

Diffusion behaviour of corrosive solution environments in carbon black filled modified polyethylene linings

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Abstract. The diffusion behaviour of water and HCl solution at different temperatures and concentrations into a modified polyethylene filled with carbon black used for lining is presented. It has shown the predominant role of nature of environment and carbon black content. In the both environments, an increase of environmental temperature increased the capacity of environmental absorption and the diffusion rate. The lower sorption capacity was observed at 40 and 60 °C while a higher at 80°C in the water. The two-stage diffusion appeared for the case of the corrosive environment at 80°C. An increase of carbon black loading was increased both diffusion rate and saturation values.

Diffusion of the environment into the polymer proposed by the following: environmental molecules diffusing into the polymer matrix through porous system, were trapped by functional groups on the carbon black surface and polymer molecule chain, and are immobilized. This explains the increase of sorption capacity when increase carbon black loading.

Keywords: modified polyethylene composites, lining, diffusion, chemical degradation.

1. Introduction

The service life of polymeric lining/coating-iron/steel system is limited by degradation and diffusion phenomenon. The polymeric lining/coating layer is required to have high resistance against its working corrosive environment, low environmental diffusion rate, and high adhesion on substrate. Polyethylene (PE) is considered as a good material for lining because of its high chemical resistance to many corrosive environments [1]. For purpose of the adhesion improvement, PE used for lining/coating was modified. This modification may effect property of PE i.e. it may change degradation resistance or diffusion behaviour in comparison with those of the original PE.

Carbon black (CB) has excellent properties, such as heat, chemical and weather resistance, light weight, and low thermal expansion [2-4]. It is widely used industrially as a deep black pigment for polymeric materials, weathering proof filler in polymer industry, and other applications [3-7]. The use of carbon black in PE lining beside as pigment additives, it may hinders the ultraviolet degradation. However, it may effect diffusion behaviour of working solution environment into the lining layer.

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This paper presents role of carbon black loading on diffusion behaviour of water and hydrochloric acid solution into a modified polyethylene (sPE) using for lining on steel.

2. Experiment

2.1. Material

A grade of linear-low-density polyethylene resin having density in range of 0.925 – 0.930 g/cm³ was used to form test pieces in this study. The resin was chemically modified to form a blend polyethylene named as sPE. Due to limits on information sharing, further details of modification process and the use of modified agent are not released. Mixtures of this blend polyethylene and carbon black were performed in accordance with ratio of 2, 3, and 4 mass% of carbon black. Rectangular sample sheets with thickness of 1.0 mm were made by hot compression molding method using these mixtures. The test pieces having dimension of 60 x 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. Materials used for investigation

Code	base polymer	Composition of modifier	carbon black composition
sPE-2	LDPE	5%	2%
sPE-3	LDPE	5%	3%
sPE-4	LDPE	5%	4%

2.2. Immersion study

Immersion experiment was carried out by simply immersing the test pieces in water and 10, 20 mass% hydrochloric acid solutions. The test pieces were fixed in a polytetrafluoroethylene holder to avoid contact surface each other, and immersed in separable flash bottles which 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 interval 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 initial mass.

To characterize mode of the environmental diffusion, penetration pattern of chloride (Cl) element into the specimens was observed by using energy dispersive X-ray spectroscopy (EDS) on cross section of sample. Scanning Electronic Microscope (SEM) was also used to observe the morphology of sample during immersion.

3. Results and discussion

The quantity of solution environment penetrating into the test polymer matrix as a function of time has been determined. Figures 1.a; 1.b and 1.c give typical examples of plots of the absorbed amount (M_t) of water, HCl 10 mass%, and HCl 20 mass% at 40, 60, and 80 °C versus immersion time for the

sPE-2, sPE-3, and sPE-4, respectively. From these curves, the environmental solution absorbed at saturation (M_∞) can be determined. Diffusion coefficient (D) was also calculated by following equation, base on initial slope method if the diffusion is considered to be Fickian mode [8 -15]:

$$\frac{M_t}{M_\infty} = \frac{4}{L\sqrt{p}} \sqrt{Dt} \quad (1)$$

In which, L is thickness of the test specimen and t is diffusion time.

3.1. Diffusion behaviour of water

Figure 1 shows weight change profiles of the polymers during immersion in the 40, 60, and 80 °C water environment. Main characteristics of the diffusion are detailed in Table 2. It is clearly seen that the sorption capacity of a polymer depends on its carbon black loading and temperature of the environment. For a polymer, the uptake amount increased with increasing temperature, indicating of the more entry of water molecules into the free volume space of the matrix polymer. The saturation increased from 0.30, 0.32, and 0.42 % (at 40°C) to 2.08, 2.17, and 2.40 % (at 80°C) for the sPE-2, sPE-3, and sPE-4, respectively. It is also note that a slight increase of the saturation value at 40°C to those at 60°C was observed whereas a large amount of uptake (more than about 5 – 7 times) was observed at 80°C. This maybe attributed to significant change of physical state of the specimens at 0°C in comparison to those at 40 and 60 °C.

