

The effect of the transport properties of epoxy based coatings on metallic substrate corrosion

P. MASTRONARDI, C. CARFAGNA

Istituto G. Donegani C.R. Napoli, Via Nuova delle Breccie, 150 Napoli, Italy

L. NICOLAIS

Polymer Engineering Laboratory, University of Naples, Napoli, Italy

An attempt is made to correlate the protective properties of different epoxy based coatings with their water transport properties. Rust formation on the support and blister growth on the varnish are strongly affected by the equilibrium uptake and diffusion coefficient of water. An evaluation of these parameters can give useful information on the capability of different paints.

1. Introduction

The protection afforded by organic coatings against the corrosion of the metallic support can be strongly affected by water transport. As a consequence of prolonged exposure to a high humidity environment, coatings can show dramatic failure in service. In fact epoxies, widely used as protective paints, are considerably sensitive to water sorption. Due to the hydrophilic character of the epoxy bond, the equilibrium water uptake can reach very high values leading to phenomena such as plasticization and subsequent depression of the glass transition temperature [1]. As a result, blister growth on the film surface can be observed after prolonged immersion in water. This phenomenon is caused by an increase of volume caused by water swelling, and by the loss of adhesion at the interface coating-support [2]. Both effects can be observed when a strong affinity between water and the polymer is present. In addition to these phenomena, related to the molecular structure of the binder, water diffusion can lead to the solvation of solvents and low molecular substances entrapped in the paint after drying.

The loss of these substances can affect the mechanical performance of the film. The desorption of solvents can produce blisters, due to the osmotic flux through the film [3]. In addition to these so-called transport properties of the cured

films, the effect of the environment on the properties of the coatings must be considered. In fact, previous results on water sorption in epoxy resins have shown that both the kinetics and the apparent equilibrium of the sorption phenomena can be strongly influenced by the temperature and humidity history which the samples have undergone prior the experiment [4-6]. An analysis [7] of the effective diffusion coefficients based on the dual mode sorption theory [8] confirmed the heterogeneous nature of the damage associated with network inhomogeneities of regions of low and high crosslinking densities. For epoxy paints, these different crosslink distributions can be strongly affected by the presence of a second phase.

In this case it is expected that the incorporation of a pigment into the matrix may change the water transport properties, depending on the pigment volume fraction, the chemical constitution, the geometry and the dispersion [9].

In a similar way, the blend of epoxy binder with hydrophobic coal tar can reduce the equilibrium value of water sorption enhancing the capability of the film mostly for immersed structures in very aggressive environments.

In a previous paper [10] it has been shown that sorption-desorption experiments can give useful information on the performance of epoxy based

TABLE I Coatings tested and their formulation

Material	Supplied by	Formulation
Venolite	Veneziani Zonca	Epoxy-Tar
Titania EP	Duco	Epoxy-Bentonite-TiO ₂
Araldite GY 250	Ciba Geigy	Epoxy

coatings. In this communication an attempt is made on the correlation between the water transport properties of epoxy films and the corrosion of the metallic support immersed in sea water. Results are also shown on the loss of adhesion and blister formation for cathodic protected samples.

2. Experimental details

2.1. Sorption kinetics and equilibria

Specimens were prepared from the materials reported in Table I, according to the technique previously described [10]. Gravimetric liquid sorption experiments were performed by weighing 3.0 cm × 1.0 cm × 0.02 cm samples on an analytical balance following immersion in water maintained at constant temperature. The samples were removed from the water, blotted, placed in a weighing bottle, weighed and finally replaced in the constant temperature pool.

Sorption data are reported as a percentage of weight gain referred to the dry weight and plotted as a function of $(t/l)^{1/2}$, where l is the thickness of the samples, ranging from 0.1 to 0.2 mm. Sorption equilibria were achieved over 60 days. Sorption equilibria in humid environments were achieved by conditioning samples at room temperature in an environmental chamber at a relative humidity ranging from 15 to 98% ± 3% RH. The relative humidity was controlled by using saturated salt solutions. All experimental points on the curves represent an average of at least three measurements.

2.2. Cathodic protection

Panels were prepared using sand blasted (grade ASa 2½ Swedish standard) and degreased mild steel sheets, 150 mm × 80 mm × 1.5 mm. The paints were brush applied in duplicate in a dust free environment maintained at 20°C. After ageing for two days at this temperature, the curing was initiated at 80°C under vacuum for 24 h and finally the temperature was brought to 110°C for a curing stage of three days.

