Effect of mechanical stress onto water uptake in epoxy systems

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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 coated substrate and affect the coating performances. Many studies related the influence of each ageing factor or a combination of them [1–7] in order to better understand the degradation mechanisms and the best way to evaluate the coating lifetime. The effect of mechanical stresses was also investigated [8–11] using different tests. However, the mechanical state of the polymer was not rigorously known in these works and no general trends were proposed.
Recently [12-16], we proposed a different approach where the true mechanical state of the polymer is considered. A visco-elastic (VE) mechanical stress (positive or negative) is applied onto epoxy coating systems. 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. However, the complex formulations of these commercial systems lead to annex processes such as lixiviation that hide the real response of the polymer.
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 this work, the model epoxy system was prepared as free film and was carefully studied in order to obtain physico-chemical and mechanical properties of the polymer. Then, steel panels were coated by the epoxy system and were immersed in saline solution. Mechanical stresses were applied onto the coated panels and EIS allowed to study the water uptake process. EIS data were analyzed using different approaches which are compared and discussed.

Experimental

The epoxy resin used 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 and amine hardener was mixed at room temperature until reaching a homogeneous liquid. After degasing, the mixture was cast between two Teflon sheets which have been beforehand degreased and cleaned with acetone. The plates were separated by a spacer in order to obtain free film thickness of 120 ± 20 µm. For coated steel panels, the liquid epoxy system was deposited onto the steel sheet and covered by a Teflon sheet. Both systems were then placed into an oven to achieve complete cross-linking.
Free films allowed to measure the limits of the visco-elastic (VE) domain as done previously [12]. Then, the coated panels were bent or compressed in order to place the polymer in a VE mechanical state (±7 and ±9MPa). Unstressed panels were also prepared. All panels were immersed in saline solution (NaCl 3wt.%) at different ageing temperatures between 30 and 60°C. Three identical coated panels were considered for each mechanical and thermal condition.

EIS measurements were performed in 3 wt.% NaCl solution using a saturated calomel electrode as reference, a graphite counter electrode, all of them set into a Faraday cage. 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 bent coated 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. All 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). Data analysis was performed by the software ZView (Scribner Associates, USA), using the imaginary part of the impedance at 10kHz or classical electrical equivalent circuits.

Results and Discussion

EIS data allowed to measure the film capacitance at 10kHz (C_{HF}) or were analyzed by classical equivalent electrical circuits in order to get the film capacitance equivalent CPE. Using the Brug's equation [17], the "true" film capacitance C_{Brug} was also calculated. The three parameters were followed during immersion time. A typical plot is presented in Fig. 1 for an unstressed panel, aged at 30°C in NaCl solution.

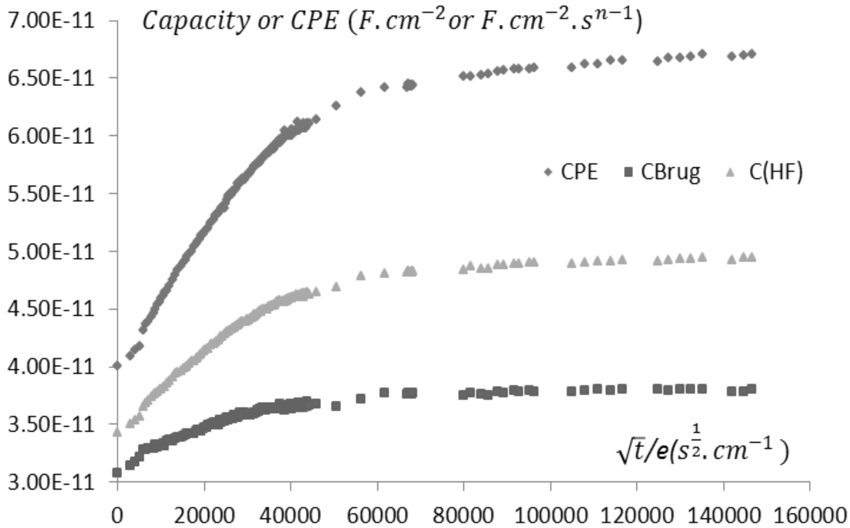

Figure 1: Evolution of the "film capacitance" with immersion time for an unstressed panel (thickness e), aged at 30°C in NaCl solution.