Table 2. Diffusion characteristics in water

Polymer	40°C		60°C		80°C	
	D [10 ⁻¹⁴ m ² s ⁻¹]	$M_\infty^{\text{exp.}}$ [%]	D [10 ⁻¹⁴ m ² s ⁻¹]	$M_\infty^{\text{exp.}}$ [%]	D [10 ⁻¹⁴ m ² s ⁻¹]	$M_\infty^{\text{exp.}}$ [%]
sPE-2	4.21	0.30	4.44	0.50	1.09	2.08
sPE-3	4.81	0.32	4.91	0.57	1.12	2.17
sPE-4	5.44	0.42	5.51	0.63	1.13	2.40

By contrast, as far as the saturation values are obtained, the maximal quantity absorbed by the polymers seem to be additive. Consideration of polymer composition (modified PE and carbon black), the maximal quantity of water absorbed can be calculated using the following relationship:

$$M_\infty^{\text{polymer calc.}} = x_1 M_\infty^{\text{modified PE}} + x_2 M_\infty^{\text{carbon black}} \quad (2)$$

in which, x_1 , and x_2 being the weight fraction of the modified PE and carbon black composition, respectively. The experimental values and calculated values in Table 3 confirm this hypothesis of additivity. The higher of experimental value than the calculated value may be attributed to synergic effect (establishment of new pores or free volume) of carbon black and modified PE when these constituents formed the polymers. An evidence of pore observation using SEM in Figure 2 may confirm this explanation.

An interesting point was found out that the mean diffusivity is higher at 60°C than at 40°C, however, it is lowest at 80°C (see Table 2). A possible explanation for this phenomenon is that effect of thermal relaxation of polymer chains at 60°C improved penetration of water molecules into the polymer matrix than those at 40°C, however, a strong relaxation of these chains at 80°C may lead to appear an internal stress that reduce penetrating rate of water molecules.

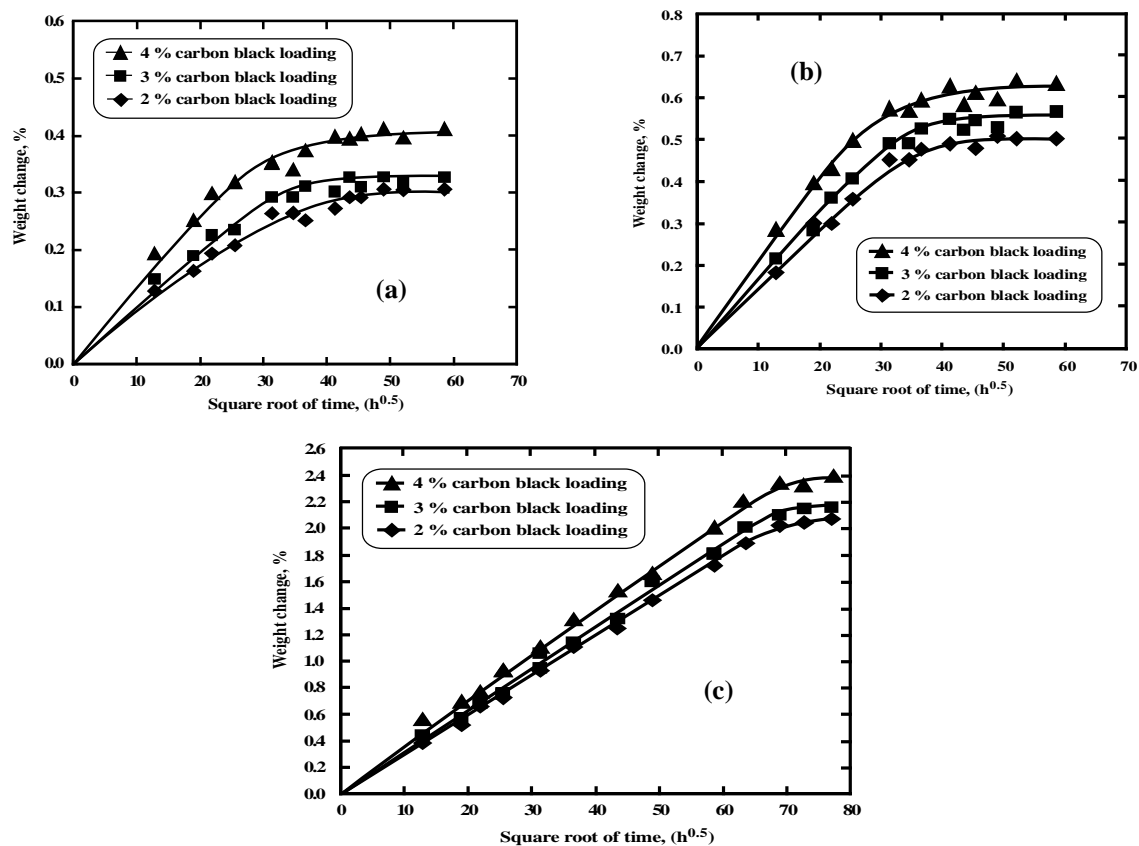


Fig. 1. Diffusion behaviour in water: a – at 40°C; b – at 60°C; and c – at 80°C.