Samples were subsequently stored in a desiccator containing anhydrous silica gel before testing. After curing, the thickness of the film was about 200 ± 20 μm. The panel edges were wax coated to

eliminate edge effects. All tests were performed using sea water at 20 ± 2°C as test electrolyte, previously filtered by 0.4 μm pore size filter; oxygen saturation was assured by air bubbling from an electrical aereator.

An Amel 551 potentiostat was used for cathodic protection of the test panels. A platinum counter-electrode and a saturated calomel electrode (SCE) closed the electric circuit. The imposed potential for protection was -950 mV (vs SCE), lower than the value -800 mV requested to protect metallic structures immersed in sea water [11-21]. However, this value best simulates the overprotection conditions characteristic of areas nearby the anodes of the cathodic protection system, not sufficiently shielded [22].

2.3. Corrosion potential

Corrosion potential-time measurements were carried out on samples similar to those of the cathodic protection test. A second set of measurements was developed on mild steel rods ($\phi = 18$ mm, $l = 150$ mm) previously sand blasted and degreased.

The painting and curing cycle was executed in the way described in the previous section. The free corrosion potential evaluation was carried out connecting the test electrode and a SCE to an HP Multimeter 3490 A. All tests were performed according to the experimental protocol previously described. Readings were taken at intervals for a period of about four months.

3. Results and discussion

The equilibrium values of water sorption, for the three different paints at constant temperature of 20°C, are reported in Fig. 1. These results are typical of low hydrophilic polymers [23]. In fact the more hydrophilic ones, have typical "S" form sorption curves, characteristic of polymers with strong hydrogen bonding sites [24]. For such materials, water uptake is higher than expected at very low penetrant activity; at high humidity, it increases almost asymptotically. In our case, only a progressive increasing of water gain is observed with water activity.

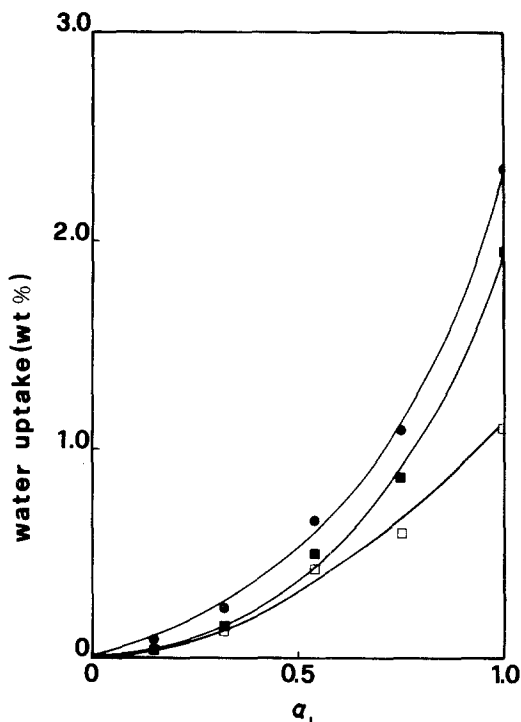


Figure 1 Water uptake against water activity for Araldite (●), Titania (■), Venolite (□), at $T = 20^{\circ}\text{C}$.

A successful description of the equilibrium solvent uptake in polymers, for non-interacting molecules has been derived as a function of the penetrant activity [25]:

$$\ln a_1 = \ln v_1 + v_2 + \chi_1 v_2^2 \quad (1)$$

where the subscripts 1 and 2 refer to the solvent and polymer, respectively, v is the volume fraction and χ_1 is a dimensionless quantity which characterizes the interaction energy per solvent molecule.

Equation 1, however, represents the limiting case for poorly mutually interacting polymer and diluent groups. χ_1 generally varies with concentration: the value (> 0.5) is indicative for poor solvation. Previous authors [26] studied the sorption of water in several polymers, including cellulose acetate, polyvinylchloride and polymethylmethacrylate and found that χ_1 either increased or decreased with a_1 . Variations of χ_1 would reflect deviation from simple Flory-Huggins behaviour and, therefore, deviations from random mixing.

The interaction parameters, calculated for the investigated coatings are reported in Table II. Their values are decreasing with increasing activity, especially for Titania and Araldite, whose water sorption isotherms show dramatic upturns at activities above 0.7.

