Study on influence of substrate and exposure corrosive environment on adhesion ability of a modified polyethylene lined on blasted steel substrate

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Abstract. This paper presents a study of the adhesion ability of a modified polyethylene (sPE) lined on blasted steel substrate. Effects of pre-treatment of the substrate surface, the exposure environments, and elevated temperature on the adhesion strength, adhesion energy was conducted. A peel analysis model was established to calculate adhesion energy (fracture energy) of the sPE lined on the substrate from the peel data. The dumbbell tensile test was conducted at the rate of 50 mm/min. as similar to the rate of peel test to find out the parameters using for the model. Adhesion ability of the sPE lined on the different pre-treatment surface substrates was investigated. The Standard specimens showed the highest peel strength-adhesion energy. The adhesion energy result (2657.5 J/m^2) for the Very low roughness specimens (smooth surface) was considered to the chemical bonding energy between the modifier/polymer and the metal oxides/metal crossing the interface. The peel strength of lined virgin PE for these substrates was also measured. The value of 743.2 J/m^2 for the Very low roughness specimens was attributed to chemical secondary bonding energy of the base polymer and the substrates. The Standard specimen was used for testing the effects of corrosive environment on its peel strength, adhesion energy, in which the polymer face was in contact with the 60°C corrosive environment while the steel face in contact with the 15°C cycling water. For the specimens exposed to the water, the reduction of 15.04% peel strength in comparison with the initial for first 864 h exposure was found while those exposed to the HCl solution was reduced about 53.94, 35.67, and 45.06 % in comparison with the initial for the first 720 h exposure. Corrosion is considered a main reason for this reduction. Chloride ion accumulated on the interface was attributed for catalysis of the corrosion process. The peel strength for dried specimens was unremarkably different in comparison with that in the wet condition.
Keywords: polyethylene lining, corrosion, adhesion energy, peel test.

1. Introduction

Polyethylene is widely used as anticorrosion lining/coating material for steel pipes because of its appropriate chemical and mechanical properties [1]. The polyethylene works as a barrier or shield to water, oxygen, and especially to corrosive elements from service environment. Adhesion strength of lined/coated polymeric layer on substrate is considered to be a significant parameter for evaluation of a polymeric lining/coating-substrate system. In order to improve adhesion strength of lined/coated polyethylene onto steel, this material has been modified (copolymerization, ter-polymerization, or graft) by incorporating polar functional groups [2-4]. It should be noticed that polyethylene is the relatively large thermal contraction coefficient during cooling of the lining/coating, about 12-14 times larger than mild steel [5]. This may result in significant residual shrinkage stress upon solidification.

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Another important feature, which may also be the effect to adhesion strength of lined/coated polyethylene on steel, is the crystallization and densification during lined/coated cooling. The crystallization is considered to play a significant role in residual stress development [6], resulting in internal strains, which may lead to induced/promoted interfacial failure. Although the adhesion strength would be improved, it maybe reduced during the exposure. The corrosion of lined/coated substrate surface which takes place by action of water, oxygen, and corrosive elements within the interface is considered as a main factor for reduction of adhesion strength.

Currently, several solutions have been applied to modification of polyethylene in order to improve its adhesion strength onto metal substrate [2-4]. However, there are many challenges connected with possibility of polymer modification, process, and utilization in term of lining/coating need to be solved. A new modified polyethylene was developed to approach the solutions of these challenges. Due to limitations of information, the detailed composition and processing of this polymer is not released.

This paper presents an investigation of adhesion reduction of this new modified polyethylene lined on steel under corrosive liquid environment. In addition, a model was established to determine the adhesion energy. The influence of the exposure environment on mechanical properties which relates to its adhesion strength is also discussed in this paper.

2. The mechanics of peel test

The peel test is schematically illustrated in Fig. 1, in which, P is an applied force at peel angle θ for a lining/coating strip having thickness h and width b, and being displaced a distance da. The adhesion energy G_a of the lining/coating on substrate maybe calculated from the energy balance approach:

$$G_a = \frac{1}{b}\left(\frac{dU_{ext}}{da} - \frac{dU_s}{da} - \frac{dU_{dt}}{da} - \frac{dU_{db}}{da}\right) \qquad (1)$$

