Blistering behavior of a Lined Fluoropolymer-steel Substrate on Exposure to a HCl Acid Aqueous Environment

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ABSTRACT: In this paper, blister formation on a lined fluoropolymer-steel substrate’s exposure to water and hydrochloride acid solution at different temperatures and temperature gradients was studied. The higher the temperature gradient between the lining and the substrate, the faster the blister will form. In the absence of a temperature gradient, the temperature also affects the formation of blisters. The higher the working environment temperature, the faster the blistering will appear. Even so, the role of temperature gradients in promoting blistering is far greater than that of temperature. The concentration of HCl solution also affects the formation of blisters. Blistering occurs more slowly in high-concentration solutions and water is determined to be the main cause of blister formation.

INTRODUCTION

Isolation of a metal from its corrosive environment by polymeric lining is considered the most general approach for corrosion protection. Effective isolation requires that polymeric materials have good barrier properties, significant chemical resistance, and remain adherent to the substrate in the presence of corroding components. The lining is also needed to improve the flow rate of the working environment as well as easy surface cleaning. However, there is no polymeric material having perfect barrier property for water, oxygen, and other corrosive elements; therefore, failures of the polymeric lining systems are observed after a period of service life. The failures are delamination, blistering, and interfacial degradation, especially for lining systems serving under a liquid environment.

Blistering is normally caused by an osmotic process. For a polymeric lining system, the polymer layer acts as a selective permeable membrane. It can be highly permeable to water, for example, whereas it is less permeable to water-soluble substances. If the water-soluble substances are present on the interface, a concentration gradient to the outer environment will be established. This concentration gradient is the driving force for additional water diffusing into the polymer to balance the concentration of solutes. In consequence, an osmotic pressure is established. When stresses resulting from the osmotic pressure exceed the critical strength of the polymer, microcracks may occur and blisters may initiate.

Blister formation may also result from temperature gradient. Thermal stress between the lining and substrate, condensation of water vapor on the interface, cathodic lamination, and polymer swelling are considered the alternative reasons for blister formation. Once a blister occurs, at first, the polymeric lining loses adhesion to the substrate. Area of adhesion loss expands with expanding of the blister. When the osmotic pressure inside the blister exceeds the breaking point of the lining material, the lining layer is broken, resulting in loss of isolation function of the layer.

Fluoropolymers are often chosen for corrosive services due to their relative cost position compared with high alloy materials and their availability. Fluoropolymer products have excellent chemical resistance to aggressive solutions. However, this material still allows corrosive substances such as oxygen, water, and acids both in the form of gases and liquids to permeate and accumulate on the interface between the substrate and the lining, creating osmotic pressure and losing the adhesion of the lining to the metal substrate. Permeation can be influenced by temperature and corrosive solution concentration.

RESULTS AND DISCUSSION

Effect of temperature gradient on blistering characteristic. Blisters appearing on the lining side are defined as...
small, medium, or large blister if their maximum dimension is less than 1 mm, from 1.0 to 5.0 mm, or over 5.0 mm, respectively. Illustration of blister classification is shown in Figure 1.

Temperature gradient and nature of corrosive environment play an importance for blister creation. Figures 2 and 3 show the effect the temperature gradient on blistering performance of the lining system exposed to water. The results pointed out that the higher the temperature gradient between the steel face and the lining face, the faster the blistering will appear.

First blisters appeared after 78 h at the temperature gradient of $80-25^\circ$C, 157 h at the temperature gradient of $60-25^\circ$C, and 348 h at the temperature gradient of $40-25^\circ$C. To further understand the role of temperature gradient in blistering, another investigation was carried out where the temperature of the steel substrate side is set equal to the temperature of the lining side. The time of blister appearance obtained by this investigation is shown in Figure 4. Without temperature gradient, the first blisters were observed after 447 h at the temperature of $80-80^\circ$C and after 1258 h at temperature of $60-60^\circ$C. However, there was no blister observed after 2468 h for specimens that underwent the temperature of $40-40^\circ$C. Therefore, it can be seen that temperature gradient promotes the formation of blistering more strongly than the temperature. For example, first blisters appeared after 348 h at the temperature gradient of $40-25^\circ$C, whereas it took 447 h for specimens taken at $80-80^\circ$C.

Many studies show that the formation of blistering when the coating system is exposed to a moist environment is due to osmotic pressure. Consider a blister having a spherical shape with volume $V$ and debonded surface area $A$ and with other parameters as shown in Figure 5. Assume that the PFA lining is inextensible and that the load $p$ is the osmotic pressure generated by the difference of water concentration in between the interface and the polymer. The load contributes uniformly over the blister surface.