TABLE II Solubility parameter (χ_1) as calculated at different relative humidity

Coatings	$\chi_1^{(0.50)}$	$\chi_1^{(0.70)}$	$\chi_1^{(1.00)}$
Venolite	3.70	3.37	3.18
Titania EP	3.30	2.94	2.55
Araldite GY 250	3.42	3.19	2.79

For these coatings, the vapour sorbed at low activities in the pre-existing microvoids may act as nuclei for clusters that probably persist and grow, especially for systems such as polymer-water which are poorly compatible [27]. For Venolite, the isotherm does not upturn so dramatically at higher activities. This suggests that sorption and transport of water vapour is predominantly controlled by morphological features. Steric conditions imposed by the presence of hydrophobic tar in the crosslinked network may be responsible for the inaccessibility of all sorption sites. The presence of tar in the blend strongly reduces the affinity with water, affecting not only the equilibrium water uptake but also the diffusion coefficients. In fact, from the data of Table III lower sorption values and diffusion coefficients are always observed for the epoxy tar film. From these considerations it can be expected that also the protective properties of these coatings should be strongly influenced by their formulation.

Fig. 2 shows the corrosion potential E_{corr} of painted panels, immersed in sea water, against time t in a semilog scale for the investigated coatings. No substantial difference is evident in the long term behaviour. Apart from the temperature effect, the potential is the same and it is not so far from the potential of free corrosion of mild steel in sea water as confirmed with a test on unpainted samples.

After four months of immersion the film was peeled off: as a result, a differently corroded metallic surface appeared (Fig. 3). In fact, while for Araldite and Titania, reddish spots, uniformly distributed on the specimen, were observed, for Venolite painted samples no corrosion products

TABLE III Equilibrium water uptakes (S) and diffusion coefficients for samples conditioned in liquid water at $T = 20^{\circ}\text{C}$

Coatings	S (g per 100 g)	D ($\text{cm}^2 \text{sec}^{-1}$)
Venolite	1.10	2.8×10^{-10}
Titania EP	1.95	15.0×10^{-10}
Araldite GY 250	2.35	46.0×10^{-10}

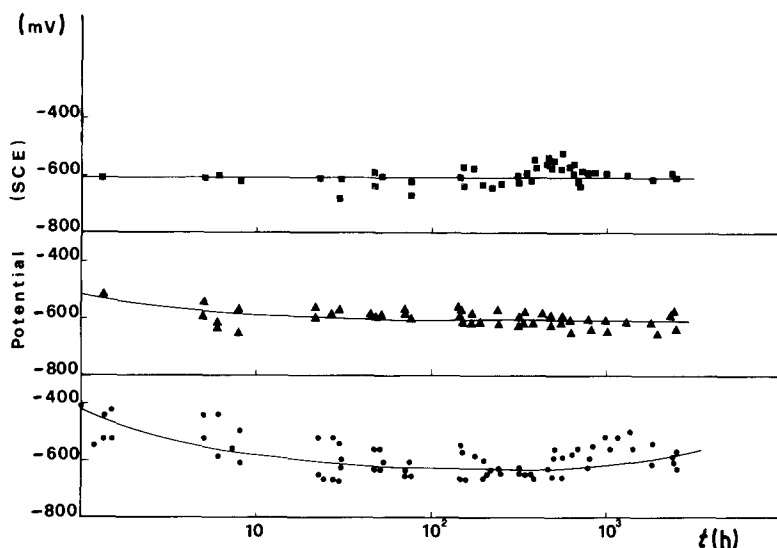


Figure 2 Potential-time behaviour of coated steel in sea water at $T = 20^{\circ}\text{C}$. Araldite (▲), Titania (■), Venolite (●).

appeared. The corroded areas show two different coloured zones: a deep green nucleus surrounded by a reddish halo; the first one is the real point of dissolution of iron, the second one is the zone of oxidation of Fe^{2+} to rust. The non-corroded areas of the samples correspond to the cathodic regions where the permeated oxygen reacts with formation of hydroxyl ions [3].

It is important to notice that the corrosion under Titania and Araldite is similar to that observed for samples immersed in a low conductive medium such as distilled water [28]. This observation supports the hypothesis that a very low ionic permeability can be guaranteed by epoxy based coatings. No particular strength was demanded to peel off the films indicating that the water uptake at the interface weakens the intermolecular forces between the metal and the film. The loss of adhesion was more intense for Titania

and Araldite, for which the rust formation can cause a larger debonding of the film.

A similar result was observed by the cathodic protection test. In fact for Araldite, after only fifteen days of immersion in sea water, several blisters appeared on the all area.