where U_{ext} is the external work done by the force P, U_s is the store strain energy in the peeling arm, U_{dt} is the energy dissipated during tensile deformation of the peeling arm, and U_{db} is the energy dissipated during bending of the peeling arm near the peel front.
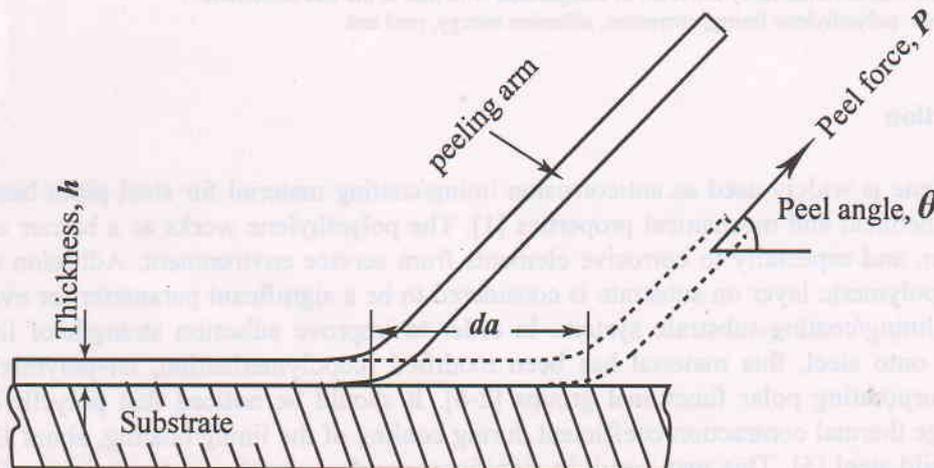
Fig. 1. Schematic of peel test.

Value of G_a reflects the energy to break the interfacial bonding forces and the energy dissipated locally ahead of the peel front in the plastic or viscoelastic zone at the crack tip. G_a is considered as a geometry-independent parameter.

$$dU_{ext} = Pda(1 + \varepsilon_a - \cos\theta)$$

$$d(U_s + U_{dt}) = bhda\int_0^{\varepsilon_a}\sigma d\varepsilon \qquad (2)$$

where ε_a is the tensile strain in the peeling arm. Therefore, G_a maybe obtained by the following equation:

$$G_a = \frac{P}{b}(1 + \varepsilon_a - \cos\theta) - h\int_0^{\varepsilon_a}\sigma d\varepsilon - G_{db} \qquad (3)$$

where G_{db} is the loss energy result from bending deformation, $G_{db} = dU_{db}/b$.

If the peeling arm is assumed to be only elastic, the adhesive fracture energy is then obtained by:

$$G_a^{eb} = \frac{P}{b}(1 + \varepsilon_a - \cos\theta) - h\int_0^{\varepsilon_a}\sigma d\varepsilon \qquad (4)$$

In case of the peel arm was made of from an infinite tensile stiffness ($\varepsilon_a=0$) and a zero bending stiffness material, the value of G_a obtains from the following equation:

$$G_a^{\infty E} = \frac{P}{b}(1 - \cos\theta) \qquad (5)$$

The maximum elastic energy G_{max}^e stored in the peeling arm for an elastic, non-working hardening material (work hardening parameter $\alpha = 0$) is given by

$$G_{max}^e = \frac{1}{2}(\sigma\varepsilon_y h) = \frac{1}{2}(E\varepsilon_y^2 h) \qquad (6)$$

where ε_y is the yield strain and E is the Young's modulus of the peeling arm. Therefore, the Eq.3 can rewrite as:

$$G_a = G_a^{eb} - G_{db} \qquad (7)$$
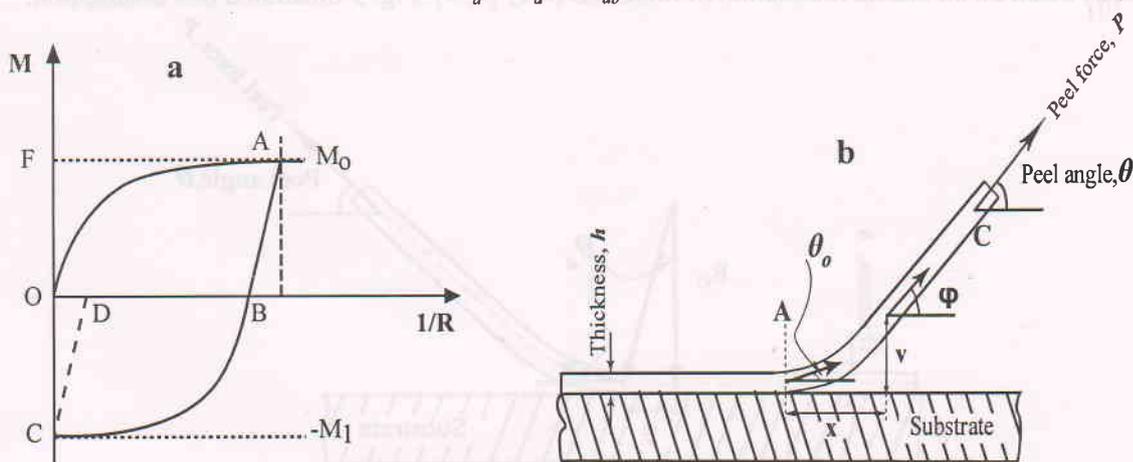
Fig. 2. Deformation of the peeling arm: (a) deformation process,
(b) large-displacement theory model of the peel test.