On blistering, parameters such as the height of the blister, $H$; the distance from center to inner surface of the blister, $s$; and the contact angle, $\theta$ change. However, they are all fixed with a given debonded strength $2s$ and have the following relationships.
The energy needed to create the blister at a given time can be calculated by

\[ E = \frac{pV}{dA} \]

in which

\[ V = \frac{1}{3} \pi R^3 (2 - 3 \cos \theta + \cos^2 \theta) \]

\[ A = 2\pi R^2 (1 - \cos \theta) \]

Noting that \( s = R\theta \), then

\[ \frac{ds}{d\theta} = \theta \frac{dR}{d\theta} + R = \frac{dR}{d\theta} \sin \theta + R \cos \theta \]

that is

\[ \frac{dR}{d\theta} = -R \left( \frac{1 - \cos \theta}{\theta - \sin \theta} \right) \]

\[ \frac{dA}{d\theta} = -R \left( \frac{\sin \theta - \theta \cos \theta}{\theta - \sin \theta} \right) \]

and

\[ dA = 2\pi n d\theta \]

Thus, the needed energy for the creation of a blister can be rewritten as

\[ E = \frac{pR}{2} (1 - \cos \theta) \]

Osmotic pressure can be calculated from eq 10. The amount of water inside a blister depends on the diffusion process and can be calculated by the following

\[ p = \frac{nR^*T}{V} = \frac{mR^*T_i}{MV} \]

where \( M \) is the water molecule number, \( R^* \) is the gas constant, \( T \) is temperature in the Kelvin scale, and \( m \) is the mass of water inside the blister which can be computed by

\[ m = Q_i A = \frac{DC}{h} \left( t - \frac{h^2}{6D} \right) A \]

in which \( Q_i \) is the amount of permeated water for a given time \( t \), \( h \) is the thickness of the polymer lining, \( D \) is the diffusivity, and \( C \) is the concentration of water inside the polymer. Hence, osmotic pressure can be computed as

\[ p = \frac{6DC}{hMR(2 - \cos \theta)} \left( t - \frac{h^2}{6D} \right) R^*T_i \]

and the energy needed for creating the blister will be computed by

\[ E = \frac{3DC(1 - \cos \theta)}{hM(2 - \cos \theta)} \left( t - \frac{h^2}{6D} \right) R^*T_i \]

The dependence of diffusivity on temperature was described by the Arrhenius mode as follows

\[ D_T = D_0 \exp(-E_0/R^*T) \]

where \( E_0 \) is energy activity of the system. Therefore, the diffusivity \( D \) over the temperature gradient can be computed by

\[ D = \int_{T_1}^{T_2} D_T dT = D_0 \int_{T_1}^{T_2} \exp(-E_0/R^*T) dT \]

By putting eq 15 into eq 13, the blister energy can be calculated by

\[ E = \frac{3D_0C(1 - \cos \theta)}{hM(2 - \cos \theta)} \int_{T_1}^{T_2} \exp(-E_0/R^*T) dT \]

\[ \left( t - \frac{h^2}{6D} \right) R^*T_i \]

A blister will occur if the blistering energy is higher than the adhesion energy of the PFA lining on the steel substrate. Based on this rule, eq 16 may explain the significant effect of the temperature gradient on the blistering performance.

**Effect of HCl Concentration.** The effect of HCl—aqueous and vapor—on blistering of the lined PFA-steel substrate system was investigated by using the experiment apparatus as shown in Figure 1b. The temperature gradient was set constant at 80–25 °C. In this experiment, a part of the lining side was exposed to HCl aqueous, whereas the other part was exposed to HCl vapor. The observed results show that blisters occur in both parts exposed to the solution and HCl vapor. However, number of blisters of the part that was exposed to HCl solution is higher than that of the part exposed to the vapor. Figure 6 shows the blistering performance of the lining system after 216 h exposure in 5% mass HCl solution.

The difference in blistering density between the two parts may be due to the different moisture and HCl content between the liquid phase and the vapor phase. In the vapor phase, the partial pressure of water is less than 333 mmHg, whereas HCl is about 0.1505 mm Hg over HCl aqueous solution. The partial pressure of moisture is many times greater than that of HCl which may indicate that blistering formed only by moisture. The results of energy dispersive spectroscopy (EDS) analysis showed that no trace of the element, Cl was detected along the PFA lining thickness (see Figure 7). The pH index of liquid inside the blisters was measured, and its value was around 6.7–7.0. From this evidence, it is confirmed that the HCl component in the vapor phase affects blister formation insignificantly.

