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Effect of mechanical stresses on epoxy coating ageing approached by Electrochemical Impedance Spectroscopy measurements

D. Nguyen Dang*, B. Peraudeau, S. Cohendoz, S. Mallarino, X. Feaugas, S. Touzain

Laboratoire des Sciences de l'Ingénieur pour l'Environnement, FRE CNRS 3474, Université de la Rochelle, France

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ABSTRACT

The present work is a new illustration of the interest to use electrochemical analysis to investigate polymer coating degradation. We focus our attention on specific effect of visco-elastic (VE) stress on the hygrothermal ageing of a model polymer DGEBA/TETA coating applied on steel panels. Two different VE stress values (stretched and compressed modes) were applied on the coated panels and these samples were hygrothermally aged in NaCl 3 wt.% solution at different temperatures. Electrochemical Impedance Spectroscopy was used in order to determine the solubility, the diffusion coefficient and the initial relative permittivity of the coating. The obtained results suggested that all of these parameters appeared as thermo-activated functions of the absolute value of the applied stress and that the stress, independent of its sign, leads to a decrease of the initial relative permittivity, solubility and diffusion coefficient. A thermodynamic approach was used to separate the enthalpy and entropic contributions of each property. It is shown that the entropic contribution plays a major role on the modification of these parameters. It means that the VE applied stress modifies the polymer chain spatial distribution. Finally, the VE stress allows a better barrier effect of the coating and then to delay the corrosion process of the metallic substrates.

1. Introduction

Organic coatings are widely used for corrosion control of metallic substrates. However, environmental factors such as water, UV or temperature cause the deterioration of the coating, leading to blistering and/or disbonding that affect the coated substrate performances. So, the prediction the coatings lifetime is very important in corrosion control. Many studies related the influence of each ageing factor or a combination of them [1–8] in order to better understand the degradation mechanisms of the coatings. This is one of the best ways to evaluate the coating lifetime. Water transfer through coating causes the degradation of the coating structure and also contributes to the corrosion of metallic substrate. The quantity of water uptake in the coating is often estimated by gravimetry with free films and/or Electrochemical Impedance Spectroscopy (EIS) with coated substrates [9]. Indeed, EIS is a non-destructive method that is able to characterize the organic coating and can be used to obtain the interfacial metallic response under the coating. However, the amounts of water in the coatings determined from EIS are often different from those obtained by gravimetry [10] and researches are still performed in order to precise the origin of such differences [11,12].

EIS is known as a powerful technique to monitor the organic coating degradation and it was used to study the effect of mechanical stresses onto water uptake [13–17]. For instance, Klüppel et al. [17] used EIS to study the degradation of organic coating applied on galvanized steel under uniaxial mechanical stress application (up to 20% of elongations) and found that stretching-induced defects occur at the interface between spherical Zn particles and the polymeric material. However, in these studies, the mechanical stresses put the polymer network of the coating either in a state of plastic deformation (irreversible process) where its properties are largely affected, or in a state of unknown deformation. No general trends were proposed concerning the effect of mechanical stresses onto water uptake process.

Recently [18–22], we proposed a different approach where the true mechanical state of the polymer is considered. A visco-elastic (VE) mechanical stress (tension-positive or compression-negative) is applied onto marine epoxy coatings. It is then considered that polymer chains are elongated or compressed but no irreversible polymer network change occurs. It was observed that the ageing of epoxy coatings in saline solution affects the mechanical properties and then, may have a significant influence on the durability. Moreover, it was shown that a visco-elastic mechanical stress had a strong influence onto the barrier properties of such coatings and also onto the initial relative permittivity [21]. However, the complex formulations of these commercial paints lead to annex processes such as lixiviation that hide the real response of the polymeric material.

* Corresponding author. Tel.: +33 5 46 45 87 67; fax: +33 5 46 45 82 41.
E-mail addresses: dang_dan.nguyen@univ-lr.fr, dangdanqt@gmail.com (D. Nguyen Dang).

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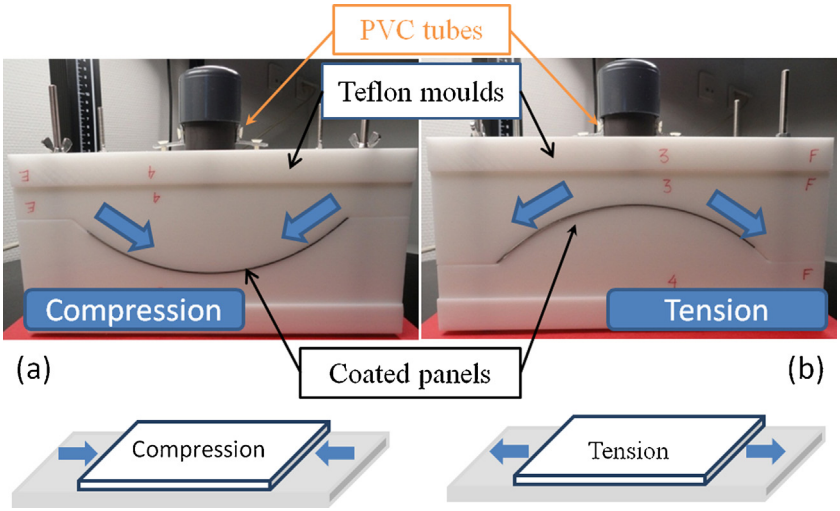

Fig. 1. Coated steel panels under stretched state (a) and compressed state (b).