The deformation process is one of predominantly bending with large displacements. In the steady state, the peeling arm is loaded rapidly up to a maximum moment at which crack propagation occurs and then is unloaded at the section moving backwards. If the adhesive is plastic material, there must be reverse bending to straighten the arm at the away part from the peel front. This process is illustrated by Fig.2.

If the peeling arm formed from polymeric materials (corresponding to $k_0>2(1-\alpha)/(1-2\alpha)$ and $\alpha<0.5$), Gdb can be calculated from the followings [7] :

$$\frac{G_{db}}{G_{max}^e} = f_1(k_0) \tag{8}$$

$$\frac{G_a^{\infty E}}{G_{max}^e} = \frac{(1-\cos\theta)}{\left[1-\cos(\theta-\theta_0)\right]} f_2(k_0) \tag{9}$$

$$f_1(k_0) = \frac{4}{3}\alpha(1-\alpha)^2 k_0^2 + 2(1-\alpha)^2(1-2\alpha)k_0$$
$$+ \frac{2(1-\alpha)}{3(1-2\alpha)k_0}\left[1+4(1-\alpha)^3\right] - (1-\alpha)\left[1+4(1-\alpha)^2\right] \tag{10}$$

$$f_2(k_0) = \frac{1}{3}\alpha\left[1+4(1-\alpha)^2\right]k_0^2 + 2(1-\alpha)^2(1-2\alpha)k_0$$
$$+ \frac{8}{3}\frac{(1-\alpha)^4}{(1-2\alpha)k_0^{\bullet}} - 4(1-\alpha)^3 \tag{11}$$

$$\theta_0 = \frac{1}{3}(4\varepsilon_y)k_0 \tag{12}$$

The term k_0 is given by $k_0=R_1/R_2$ where R_0 is actual radius of curvature at the peel front and R_1 is the radius of curvature at the onset of plastic yielding, given by $R_0=h/2\,\varepsilon_y$.

Eq.12 is derived from concept of root rotation in which the deformation has is considered as an elastic beam on an elastic foundation of thickness ($h/2$) [8, 9]. Fig. 3 illustrated this assumption.
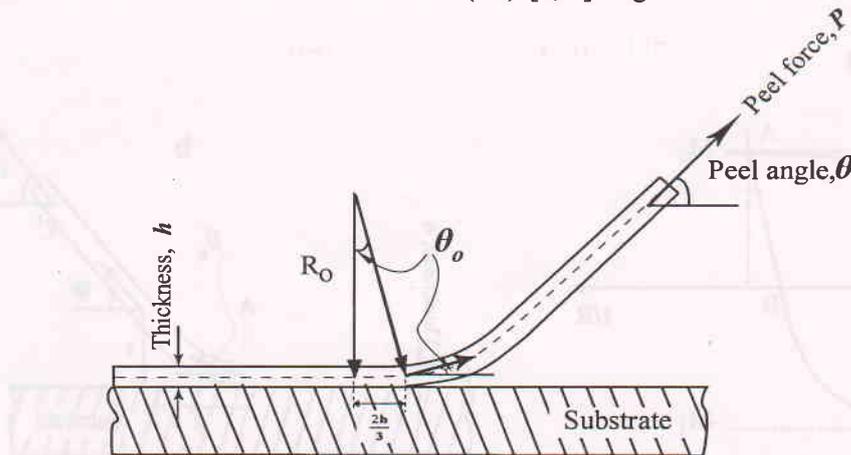
Fig. 3. Root rotation at the peel test.

3. Experimental details

3.1. Material

A medium polyethylene having density in range of 0.925 – 0.930 g/cm^3 was used as base polymer for this study. The polymer was chemically modified. An amount of 5 mass % of modification chemical together with 1 mass% of carbon black was used in the modification to form the sPE. In limitation of sharing information, the detail information of the modifier was not released.