It is the same phenomenon for specimens tested in the 15% mass HCl solution (see Figure 8). However, delamination of the PFA lining was observed for specimens exposed to 30% mass
HCl solution. Figure 9 shows that blisters appear after about 577 h with the test specimens in the 30% mass HCl solution exposure area, whereas some corroded parts were found in the vapor exposure area.

EDS analysis was also conducted on cross section of the specimens and is shown in Figure 10. Chloride element was found on the interface between the lined polymer and the substrate of the part exposed to the HCl vapor phase. It confirms that HCl gas permeated into the lined PFA, reached to and corroded the interface, and resulted in loss of adhesion of the lined PFA. It is the main reason of the lining delamination.

For the coating system, blistering is a dangerous phenomenon but the loss of adhesion seems even more dangerous. Experimental results show that for devices that use PFA lining to prevent the corrosion of HCl acid solution, it is necessary to minimize the lining in contact with the HCl vapor phase.

The effect of HCl acid concentration on the formation of blisters is shown in Figure 11. Experimental results show that the higher the concentration of HCl, the longer time it takes to form blisters. Specifically, to form a blister, the time required for the specimens exposed to the 30% HCl acid solution was 577 h, to
the 15% HCl acid solution was 348 h, and to the 5% acid solution was 218 h, whereas to water was only 78 h. This suggests that water is important for blister formation. Water in the HCl acid solution diffuses into the PFA lining faster than the HCl component and soon approaches, accumulating on the interface, generating osmotic pressure which is the driving force to form blisters. In the vapor, HCl in the gaseous form seems to easily diffuse into the lining polymer and reach the interface, corroded steel part in the interface by specific reactions.21,22 The green color of the delaminated surface indicates the presence of FeCl₂, a product of the corrosive reaction between Fe and HCl, whereas the brown color may attribute to FeCl₃, a corrosion product between Fe₂O₃ and HCl.

## CONCLUSIONS

The effect of temperature gradient and HCl concentration on blistering of PFA-lined steel system in contact with water and HCl acid solution was studied. The higher the temperature gradient between the lining and the substrate, the faster the blister will form. In the absence of a temperature gradient, the temperature also affects the formation of blisters. The higher the working environment temperature, the faster the blastering will appear. Even so, the role of temperature gradients in promoting blistering is far greater than temperature. The concentration of HCl solution also affects the formation of blisters. Blistering occurs more slowly in high-concentration solutions and water is determined to be the main cause of blister formation. When the specimens were exposed to HCl vapor generated from the HCl solution, blisters were also formed, especially, at high concentrations of HCl; loss of adhesion of PFA lined on the steel substrate was also observed.

## EXPERIMENTAL

**Materials.** Fluoropolymer lining system specimens made of fluoropolymer named as PFA from Nippon Fusso Co. Ltd, Japan, lined on carbon-steel substrate having side of 85 mm by 85 mm with lining thickness of 1 mm were utilized in the study. The specimens were dried in a drying oven at 50 °C for at least 100 h to ensure that no free water remained before conducting the experiments.

**Blistering Study.** The blistering experiment was carried out by installation of the specimens into the corrosive aqueous environment and the acid vapor—aqueous apparatus as shown in Figure 12a,b, respectively. The polymer side of the specimens was in contact with de-ion water or the HCl solution, whereas the steel side was in contact with recycle-cooling water.

Temperature of the corrosive solution (Tₛ) was set constant at 40, 60, and 80 °C, whereas the temperature of the recycle-cooling water (Tᵣ) was set constant at 25 °C. Water and 5, 15, and 30% concentration in mass percentage of HCl solution was used as the corrosive environment. At interval times, the specimens were taken out and wiped by a filter paper to remove attached solution on their surfaces for observation of blisters by using the microscope TGG200HD2 model from Shodensha Company, Japan. Permeated depth of the chloride element into the lined polymer was studied by application of the energy X-ray spectrometer method on the cut-cross section surface of the exposed specimens. A JSM-5310LV [for scanning electron microscopy] combined with JED 2100 (for EDS) were used for this investigation.

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**Notes**

The author declares no competing financial interest.

## ACKNOWLEDGMENTS

The author is grateful to the Department of Science & Technology of the Hanoi City (Vietnam) for financial support (Grant TC.03-2016-03).

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