SORPTION AND DIFFUSION OF ALKALINE SOLUTION IN ORGANIC COATINGS AT AMBIENT AND ELEVATED TEMPERATURES

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SORPTION AND DIFFUSION OF ALKALINE SOLUTION IN ORGANIC COATINGS AT AMBIENT AND ELEVATED TEMPERATURES

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Introduction

When a polymer-coated steel panel containing large defects is exposed to aggressive environments, such as salt water, corrosion (anodic reactions) takes place at the defects and cathodic processes occur underneath the coating around the defects (1, 2). For coated panels having no detectable defects, pathways or small pores through the coatings are first formed (3). Anodic reactions then take place at the base of the pathways or pores, and cathodic reactions occur around the pathways. The cathodic areas have a high pH (>11). This has been verified by a strong violet coloration in a clear coating containing a phenolphthalein pH indicator (4) or after spraying with the same indicator over the delaminated area (5). Indeed, a pH value of 14 has been reported at the cathodic delamination front of coated steel exposed to 3.5 % NaCl solution (6). The strong alkalinity at the cathodic sites has been attributed to the oxygen reduction reaction (1,2):

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

where the electrons are supplied from the anodic reactions. Thus, the surface of the coating surrounding the cathodic blisters and cathodic delaminated areas are subjected to a strong alkaline environment. This study investigates the sorption and diffusion characteristics at 60 °C and at ambient temperature (22 °C) of an alkaline solution in an amine-cured epoxy and an isophthalate polyester coating. A knowledge of the sorption characteristics of alkaline solutions in polymer coatings would provide a better understanding of their protection performance against corrosion of metals in electrolytes.

Experimental Procedures

Polyester films of 250 μm ± 10 μm were prepared by molding the mixture of 100 parts of an isophthalate ester resin and 2 parts of a methyl ethyl ketone peroxide catalyst between two sealed plates. Films were allowed to gel at ambient condition (22 °C and 45 % RH), followed by a 2 h 150 °C cure in an air-circulating oven. Epoxy films of 300 μm ± 8 μm were prepared by mixing 100 parts of a diglycidyl ether of bisphenol A (epoxide equivalent weight = 189 g) and 42 parts of a polyether-triamine (amine equivalent = 83 g). After degassing, the coating was applied to smooth aluminum foil using a draw down applicator. Films were cured at ambient conditions for 24 h, followed by heating for 2 h at 120 °C in an oven. The alkaline test solution contained 0.23 mol/KOH, 0.14 mol NaOH and 2.0×10^{-3} mol/L $Ca(OH)_2$ in distilled water. This solution had a pH of 13.5 and was used to simulate a concrete pore solution. The results of the study are therefore, directly applicable to polymer-coated reinforced steel.

Free standing films having dimensions of 25 mm x 25 mm were immersed in the test solution contained in screw-top glass jars placed in a sand bath maintained at 60 °C ± 2 °C, with each jar containing one specimen. Specimens were periodically removed from the solution, rinsed thoroughly with distilled water, blotted dry, and weighed using an automatic balance. The same procedure was applied for measurements at ambient temperature, except that no sand bath was used. Six specimens were employed for each coating. Film thicknesses were measured at three different locations on each specimen using a micrometer. Solution uptake in the coatings was measured as a change in mass with respect to the initial film mass. The bulk diffusion coefficient, D, of the solution was calculated from the uptake data using the sorption kinetics approach (7). Solubility of the alkaline solution in the films was calculated as the product of the sorption at equilibrium and film density, the latter being measured by the water displacement method. Glass transition temperatures (T_g) of the coatings before and after saturation in the test solution at 60 °C and 22 °C were measured by differential scanning calorimetry (DSC).

Results and Discussion

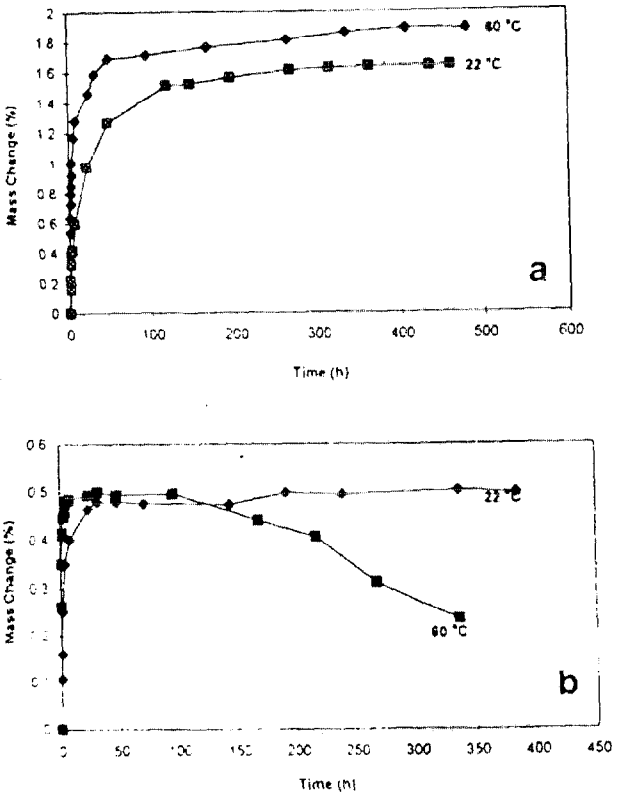

Figure 1. Alkaline uptake at two temperatures for epoxy (a) and polyester (b) coatings.