Fig. 4a shows the painted plate after six months of immersion in sea water, in a condition of cathodic protection. The small brownish spots are due to the product of corrosion arising from periodic loss of current during the test. The pH value of the solution under the blisters was higher than 10. This could be expected as a consequence of cathodic reduction of oxygen on the steel surface. The observation that under these areas no carbonates were detected, supports the previously hypothesis of poorly ionic permeability through epoxy coatings. The alkaline solution causes severe loss of adhesion at the metal-film interface interacting with polar groups of the polymer. This is particularly evident for Araldite, which is an epoxy resin very sensitive to alkaline products. Figs. 4b and 4c show the back side of the peeled off film of Titania and Venolite, respectively.

For Titania, blisters were observed after three months; for Venolite, only after six months did blisters appear, to a lesser extent and smaller with respect to the other paints. It is important to notice that while for Titania and Venolite blisters appeared as small bubbles slightly increasing in number and magnitude during the experiments, for Araldite the blisters appeared after fifteen days and were practically constant during the test. In a very simple way this may be a consequence of the different sorption kinetics. In fact for Araldite,

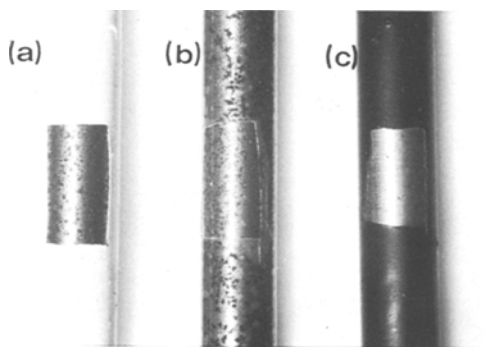


Figure 3 Appearance of the Titania (a), Araldite (b) and Venolite (c) coated steel samples after four months exposure to sea water.

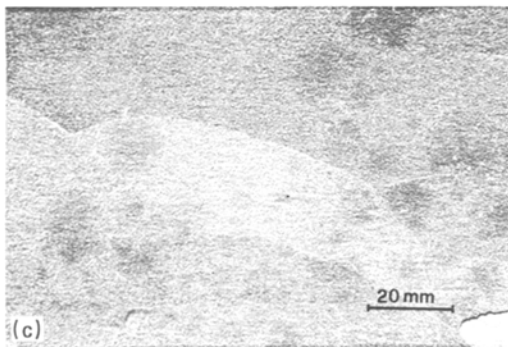
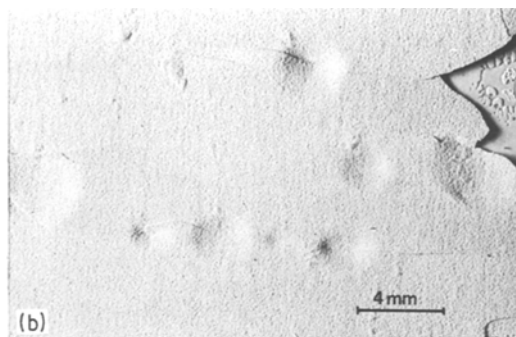
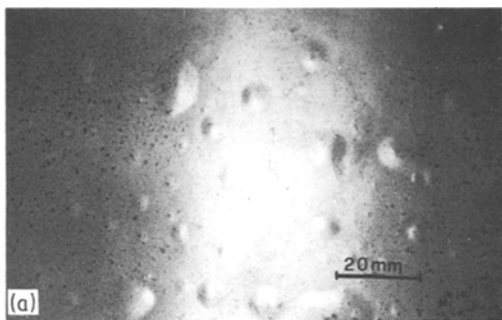


Figure 4 (a) Blister formation on Araldite coated steel samples. (b) Blister formation on Titania coated samples. (c) Blister formation on Venolite coated samples.

the higher diffusion coefficient causes a sharp water uptake leading to a rapid plasticization.

Without probing into the mechanism of the blister growth, it seems that the greater the concentration of polar epoxy groups the greater is the water gain and the easier is the local debonding of the film. The phenomenon is much more evident for cathodic protected samples, for which the formation of hydroxyl ions at the metal-coatings interface enhances the effects of dipolar interactions.

4. Conclusions

In conclusion a good knowledge of the transport properties of the polymeric coatings can give useful information of the capability of a protective paint. It is clear that in order to fully characterize a paint it is necessary to investigate also the oxygen permeability, which will affect the corrosion rate of the metallic substrate.

Moreover, if a qualitative comparison of the performance of different paints, especially as regards to the loss of adhesion at the interface, is requested, the evaluation of the equilibrium water uptake and the diffusion coefficient of the resin is necessary. Furthermore the investigation of corrosion potential of the painted metal *per se* is not sufficient for the correct evaluation of the protective properties of organic coatings.

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