Diffusion data in Table 2 also illustrated influence of carbon black loading on diffusion behaviour of water into the polymers. As seen in Table 2, an increase of carbon black loading leads to an increase of M_{∞} and D . However, the significance of carbon loading on diffusion behaviour is minor in comparison with those of temperature. The effect of carbon black constituent on mechanism of penetration of water into the polymers would be proposed as the following: water diffuses through the polymer matrix and is irreversibly trapped by carbon black particles until all oxygenated sites are saturated [16-18]. The water fixed on surface of carbon black particles is thus immobilized and do not participate in further diffusion [16]. Considering of this explanation, it would hypothesize that if a polymer having carbon black loading content higher than over an criterion will lead to low-down diffusion rate.

Table 3. Saturation absorption in water

Polymer	40°C		60°C		80°C	
	$M_{\infty}^{\text{calc.}}$ [%]	$M_{\infty}^{\text{exp.}}$ [%]	$M_{\infty}^{\text{calc.}}$ [%]	$M_{\infty}^{\text{exp.}}$ [%]	$M_{\infty}^{\text{calc.}}$ [%]	$M_{\infty}^{\text{exp.}}$ [%]
Modified PE	0.26	-	0.36	-	1.90	-
Carbon black	2.26	-	7.36	-	10.90	-
sPE-2	0.30	0.30	0.5	0.50	2.08	2.08
sPE-3	0.32	0.32	0.57	0.57	2.17	2.17
sPE-4	0.34	0.42	0.64	0.65	2.26	2.40

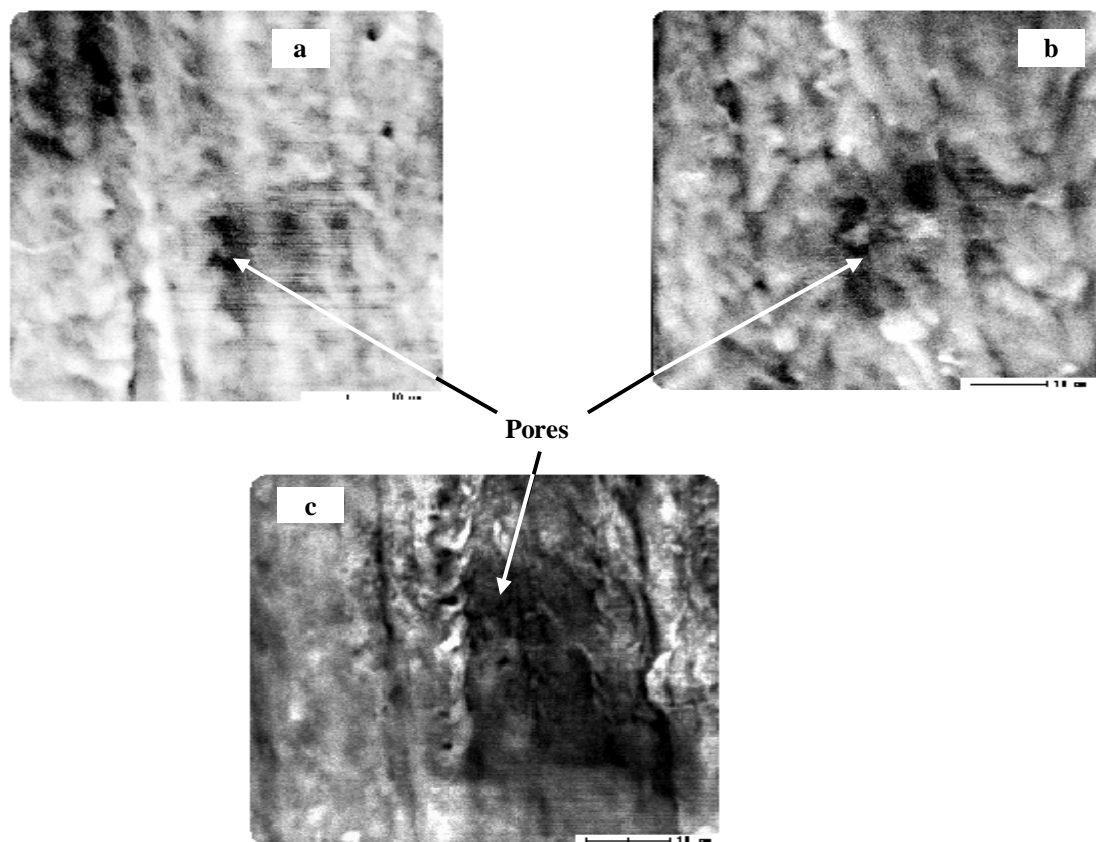


Fig. 2. SEM images of laminated polymer: a- sPE-2; b-sPE-3; and c-sPE-4.