Figure 1 displays the sorption characteristics, and Table 1 includes data on T_g changes with exposure, solubility, and diffusion coefficient of the two coatings immersed in the solution at 22 °C and 60 °C. T_g of the epoxy decreased substantially and T_g of the polyester reduced slightly after exposure at both temperatures. Both the sorption rate and solubility were greater at 60 °C than at 22 °C for both coatings. Further, once an equilibrium sorption was reached, little change in mass was observed, even up to 400 h immersion, at either

Table 1. T_g, D, and sorption properties of coatings before and after immersion to alkaline solution at 22°C and 60°C.

Property	Epoxy			Polyester		
	1[a]	22°C	60°C	1[a]	22°C	60°C
T_g °C	80.1	68.3	68.4	105.0	101.3	98.3
Solubility (mg/cm^3)[b]	---	18.6	21.4	---	5.8	6.1
D, 10^{-9} (cm^2/s)	---	0.7	9.8	---	8.9	34.1

T_g was measured on saturated specimens using DSC at 10°C/min heating rate; (a) Before exposure; and (b) Mass of water per unit volume of the specimen.

temperature for the epoxy or at 22°C for the polyester. However, a mass loss was observed for the polyester after 100h immersion at 60 °C. This mass loss was probably due to the base-catalyzed hydrolysis of the ester groups, as evidenced by FTIR analysis of the test solution (8). These results suggest that conductive pathways may develop in a coating film surrounding the cathodic blister and cathodic delaminated areas when an isophthalate polyester coated steel panel is exposed to a warm corrosive environment. The consequence of pathway formation

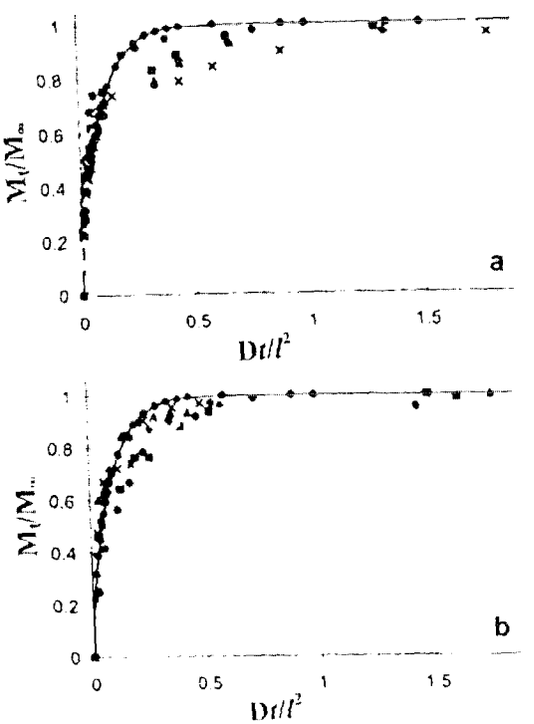

Figure 2. Reduced sorption curves for epoxy (a) and polyester (b) coatings immersed in alkaline solution at 60 °C. (Different symbols represent data for six different specimens, and solid lines are from Fickian diffusion theory)

implies that ions from the environment probably migrate to the metal surface under the coating.

Figure 2 shows the reduced sorption curves for the two coatings immersed in the test solution at 60 °C. Values for M_∞(sorption at equilibrium) of the polyester were taken at 25 h immersion (from Figure 1b). Experimental data (including for ambient temperature exposure) fit well with theoretical curves up to M_t/M_∞ (sorption at time t/sorption at equilibrium) = 0.7, indicating that the diffusion of the alkaline solution in the two coatings followed a Fickian process. Despite a higher T_g and a lower solubility, the diffusion coefficients of the polyester at 22 °C and 60 °C were, respectively, approximately 12 times and three times higher than those of the epoxy. Further, the D value of the epoxy at 60°C was 14 times greater than its value at ambient temperature. However, the difference of D between the two temperatures for the polyester was only one third of that of the epoxy coating. The larger D difference between ambient and elevated temperature for the epoxy was probably because the 60 °C exposure temperature approached the T_g of the saturated specimen. This interpretation is consistent with the literature, which showed that the diffusion of water above T_g in most polymers is several orders of magnitude greater than that at temperatures below T_g (9).

Conclusions:

Sorption and diffusion of amine-cured epoxy and isophthalate polyester coating in a pH 13.5 alkaline solution at 22 °C and 60 °C were investigated. Diffusion of the solution in both coatings at ambient and elevated temperatures followed a Fickian process. However, the increase of the epoxy coating diffusion coefficient was more than three times that of the polyester when the immersion temperature was increased from ambient to 60 °C. The results also showed that there was no evidence of mass reduction up to 400 h exposure at either ambient or elevated temperature for the epoxy coating or at ambient for the polyester. However, a mass loss, believed to be due to base-catalyzed hydrolysis, was observed for the polyester at elevated temperature. This degradation may result in the pathway formation through the coating, which may lead to accelerated corrosion of coated metals.

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