of the MAPE in water is lower than those of the sPE ; on the contrary, the MAPE's sorption capacity is higher than the sPE's in the HCl solution. This may suggest that MAPE and sPE exhibit different resistance to the environment as a result of the incorporated maleic anhydride and modifier.

The diffusion coefficients of the solutions into the MAPE and sPE are presented in Table 4. HCl concentration considerably influences the diffusivity. Diffusivities of water and HCl 10 mass % into the MAPE and sPE are smaller than those into the PE. However, the diffusivity of 20 mass % HCl into MAPE and sPE is higher than those into the PE. The modifiers have contributed to this effect.

4. Conclusion

Degradation of the modified polyethylene (sPE) was evaluated by exposure to corrosive environments.

The virgin polyethylene (PE) and maleic anhydride polyethylene (MAPE) were also exposed in the same environments for comparison of their degradation with those of the sPE's. Within the testing time, the MAPE and sPE degraded in HCl solution at 80 °C while the PE remained stable under these conditions. This degradation resulted from the incorporated modifiers in polymers.

Within the test period, two-stage diffusion was observed for the MAPE and sPE immersed in HCl solutions at 80 °C, while Fickian diffusion mode was observed in water and HCl solution at 40 and 60 °C. Water diffused predominantly in the first stage while the HCl component did in the second stage. The solutions that diffused into the PE obeyed the Fickian mode only. Sorption capacity of the polymers and diffusion coefficient of the environments into the polymers were also discussed. High concentration of HCl in the second saturation resulted in the degradation of the polymers.

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塩酸水溶液曝露されたライニング用ポリエチレンの劣化

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要 旨

本報は塩酸水溶液における防食ライニング用無水マレイン酸およびその他の変性ポリエチレンの劣化挙動を検討したものである。二種類の変性ポリエチレンについて0, 10, 20%の塩酸濃度, 40, 60, 80℃で劣化挙動を調査した。比較として未変性のポリエチレンについても同様の条件で試験した。重量変化, 塩素の浸透, 化学構造変化について調べた。

浸漬試験の結果, 未変性ポリエチレンでは水と塩素の浸透が単純にFickの法則に従ったのに対し, 変性ポリエチレンは二種類ともに水と塩素の浸透が低温領域でのみFickの法則に従い, 80℃の塩酸水溶液浸漬では二つの飽和ステージが見られた。サンプルに劣化は見られたが, ポリエチレン樹脂そのものは化学的な劣化は確認されなかった。高分子の変性化学成分に起因するIRスペクトルに, 高温になるほど大きな劣化が確認された。EDSによる塩素マッピングから塩素がポリマー中へ浸透する挙動を評価した。