3.2. Specimen Preparation and Experiments

Mild steel panels, having dimension of 85.0x85.0x3.5 mm, were sand-blasted in accordance with the Japanese Industrial Standard. Five orders of surface roughness, the Very low, Low, Medium, High, and the Standard, were prepared. The panels were lined with the based polyethylene (virgin PE) and the sPE, using hot compression molding performance within 8 hr after being sand-blasted. The lined polymer thickness was average of 1.5 mm. An exposure apparatus was designed, fabricated for testing these specimens under accelerated corrosive environment (Figure 4). The exposed specimens were then measured for adhesion strength. The lined polymer open-face was exposed to the 60°C water and 5, 10, 15 mass% of HCl solutions while the steel open-face side was exposed to the 15°C cycling water.
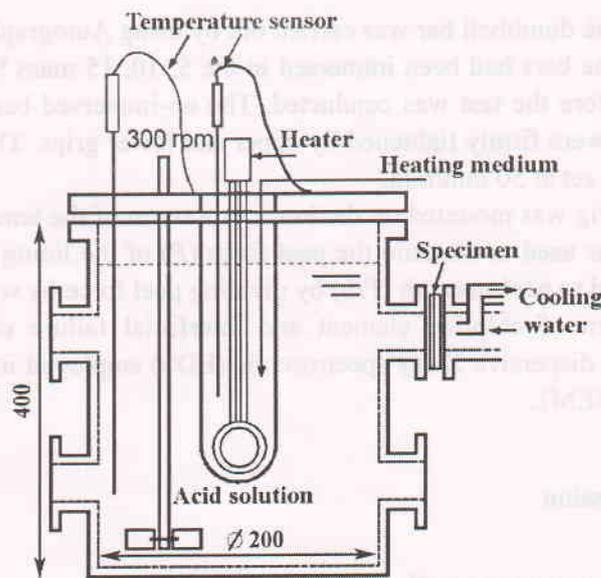
Fig. 4. Schematic diagram of accelerated exposure apparatus.

Dumbbell bar shape specimens were performed in accordance with Japanese Industrial Standard JIS K7115 for mechanical measurements. The polyethylene which was used to perform the dumbbell specimens is the same as those used for the lined specimens.

3.3. Characterization
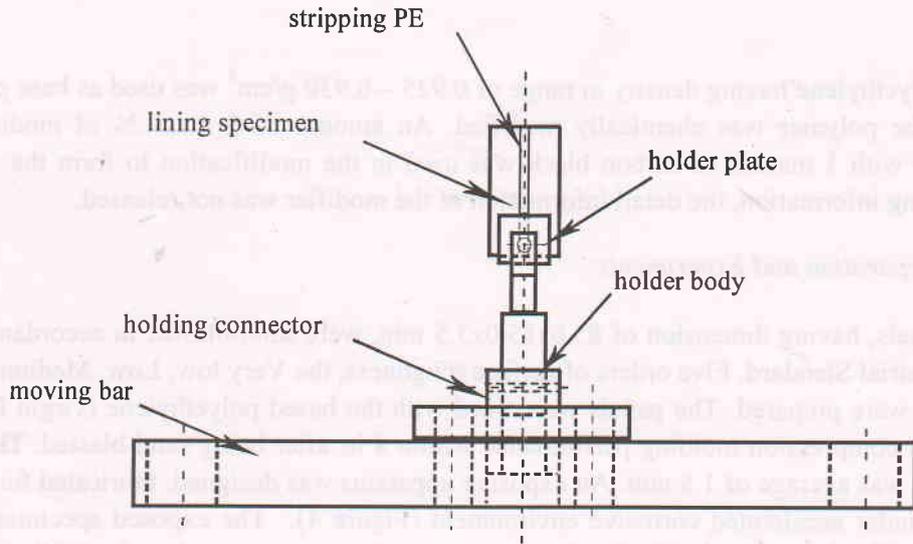
Fig. 5. Lower part of peel test.

Tensile stress of the dumbbell bar was carried out by using Autograph tensile test machine at 20°C and 30% humidity. The bars had been immersed in the 5, 10, 15 mass % hydrochloric acid solutions and water at 80°C before the test was conducted. The un-immersed bars were also conducted. Both ends of the specimen were firmly tightened by upper and lower grips. The initial distance was 50 mm and the strain rate was set at 50 mm/min.

An 180° peel test rig was mounted on the lower cross-arm of the tensile tester, as shown in Fig. 5. A 0.5 kN load cell was used to measure the peel force (*P*) of the lining strip having 5 mm width (*b*) and was then converted to peel strength (*P/b*) by dividing peel force by width.

Distribution pattern of chloride element and interfacial failure of striped polyethylene were analysed by an energy dispersive X-ray spectroscopy (EDS) employed in conjunction with a scanning electron microscopy (SEM).

