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A bulk and localised electrochemical assessment of epoxy-phenolic coating degradation

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ABSTRACT

Water absorption is believed to be one of the main causes leading to the deterioration and degradation of protective organic coatings. Water uptake in coatings on metal may be measured, for example, by changes in electrical impedance (e.g. capacitance and resistance) as a function of time. Generally coating capacitance is expected to increase during initial stages of water uptake (due to the greater dielectric constant of water) while coating resistance is expected to decrease (due to the lower resistivity of water compared to most polymers). However, here we present evidence that water ingress is not the main determinant of damage in epoxy-phenolic can coatings. Thus, as the degree of cure is increased, the water saturated coating capacitance and resistance both increase while the time-to-failure also increases. We suggest that these observations are due, respectively, to an increase in the free polymer volume (permitting more water uptake) and to an increase in the charge transfer resistance at the metal-polymer interface (due to a higher density of polymer-to-substrate bonding). These results and interpretations are supported by local electrochemical impedance spectroscopy which has confirmed water absorption, coating failure and increased coating resistance for highly cured capacitive systems, at the microscale.

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1. Introduction

Electrochemical Impedance Spectroscopy (EIS) is a widely used corrosion evaluation tool, based on an electrical analogue of corrosion processes using simple electrical circuits typically comprising of resistive and capacitive elements. Common applications include metallic interfaces [1,2], resistive organic coatings [3,4], and membranes [5,6] in a variety of aggressive [7] or inhibiting environments [8,9]. Organic coating research has found this technique particularly appealing for estimating coatings life-span [10], physical properties, morphology [11], and for the detection of delamination, like blistering and loss of adhesion [7,12]. However, EIS data interpretation can often give misleading results, considering that the recorded frequency spectrum corresponds to the averaged current across the whole exposed surface [13,14]. Recently developed localised electrochemical impedance spectroscopy (LEIS) has improved understanding of coating systems protection in the microscale [15–17]. The combination of the two techniques offers enriched data analysis and spatial resolution to the complex electrochemical characteristics of a corroding coating surface [17,18].

A large proportion of the ongoing electrochemical research on organic coatings is focused on pre-scribed or defect containing samples, in order to simplify testing procedures and analysis, but also to accelerate the corrosion initiation process. Results commonly generate useful empirical knowledge, but our mechanistic understanding is still far from complete. Early researchers have expressed the need to answer simple questions about the onset of coating degradation [19]. This information would reduce time spent on designing and testing new paint formulation recipes, which are required for attaining new resistant coating systems.

Today, it is generally acknowledged that a continuous and uniform coating, unpigmented and free from inherent defects, can protect the underlying substrate by a combination of barrier [20] and adhesive properties [21]. The barrier property of a coating can be described as its ability to hinder water, ions and oxygen permeation through the polymer network. However, it is unclear whether loss of adhesion occurs as a consequence of the presence of aggressive species at the metallic interface, or whether corrosion initiates at regions of reduced adhesion, where enough free metal and electrolyte accumulation can form an electrochemical cell.

Examining coated and free standing film systems, Mayne et al. have come across a specific type of heterogeneity between coating regions, relative to the conductivity of the electrolyte. Regions prone to failure showed coating resistance relative to the chloride

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content of the electrolyte and were categorised as “D”. On the other hand, the corrosion resistant regions which exhibited the opposite behaviour were labelled as “I” [22–25]. Micro-hardness tests on these regions suggested “D” areas were insufficiently crosslinked regions compared to the “I” [24]. Nguyen’s theoretical description of coating breakdown [26] advanced the absorption theory even further suggesting the less crosslinked coating regions, and more “hydrophilic regions”, that will absorb water preferentially and act as corrosion initiation sites.

Recent work, published by Morsch et al. on epoxy-phenolic lacquers, showed that prolonged curing at 200 °C can increase the coating crosslinking degree. Opposite to what is usually described in literature, higher water content was detected under humid conditions on coatings with increased curing degree. This statement, even though contradictory to Nguyen’s degradation model [26], can be attributed to the increasing free-volume introduced in the polymer with further curing, leading to coating swelling, lower coating density and subsequently increased water capacity [27]. Free volume presence in epoxies is responsible for many vital coating properties. For instance, counterintuitively, water uptake in epoxies decreases when the coating is exposed to high temperature electrolyte, and vice versa, as the molecular vibrations reduce the available free volume [28]. What is more, polymer rearrangements induced by further curing are also expected to influence the coatings bulk polarity and dielectric constant [29].