In order to avoid the influence of pigments, adjuvants and other fillers that exists in commercial coating formulations, a model epoxy system DGEBA/TETA was chosen to obtain the response of the sole polymer. In a previous work [23], this model epoxy system was prepared as free films and was carefully studied to determine its physico-chemical and mechanical properties. In this study, steel panels are coated by the same model epoxy system and are immersed in saline solution. Mechanical stresses are applied onto the coated panels and the water uptake process is followed by EIS. The EIS data are analysed using different approaches which are compared and discussed in order to precise the influence of a VE stress onto the barrier properties of organic coatings.

2. Experimental

The epoxy resin was a Diglycidyl Ether of Bisphenol A (DGEBA) and the curing agent was triethylentetramine 60% (TETA). All materials, from Sigma–Aldrich, have been used as received without further purification. Stoichiometric mixture of epoxy resin and amine hardener was mixed at room temperature until reaching a homogeneous liquid. After being degassed, the mixture was cast between two Teflon sheets which had been beforehand degreased and cleaned with acetone. A spacer separated the plates in order to obtain free film thickness (d) of $120 \pm 20\,\mu m$ (measured using an Elcometer 345 coating thickness gauge). For coated steel panels, the liquid epoxy system was deposited onto the steel sheet and covered by a Teflon sheet. The thickness of coatings was similar with free film. Both systems were then placed into an oven to achieve complete cross-linking as already described elsewhere [23].

Free films allowed measuring the water uptake by gravimetry and the limits of the visco-elastic domain as done previously [18,23]. The EL/VE and VE/VP limits were respectively estimated at 6 and 12 MPa for initial cured network [23]. Therefore, two VE stress values ±7 and ±9 MPa were chosen and were applied to the coated panels by bending the panels between two pieces of Teflon mould (Fig. 1). The application of these mechanical stresses put the epoxy coating in a VE mechanical state where no irreversible structural deformation occurs. Consequently, only elastic strain energy was imposed to the material. All the studied mechanical states are in a plane stress state, under tension or compression.

Unstressed panels were used as the reference. For stressed panels, two curved PVC tubes (3 cm diameter) were designed in order to allow their application on the concave side or the convex side of the stressed panels. So, with these O-ring seal type cells, it was possible to perform EIS measurements on both sides of the stressed panels without interrupting the stress–strain state of the panels. PVC tubes were filled with a saline solution (NaCl 3 wt.%) at four different ageing temperatures: 30, 40, 50 and 60 °C. Three identical coated panels were considered for each mechanical and thermal condition.

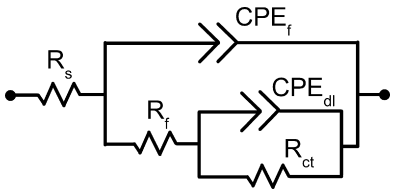

Fig. 2. Equivalent electrical circuit used to fit EIS data.

EIS measurements were performed into the ageing oven using a saturated calomel electrode as reference, a graphite counter electrode. So, the EIS measurements were realized at the same temperature of ageing. EIS measurements were performed with a Gamry Femtostat FAS 1 at the free corrosion potential. The ac frequency was swept between 100 kHz and 100 mHz with a 20 mV rms perturbation amplitude (9 points/decade). ZView software was used to perform the data analysis (Scribner Associates, USA). The film capacitance (C_{HF}) was firstly determined using the imaginary part of the impedance $Im(Z)$ at high frequency (f = 10 kHz) [24,25]:

$$C_{HF} = -\frac{1}{2\pi \times f \times Im(Z)} \quad (1)$$

EIS data were also analysed by classical electrical equivalent circuits (EEC) (Fig. 2) including Constant Phase Elements (CPE) [25]. Then, by using the Brug's approach [26] and considering only the solution resistance R_S which is much lower than other resistances, the "true capacitance" C_{Brug} was calculated as:

$$C_{\mathrm{Brug}} = Y_0^{1/n}\left(\frac{1}{R_S}\right)^{(n-1)/n} \quad (2)$$

where Y_0, n are the CPE_f parameters.

The water uptake was estimated from the Brasher and Kingsbury (BK) relation [27] using the different approaches (CPE, C_{Brug}, C_{HF}):

$$\chi_V(\%) = \frac{\log\left(C_t/C_0\right)}{\log\varepsilon_w} * 100 \quad (3)$$