4. Results and discussion

4.1. Effect of the environment to tensile property

Figure 6 represents the stress-strain curves of the initial sPE and the immersed sPE dumbbells in various solutions at 80°C. The main mechanical parameters of the dumbbell tests are detailed in table 1. The environment affected to the mechanical properties of the material. After 1200 h immersed in the solutions, the yield stress, yield strain, Young's modulus were reduced. A previous works [10, 11] have evidenced that the environment was absorbed into the piece tests, then reacted with the modifier, caused the change of chemical structure of the materials. The reduction in value of these parameters may attribute to this chemical structure change of sPE. Young's modulus reduced with increasing HCl

concentration while yielding stress changed considerably with the HCl concentration (table 1). It notes that the work-hardening parameter was equal to zero value for the initial sample, and was not changed after 1200 h immersion in all solutions.
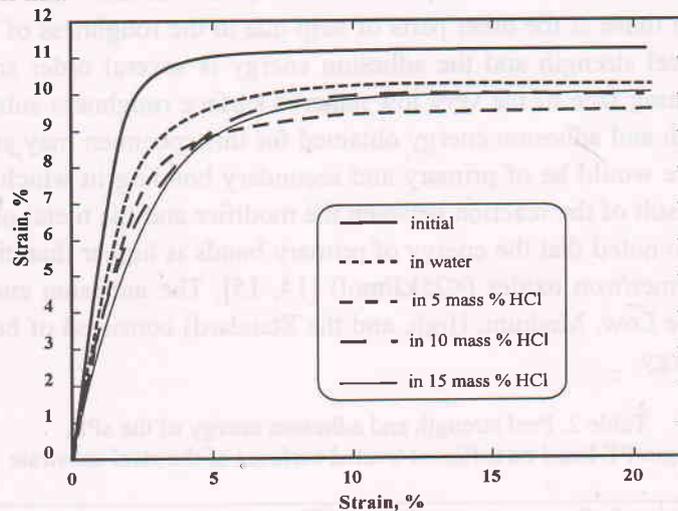
Fig. 6. Stress-strain curve of the sPE immersed in various environments at 80°C for 1200 hrs.

Table 1. Effect of exposure environment on tensile property of the sPE

Exposure Environment	Young's Modulus, E, (MPa)	Work-Hardening Parameter, α	Yielding Stress, σ_y, (MPa)	Yielding Strain, ε_y, (%)
Initial	578.63	0	11.20	1.936
Water	406.92	0	10.17	2.502
5 mass % HCl	345.98	0	9.49	2.742
10 mass % HCl	280.19	0	9.94	3.55
15 mass % HCl	268.11	0	9.95	3.71

4.2. Effects of substrate surface pre-treatment

Peel strength of the sPE on the blasted steel substrate is considered the result from mechanical interlocking and chemical bonding. According to the mechanical interlocking theory of adhesion, good adhesion occurs when an adhesive penetrates into pores on the surface of a substrate, and locks mechanically to the substrate. However, many studies suggested that interlocking may improve adhesion but only itself would not attain a good adhesion [12,13]. Improvement of surface roughness results in increase of surface area, enhancement of wettability of the substrate surface, which leads to the increase of mechanical adhesion. The chemical adhesion strength results from bonding between polymer functional group/coupling chemicals and the metal oxide/metal element of substrate at the interface.

Figure 7 shows the peel strength and adhesion energy of the sPE lined on different treated surface steel substrates. Order of the surface roughness was ranged from the very low (smooth surface) to the

standard (roughest surface). The results showed that the peel strength and adhesion energy increased with increasing lining surface roughness. It should be noted that the value of peel strength and adhesion energy based on the width at the open face of strip. The actual width of the strip at the lined face may be higher than those at the other parts of strip due to the roughness of surface before lining. Therefore, the actual peel strength and the adhesion energy is several order smaller than measured value. Assuming that lining face of the very low adhered surface roughness substrate is ideal smooth surface, the peel strength and adhesion energy obtained for this specimen may attribute to result from chemical bonding. There would be of primary and secondary bonding in which the primary bonding may be expected as a result of the reaction between the modifier and the metal oxides/ metal elements at the interface. It is also noted that the energy of primary bonds is higher than those of the secondary chemical bonds of polymer/iron oxides (<25kJ/mol) [14, 15]. The adhesion energy obtained for the other test specimens (the Low, Medium, High, and the Standard) consisted of both chemical bonding and the interlocking energy.

Table 2. Peel strength and adhesion energy of the sPE,
virgin PE lined on different treated surfaces of the steel substrate