In this work, a simplified, “stripped back”, epoxy-phenolic lacquer, based on a formulation for food cans, is used due to its clear, transparent and well defined composition. The lacquer is applied on tin-free (ECCS, Electrolytically Chromium Coated Steel) and traditional tins, which are widely used for food can packaging products. Epoxy-phenolics are popular in the food packaging industry for their exceptional adhesion, chemical and electrical resistivity. Their characteristics render them a good choice of barrier coatings for avoiding corrosion caused by the aggressive internal can conditions, but also by hindering metallic contamination of the can content [21,30–32]. Additionally, the absence of inhibiting and other leaching additives, present in most commercially available coating systems, facilitates electrolyte diffusion studies.

The purpose of the electrochemical techniques applied in this research is to detect and identify those macroscopic phenomena responsible for coating degradation from the early immersion stages, as well as their spatial extent at the microscale. Water content is estimated through traditional capacitance studies, and the coating performance at different degrees of cure is assessed with respect to the time exposed in the electrolyte. The detection ranges and limitations of each technique are discussed. The effect of water content and crosslinking degree on the coating system performance is used to validate Mayne’s and Nguyen’s models for coating degradation, as well as, previously published findings of the same coating system, obtained by FT-IR in humid conditions [27].

2. Experimental

2.1. Materials and sample preparation

Degreased ECCS substrates were used for the application of a stripped-back (i.e. not formulated and thus free of additives) stoichiometric epoxy-phenolic lacquer, supplied by AkzoNobel N.V. The deposition techniques used for the coatings production was spin-coating for 30 s at 1000RPM or 2000RPM and roller-coating. The samples were then cured in a fan assisted oven at 200 °C for 10, 20 or 30 min, to introduce different curing degrees. Differential scanning calorimetry (DSC) measurements were previously described by Morsch et al. [27] and showed that the lacquer’s Tg

increased with longer curing times and that residual uncured material that was present in the 10 min samples disappeared after longer curing. Coating samples remained stored in a desiccator at least 24 h before electrochemical testing. An electrical connection to the substrate was established and a tube was attached on the coating surface with a mixture of bees wax and colophony resin (3:1), leaving 12.5 cm² of exposed area. The samples used for localised electrochemical testing were mounted in araldite resin and their edges were sealed with the same wax-colophony mixture.

For the dry EIS measurements, coatings of the same lacquer were produced by spin-coating at 1000RPM on ECCS substrates, followed by direct oven curing at the same temperatures and times. After curing, a gold layer was deposited on the epoxy-phenolic surface and the sample edges were mechanically removed to ensure there was no electrical contact between the coating surface and the metallic substrate. In this way the dielectric properties of the dry polymer film can be assessed using a parallel plate electrode arrangement [33,34].

2.2. Methods

2.2.1. Microscopy

Examination of the coatings (for their thickness and the presence of defects) both before and after exposure was carried out by means of Scanning Electron Microscopy (SEM, Zeiss EVO-50) at 15 keV electron beam energy. For SEM cross section observations, the coating surface was gold-coated to help distinguish the organic coating from the mounting resin. The surface topography of these transparent systems was revealed with a 3D Laser Scanning Microscope (Keyence VK-X210) using a 408 nm laser source.

All coatings were also inspected by optical microscopy to ensure uniformity. The majority of defects occurring on this coating system were pinholes, caused by the presence of air-bubbles in the lacquer during the coating process. These defects, ranging approximately from 200 μm to 25 μm in diameter, were easily detected and, in this way, such samples were eliminated from the testing procedure.

2.2.2. Electrochemical impedance spectroscopy

Electrochemical impedance measurements were recorded at room temperature in the 0.01 Hz–10 kHz frequency range using a 10 mV AC perturbation with respect to the open circuit potential of the system, to ensure linearity. Data acquisition required a three electrode setup, consisting of a saturated calomel reference electrode ($E_{SHE} = E_{SCE} - 241$ mV at 21 °C) and Pt ring counter electrode, all enclosed in an earthed Faraday cage. Finally, a Gamry Reference 600 potentiostat was employed for EIS measurements, in combination with Zview analysis software, by Scribner Associates Inc. The specific equipment was chosen to ensure instrument reliability when measuring highly resistive systems as the specific organic films [35].

Measurements took place immediately after immersion in an aerated 0.1 M NaCl aqueous solution and were repeated every 2 h for the first three days, and then every 24 h. Those samples which instantly showed a connection to the substrate, assumed to arise from defects that allowed charge transfer between the electrolyte and the substrate, were excluded from this study.

Changes in the measured electrical impedance with time are typically found in highly resistant intact coating systems when facing gradual degradation with exposure to a corrosive electrolyte [36–38]. The main models used in this paper to describe the coating behaviour are shown on Fig. 1. The coatings initially exhibited an almost purely capacitive behaviour, and were fitted with model A, described by a solution resistance (R_s) and a coating capacitance (C_{coat}). As water absorption was expected to take place through the coating and to develop conductive pathways [26], a new resistive component of the impedance was revealed (model B), correspond-

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