As shown in Figure 1, the three electrochemical parameters (C_{HF}, CPE and C_{Brug}) present a linear increase during the first period of immersion corresponding to water absorption within the coating. It can be noticed that the slopes are different. Moreover, the three parameters present different values for the second stage which corresponds to water saturation. From these curves, the water uptake can be calculated using the Brasher and Kingsbury equation [18]: 5.8% using C_{Brug}, 8.0% using C_{HF}, 11.8% using CPE. These results show that the data analysis has to be chosen with great care in order to avoid wrong water uptake estimation.

The evolution of the three parameters allowed to calculate the initial permittivity (dry state) ε_r^0 of the coating (Fig. 2) and the diffusion coefficient (Fig. 3) depending on the applied mechanical stress σ. The mechanical stress significantly affects the dry permittivity of the coating, independently of the stress sign. This may be explained in terms of polymer chain orientation that is modified by the applied stress: tension and compression influence the chain orientation parallel to the stress axis. It must be noted that same trends are obtained using the three electrochemical parameters, where the temperature influence is low.

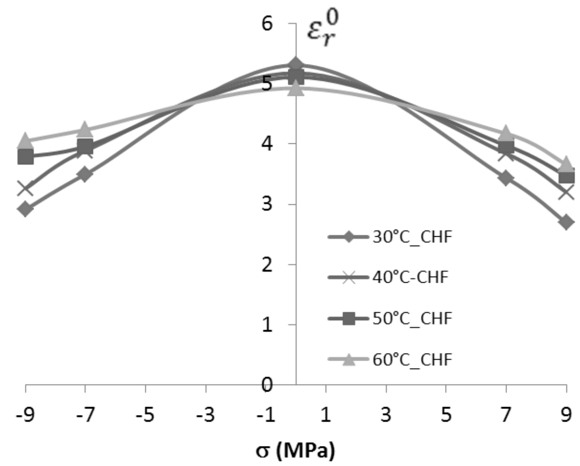

Fig. 2: Evolution of ε_r^0 with σ using C_{HF}.

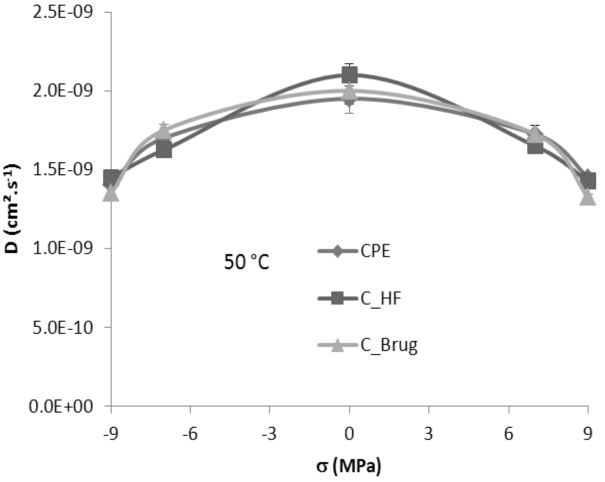

Fig. 3: Evolution of D with the stress σ.

The evolution of the diffusion coefficient, calculated using the three electrochemical parameters, is also affected by the applied stress: this may be interpreted by a decrease of available polar groups that may form O-H bonds with diffusive water.

Conclusions

These results show that EIS allows to evidence the influence of a visco-elastic mechanical stress onto water uptake in epoxy systems. Different EIS analyses were applied and similar trends were obtained, even if some absolute values for extracted parameters have to be considered with great care.

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