Surface Roughness	Peel Strength, P (N/mm)		Stripped Thickness, h, (mm)		Adhesion energy, Ga, (J/m2)	
	Lined sPE	Lined PE	Lined sPE	Lined PE	Lined sPE	Lined PE
Very low	6.98	3.29	1.5	1.5	2657.5	743.2
Low	8.43	3.94	1.6	1.5	3442.8	1020.0
Medium	9.34	4.12	1.5	1.4	4168.6	1155.9
High	9.52	5.53	1.4	1.5	4440.2	1805.9
Standard	13.97	-	1.5	-	7547.1	-
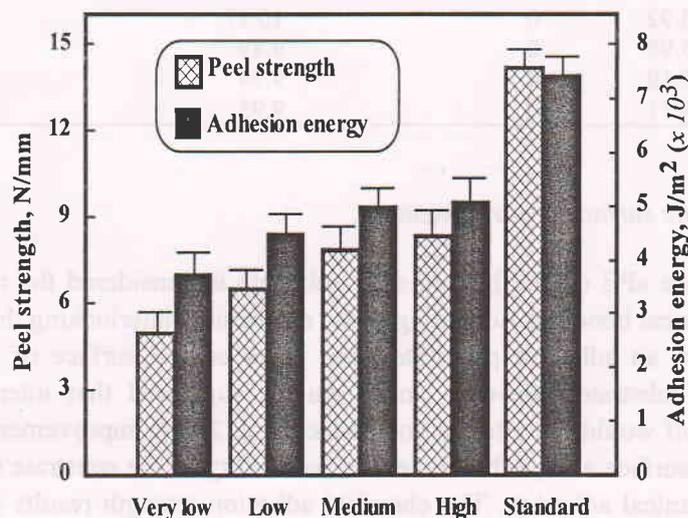
Fig. 7. Peel energy and adhesion strength of the sPE lined on different steel surface roughness.

Effect of the modifier on adhesion energy/ peel strength was investigated. Figure 8 shows the adhesion energy/peel strength of the lined virgin PE on different treated substrates. Given the smooth substrate case (the very low surface roughness), the fourfold lower adhesion energy than those of the lined sPE indicates that the modifier contributed to enhancement of the virgin polyethylene on steel. The virgin PE adhered to surface of the smooth surface specimen may be a consequence of the secondary chemical bonds between polymer and metal oxides/metal elements at the interface.

Table 2 details the peel strength and adhesion energy of the sPE, virgin PE lined on substrates with different surface roughness.
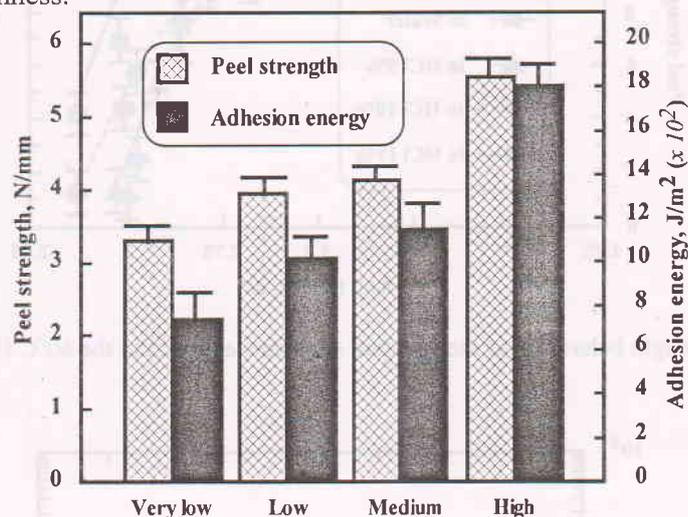
Fig. 8. Adhesion energy and peel strength of the virgin PE lined on different steel surface roughness.

4.3. Effect of environment on adhesion ability

Figure 9 and 10 show behaviours of the peel strength and adhesion energy for the Standard specimen under severe conditions respectively. The polymer open-face was in contact with the 60°C corrosive solution while the steel open-face was in contact with the 15°C cycling water. Results showed that the corrosive solution influenced significantly the peel strength, adhesion energy of the lined sPE on the substrate. For the water case, the peel strength was reduced about 15.04% (from 13.96 to 11.90 N/mm) for the first 864 h exposure while it reduced quickly (about 60.84% in comparison with initial value) for the next 178 h exposure. For the HCl solutions, peel strength reduction started early after the specimens had been exposed. The HCl concentration was effected on the peel strength reduction. After 720 h exposure, the peel strength reduction was about 53.94%, 35.67%, and 45.06% in comparison with the initial value for the HCl solution of 5, 10, and 15 mass%, respectively. The peel strength reduction may be explained by: (a)- the interfacial stress generated by difference of thermal expansion between the steel substrate and the lined sPE; (b)- corrosion of substrate caused by the diffused solution accumulating at the interface. It is found that the effect of the interfacial stress was insignificant on the overall peel strength reduction (Figure 11). Rust, chloride element found at the interface (Figure 12) were considered to be the corrosion products. For the interfacial corrosion aspect, the corrosive species may take over the chemical bonds between the