3.2. Diffusion behaviour of corrosive solution environment

Hydrochloric acid solution is considered to be corrosive environment in this study. Figure 3, 4 show the weight change profiles of the specimens during immersion. The diffusion data is listed in Table 4. It can be seen that nature of environment and filled carbon black content influenced on diffusion behaviour.

Significance of nature of environment was confirmed again in case of the corrosive environments. For instance, similar to the case of water, the Fickian diffusion was also observed at 40 and 60°C. However, an interest was found that the two-stage diffusion appeared at 80°C. The two-stage diffusion appeared in the corrosive environment at high temperature (80°C) indicates that there was of a synergic effect of thermal and corrosive component. Chloride mapping analysis using EDS showed that a few chloride elements were observed for first saturation while they were much for second saturation (see Figure 5). Therefore, it would be said that water component diffused predominantly during first stage whereas diffusion of chloride element took over during the second stage. Finding of chemical bond of Cl with functional group of the modified polymer [19] may affirm this hypothesis.

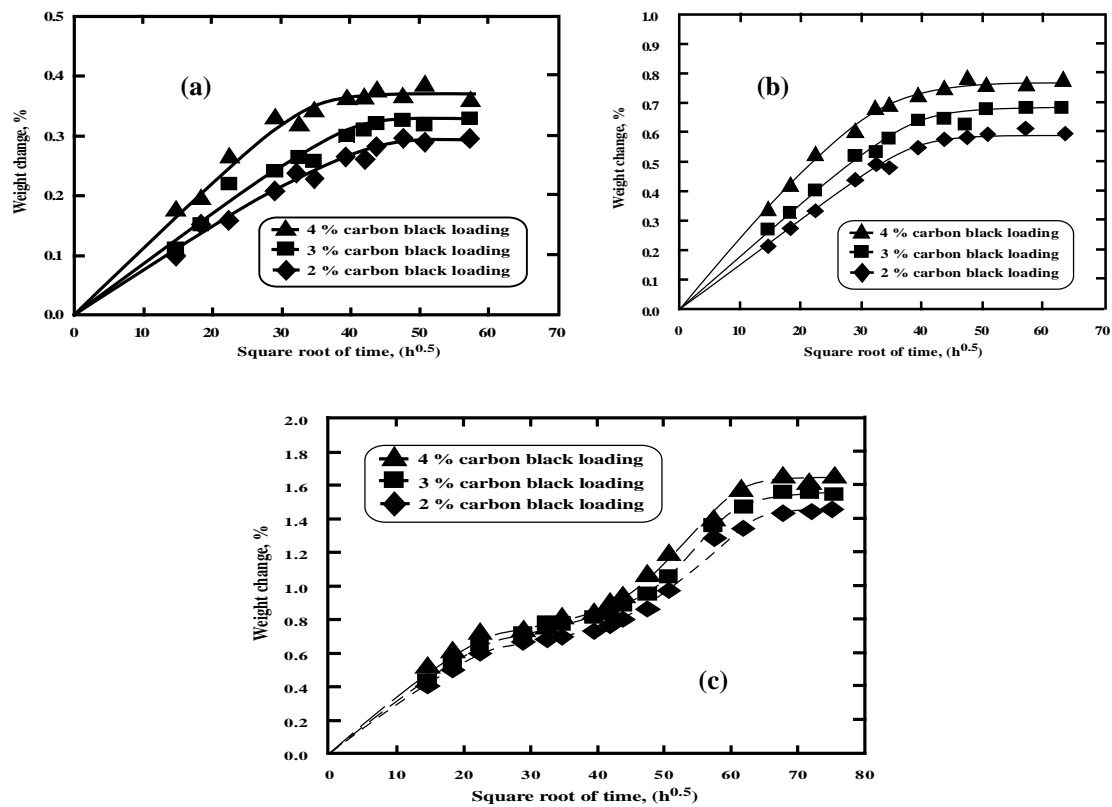


Fig. 3. Diffusion behaviour in HCl 10 mass% solution: a – at 40°C; b – at 60°C; and c – at 80°C.

Table 4. Diffusion characteristics in corrosive environment

Polymer	HCl 10 mass%							
	40°C		60°C		80°C			
	D	$M^{\text{exp. } \infty}$	D	$M^{\text{exp. } \infty}$	1 st stage		2 nd stage	
	[10 ⁻¹⁴ m ² s ⁻¹]	[%]	[10 ⁻¹⁴ m ² s ⁻¹]	[%]	D [10 ⁻¹⁴ m ² s ⁻¹]	$M^{\text{exp. } \infty}$ [%]	D [10 ⁻¹⁴ m ² s ⁻¹]	$M^{\text{exp. } \infty}$ [%]
sPE-2	3.19	0.30	3.49	0.59	8.10	0.67	3.90	1.44
sPE-3	3.41	0.33	3.78	0.68	8.11	0.71	3.34	1.58
sPE-4	4.39	0.38	4.78	0.77	8.92	0.79	4.96	1.63

Polymer	HCl 20 mass%							
	40°C		60°C		80°C			
	D	$M^{\text{exp. } \infty}$	D	$M^{\text{exp. } \infty}$	1 st stage		2 nd stage	
	[10 ⁻¹⁴ m ² s ⁻¹]	[%]	[10 ⁻¹⁴ m ² s ⁻¹]	[%]	D [10 ⁻¹⁴ m ² s ⁻¹]	$M^{\text{exp. } \infty}$ [%]	D [10 ⁻¹⁴ m ² s ⁻¹]	$M^{\text{exp. } \infty}$ [%]
sPE-2	2.65	0.55	3.96	0.96	25.59	0.92	6.88	2.21
sPE-3	3.05	0.61	4.07	1.05	23.85	1.04	19.59	2.49
sPE-4	3.46	0.69	4.45	1.15	22.29	1.14	22.29	2.70