modifier/polymer and the metal/metal oxides crossing the interface due to their higher chemical potential than those of the bonds (primary, secondary bonds).
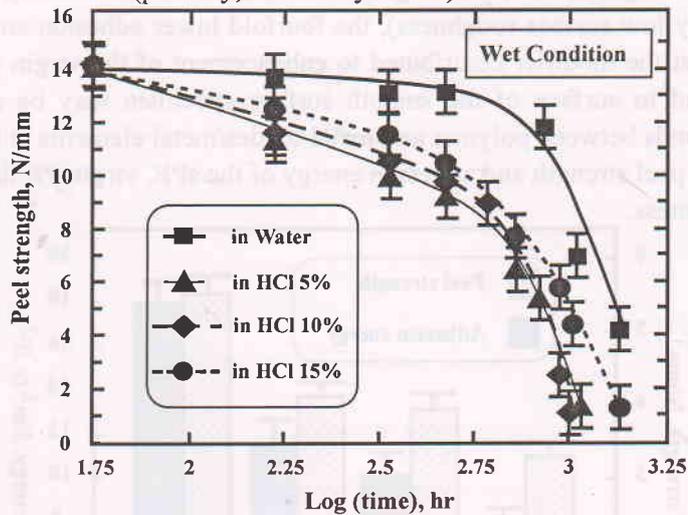
Fig. 9. Peel strength behaviour of the standard specimen exposed to the 60°C HCl solutions.
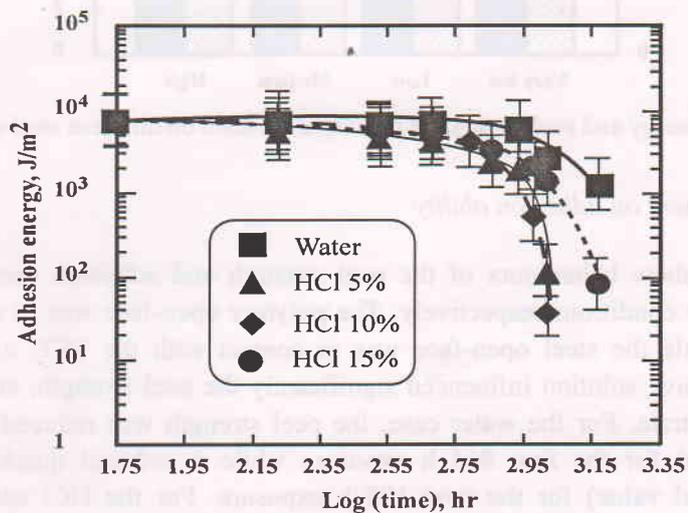
Fig. 10. Adhesion energy profile of the standard specimen exposed to the 60°C HCl solutions.

Another phenomenon related to the corrosion aspect is the flattening of substrate surface which leads to reduction of the interlocking between the lined sPE and the substrate. Therefore, peel strength reduction depends on the rate of corrosion reaction i.e., on the diffusion rate of the solution into lined polymer and chemical potential of the corrosive species. The previous work [11] showed that the meant diffusivity of the 60°C water, HCl 5, 10, and 20 mass% solutions into the sPE was 5.32, 5.33, 2.82, and 3.78 x10^{-14} m^2/s, respectively. For the water solution case, that the peel strength remained as the initial for first 560 h exposure may suggest that the corrosion process took place slowly in this

stage. When the amount of corrosive species (water, oxygen) at the interface exceeded a critical value, the corrosion took place quickly, resulting in the fast reduction of the peel strength. Chloride ion catalysed the corrosion process, resulted in the peel strength reduction in early. The quick reduction of the peel strength in the later stage for all solutions may attribute to lose the interlocking by surface flattening.
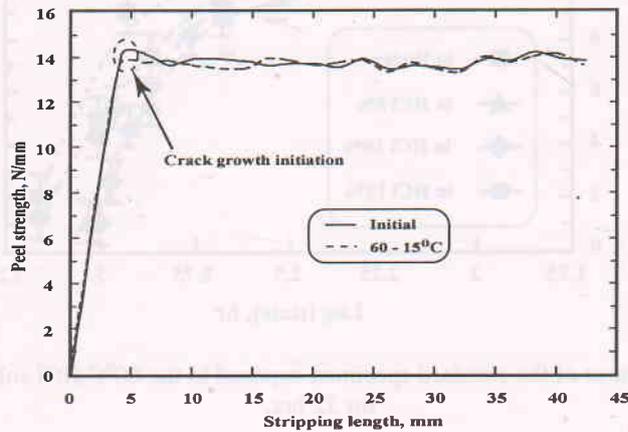
Fig. 11. Peel strength profile of typical samples.
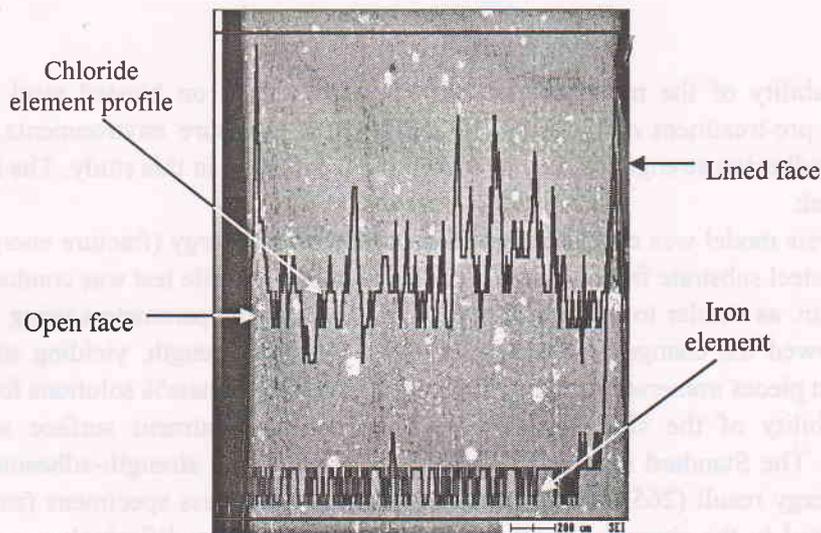
Fig.12. Iron and chloride element profiles on strip cross-section of specimen exposed.