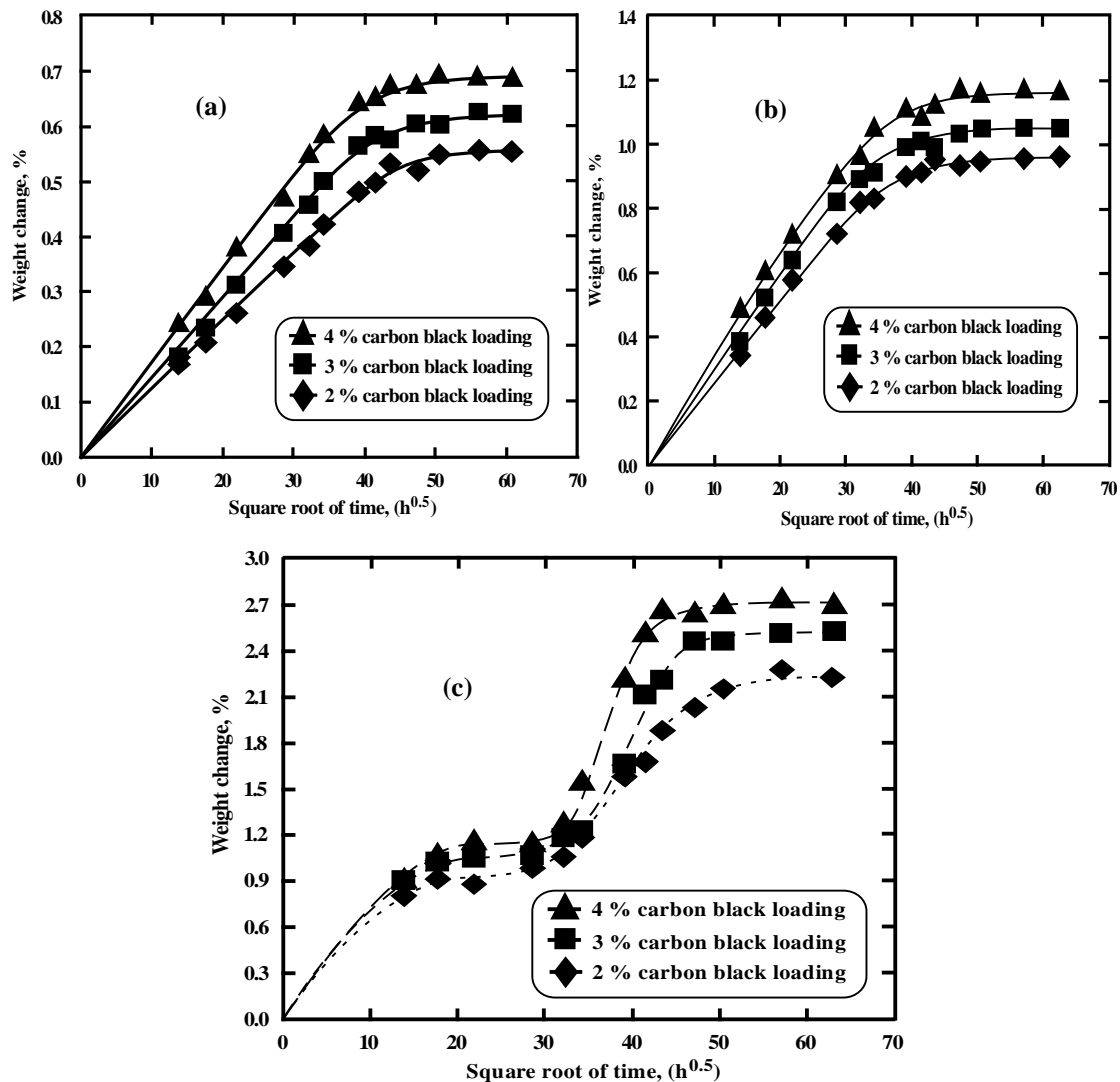


Fig. 4. Diffusion behaviour in HCl 20 mass% solution: a – at 40°C; b – at 60°C; and c – at 80°C.

The sorption capacity, diffusion rate is considerably influenced by the concentration and temperature of the exposed environment. As shown in Table 4, for the same HCl concentration solution, M^{exp}_{∞} and D increased with increasing temperature, similar tendency to those for the case exposed in water, whereas at the same temperature, the only sorption capacity increased with increasing HCl concentration while diffusion rate changed considerably with the HCl concentration. It also notes that the sorption capacity of the polymers exposed to HCl 10 mass% at 40 and 60 °C was a little higher than those to water at 40 and 60 °C, however, it was about double for the polymers exposed to HCl 20 mass% at the same temperature. Estimation of specific density of HCl solution was showed that it is about 4.7 and 9.8 % (corresponding to HCl 10 mass% and HCl 20 mass% solution) higher than those of water. Therefore, the little higher sorption capacity for samples exposed to the HCl 10 mass% solution at 40 and 60 °C maybe attributed to increase of the specific density. Beside a minor influence of the specific density, significant increase of sorption capacity when samples

exposed to HCl 20 mass% is considered by a change of micro structure of samples. SEM analysis showed that more number of pores was observed for saturated sample. Figure 6 is an example confirming this observation. Establishment of new pores during immersion may result from a reaction of polymer's polar group with HCl component [17].

Table 5. Calculated and experimental sorption capacity in corrosive environment

Polymer	HCl 10 mass%							
	40°C		60°C		80°C			
	$M_{\infty}^{\text{calc.}}$	$M_{\infty}^{\text{exp.}}$	$M_{\infty}^{\text{calc.}}$	$M_{\infty}^{\text{exp.}}$	1 st stage		2 nd stage	
	[%]	[%]	[%]	[%]	$M_{\infty}^{\text{calc.}}$	$M_{\infty}^{\text{exp.}}$	$M_{\infty}^{\text{calc.}}$	$M_{\infty}^{\text{exp.}}$
					[%]	[%]	[%]	[%]
Modified PE	0.24	-	0.41	-	0.59	-	1.16	-
Carbon black	3.24	-	9.41	-	4.59	-	15.16	-
sPE-2	0.30	0.30	0.59	0.59	0.67	0.67	1.44	1.44
sPE-3	0.33	0.33	0.68	0.68	0.71	0.71	1.58	1.58
sPE-4	0.36	0.38	0.77	0.77	0.75	0.79	1.72	1.63

Polymer	HCl 20 mass%							
	40°C		60°C		80°C			
	$M_{\infty}^{\text{calc.}}$	$M_{\infty}^{\text{exp.}}$	$M_{\infty}^{\text{calc.}}$	$M_{\infty}^{\text{exp.}}$	1 st stage		2 nd stage	
	[%]	[%]	[%]	[%]	$M_{\infty}^{\text{calc.}}$	$M_{\infty}^{\text{exp.}}$	$M_{\infty}^{\text{calc.}}$	$M_{\infty}^{\text{exp.}}$
					[%]	[%]	[%]	[%]
Modified PE	0.43	-	0.78	-	0.68	-	1.65	-
Carbon black	6.43	-	9.78	-	12.68	-	29.65	-
sPE-2	0.55	0.55	0.96	0.96	0.92	0.92	2.21	2.21
sPE-3	0.61	0.61	1.05	1.05	1.04	1.04	2.49	2.49
sPE-4	0.67	0.69	1.14	1.15	1.16	1.14	2.77	2.70

Carbon black loading was also influenced on diffusion characteristics. The diffusion rate and saturation value increased with increasing carbon black content. As mentioned in previous part, an increase of carbon black content leads to the increase of porous density or free volume of polymer resulted therefore in increase value of M_{∞} and D . An another considering reason explaining the influence of carbon black content is that the more carbon black content leads to much number of environmental molecules trapped by the carbon black particle led to an increase of M_{∞} . However, the diffusion rate was lower than those exposed to water. This observation would be explained as the following: water and HCl molecules diffuse competitively through the polymer matrix and is irreversibly trapped by the carbon black particles until all oxygenated sites are saturated. The competition between these two components resulted in lower-down process. However, the diffusion and trapping corresponding to water component was predominant over HCl component. The chloride mapping analysis during immersion confirmed this hypothesis. Figure 5 is an example of the chloride mapping analysis result.

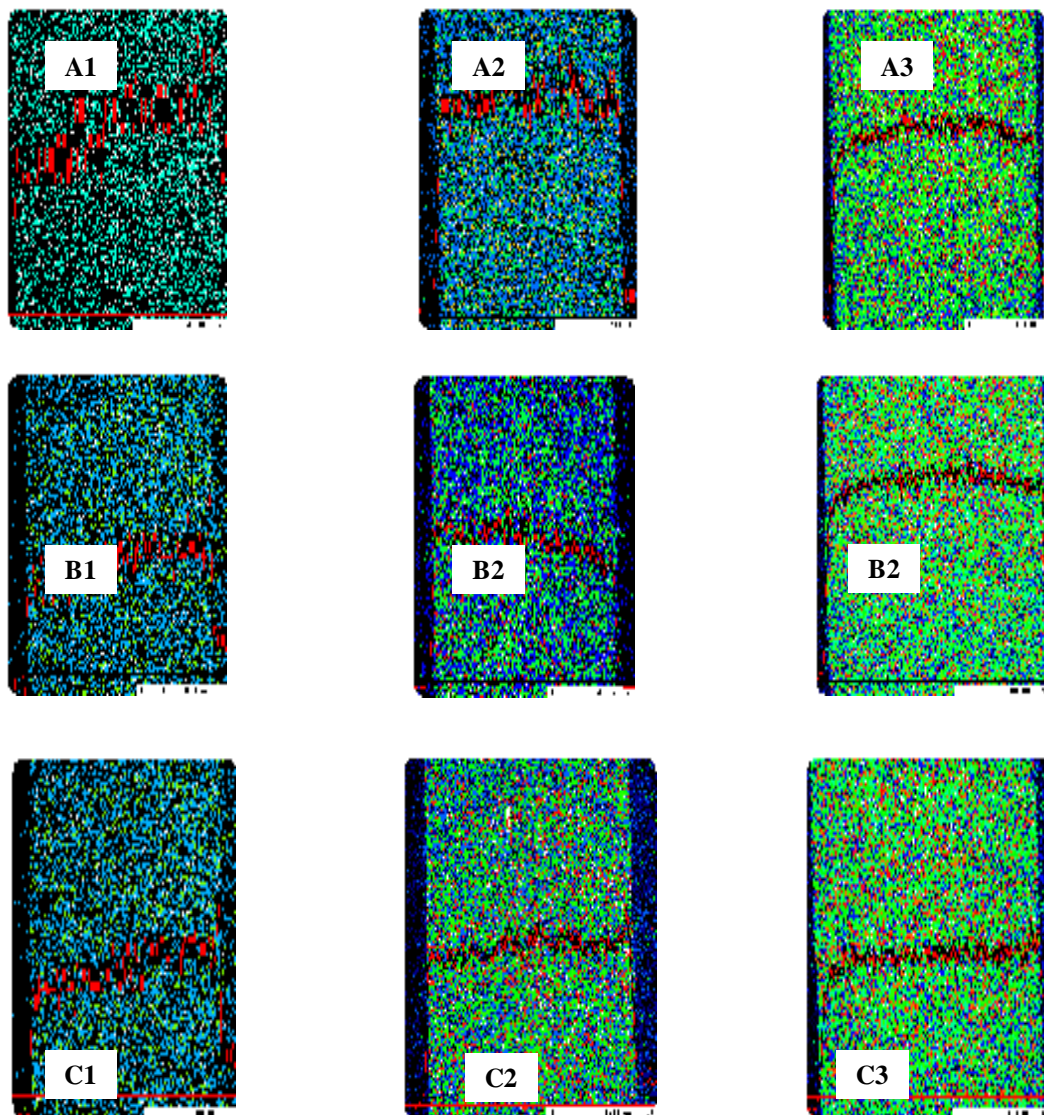


Fig. 5. EDS chloride mapping of samples: A 1-3 – sPE-2; B1-3 – sPE-3; and C1-3 – sPE-4 for 144, 480, and 2345 h immersion respectively in the 80°C HCl 20 mass% solution.

With application of the same law of additivity used previously for the case of water environment to the case of corrosive environment, the calculated saturation value was obtained and detailed in Table 5.