Figure 13 shows the peel strength pattern of the specimens after 72 h drying at $50^{\circ}C$. It can be seen that there was no remarkable change of peel strength between the wet and dried condition. It may suggest that bonding recovery did not take place when water was removed out of the interface. A little lower value at a particular point for the dried condition in comparison with those of the corresponding point for the wet condition may attribute to the higher corrosion reaction rate at the dried temperature during the drying.
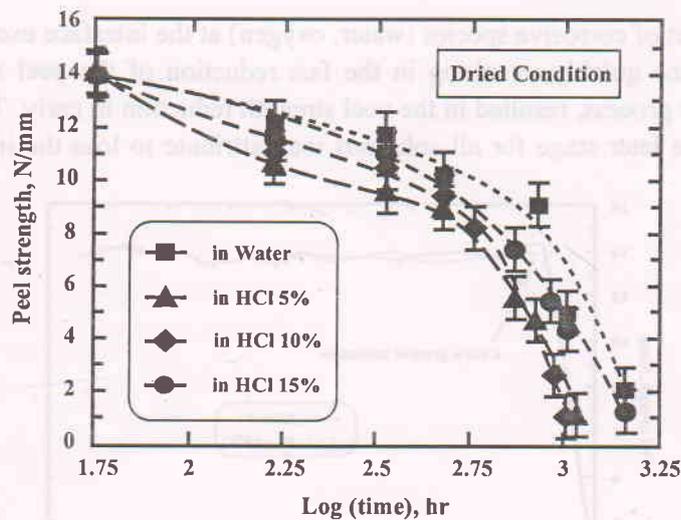
Fig. 13. Peel strength behaviour of the standard specimen exposed to the 60°C HCl solutions after drying at 50°C for 72 hrs.

5. Conclusions

The adhesion ability of the modified polyethylene (sPE) lined on blasted steel substrate was studied. Effects of pre-treatment of the substrate surface, the exposure environments, and elevated temperature on the adhesion strength, adhesion energy was conducted in this study. The followings are conclusions obtained:

1. A peel analysis model was established to calculate adhesion energy (fracture energy) of the sPE lined on the steel substrate from the peel data. The dumbbell tensile test was conducted at the rate of 50 mm/min. as similar to the rate of peel test to find out the parameters using for the model. The test showed the change of Young's modulus, yielding strength, yielding strain when the dumbbell test pieces immersed to the 80°C water, HCl 5, 10, 15 mass% solutions for 1200 h.

2. Adhesion ability of the sPE lined on the different pre-treatment surface substrates was investigated. The Standard specimens showed the highest peel strength-adhesion energy. The adhesion energy result (2657.5 J/m^2) for the Very low roughness specimens (smooth surface) was considered to the chemical bonding energy between the modifier/polymer and the metal oxides/metal crossing the interface. The peel strength of lined virgin PE for these substrates was also measured. The value of 743.2 J/m^2 for the Very low roughness specimens was attributed to chemical secondary bonding energy of the base polymer and the substrates. The higher value of adhesion energy for other specimens resulted from mechanical energy (interlocking) and chemical bonding energy (primary, secondary bonds).

3. The Standard specimen was used for testing the effects of corrosive environment on its peel strength, adhesion energy. The effect of thermal expansion difference between the sPE and the Standard specimen on the peel strength was insignificant. For the specimens exposed to water, the reduction of 15.04% peel strength in comparison with the initial for first 864 h exposure

was found while those exposed to the HCl solution was reduced about 53.94, 35.67, and 45.06 % in comparison with the initial for the first 720 h exposure. Corrosion is considered a main reason for this reduction. Chloride ion accumulated on the interface was attributed to catalysis of the corrosion process. The peel strength for dried specimens was unremarkably different in comparison with that in the wet condition.

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