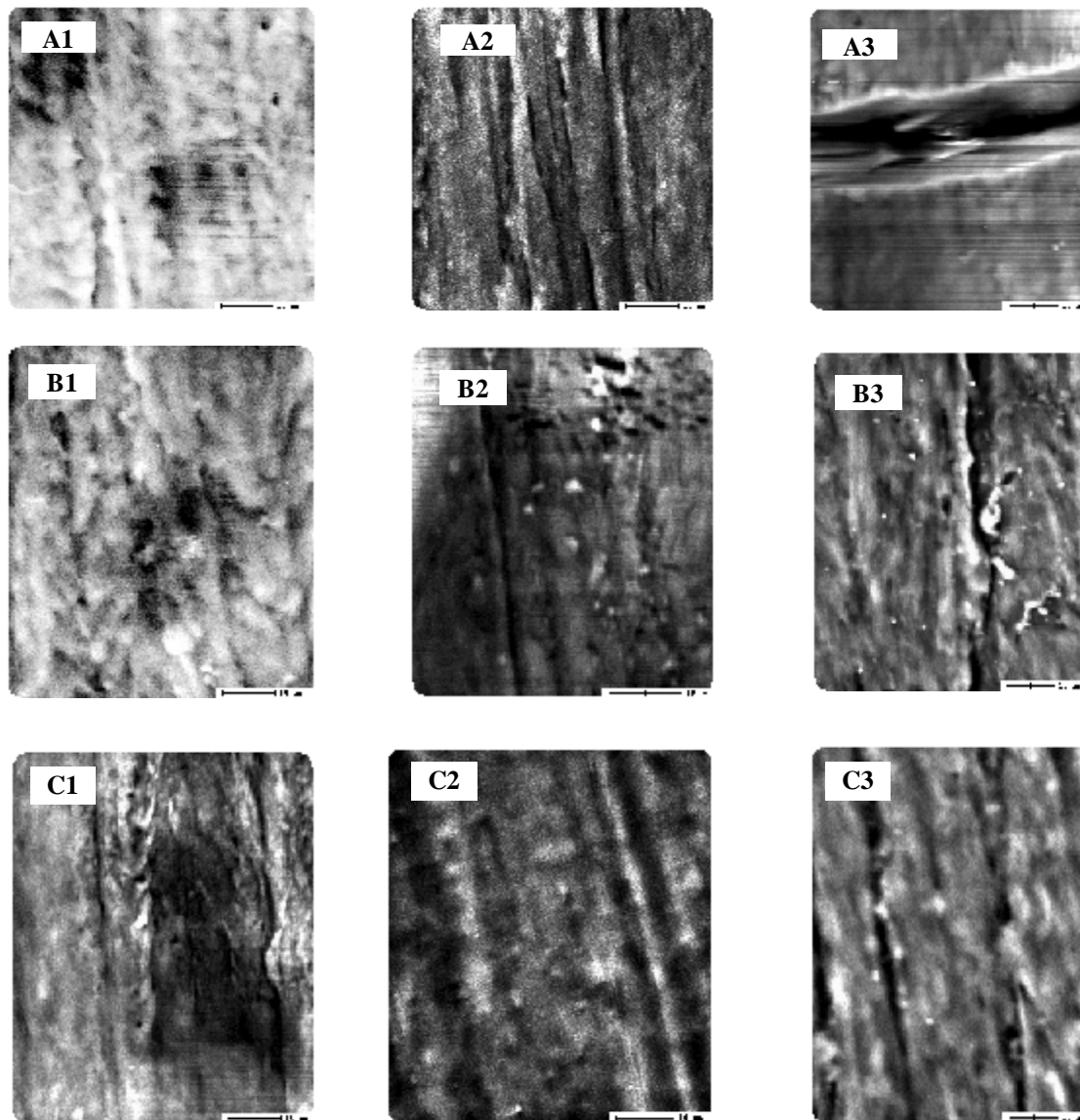


Fig. 6. SEM images of polymer: A 1-3 – sPE-2; B1-3 – sPE-3; and C1-3 – sPE-4 for 0, 480, and 2345 h immersion respectively in the 80°C HCl 20 mass% solution.

4. Conclusion

The study of the diffusion behaviour of water and corrosive solution environment in a carbon black filled modified polyethylene using for lining application has shown the predominant role of nature of environment and carbon black content. In the both environments, an increase of environmental temperature increased the capacity of environmental absorption and the diffusion rate. Sorption capacity of polymer in corrosive environment at low temperature (40 and 60 °C) was higher

than those in the water while it was lower at 80°C. The two-stage diffusion appeared for the case of the corrosive environment at 80°C. An increase of carbon black loading was increased both diffusion rate and saturation values.

Diffusion of the environment into the polymer is proposed by the following: environmental molecules diffusing into the polymer matrix through porous system, were trapped by functional groups on the carbon black surface and polymer molecule chain, and are immobilized. This explains the increase of sorption capacity when increase carbon black loading.

The results of this study suggest that in order to improve the resistance of water and HCl solution penetration, the modified polyethylene should mix with carbon black at low content. The working temperature for these polymer linings in these environments should not be exceeded over 60°C.

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