Electrochimica Acta 231 (2017) 162–170

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Water uptake in free films and coatings using the Brasher and Kingsbury equation: a possible explanation of the different values obtained by electrochemical Impedance spectroscopy and gravimetry

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ARTICLE INFO

Article history:
Received 21 October 2016
Received in revised form 6 February 2017
Accepted 9 February 2017
Available online 10 February 2017

Keywords:
water uptake
Brasher and Kingsbury
gravimetry
EIS
DMA
SECM

ABSTRACT

For many years, the water uptake in organic coatings was measured by EIS and/or gravimetry but differences in water content values were found in almost all studies. The Brasher-Kingsbury equation used in the electrochemical analysis (EIS) is often criticized because elementary assumptions may be unvalid. The origin of the discrepancy between both methods is still of interest because many questions remain open and this study aims to provide new insights to these questions.

In this work, free films and coatings of a model epoxy-amine system were immersed in a 3 wt.% NaCl solution. The water uptake in free films was evaluated using gravimetric measurements and EIS, using the Basher-Kingsbury equation. The mass of free-films used in the EIS tests was measured and compare to gravimetric measurements while the water uptake (EIS) in free films was compared to that obtained with coatings. It was found that the mass increase of free films tested with EIS was in agreement with gravimetric measurements but was always lower than the water uptake obtained by EIS. Moreover, the water uptake in free films (EIS) was different from that obtained with coatings. In all cases, it was found that the Basher-Kingsbury equation overestimated the water uptake.

It appears that the differences between EIS and gravimetric measurements can be analyzed in terms of geometrical effects. Indeed, the swelling in free films and coatings can be monitored by DMA and SECM during ageing. Finally, by mixing the experimental swelling data and the Brasher-Kingsbury equation, the same value of water uptake was obtained by EIS and gravimetry for coatings.

1. Introduction

Organic coatings are widely used for corrosion control of metallic substrates and many efforts are done in order to evaluate their performances under natural or artificial ageing [1–12]. The water uptake is a key parameter to evaluate the durability of organic coatings together with wet adhesion and the evolution of the physico-chemical and mechanical properties during ageing [13–16].

The quantity of water uptake in organic coatings is usually estimated by EIS (Electrochemical Impedance Spectroscopy) because EIS is a non-destructive method that is able to characterize the organic coating and also to obtain the interfacial metallic response under the coating. The percentage by volume of water uptake χ_V can be calculated by using the relation (Equation (1)) proposed by Brasher and Kingsbury in 1954 [17], based on the original work of Hartshorn [18]:

$$\chi_V = \frac{100.\log\left(\frac{C_m(t)}{C_m(t=0)}\right)}{log\varepsilon_w} \quad (1)$$

where ε_W is the water permittivity (76.6 at 30 °C);
$C_m(t)$ is the measured capacitance at any time t;
$C_m(t=0)$ is the measured capacitance at zero time.

In this approach, the relative permittivity of the system can be expressed as:

$$\varepsilon_r = \varepsilon_p^{f_p}.\varepsilon_w^{f_w}.\varepsilon_a^{f_a}.\varepsilon_f^{f_f} \quad (2)$$

where ε_p, ε_w, ε_a and ε_f are respectively the relative permittivity of the polymer, water, air and fillers at the temperature T and f_i are the volume fractions for each component i. Since ε_p is usually between3 and 8 [19] while that of water is about 80 at room

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http://dx.doi.org/10.1016/j.electacta.2017.02.051
0013-4686/

temperature, the water ingress leads to an increase of f_w and then to an increase of the global permittivity ε_r. The Brasher and Kingsbury (B&K) equation was used by many researchers for more than 60 years to obtain the water uptake in thin coatings (less than 1 μm) [20] or coatings thicker than 100 μm [16,21–26].

Many authors also used gravimetry to measure the water uptake in free films of the same polymer material that is then obtained by applying on a non-adherent substrate [19,27–33]. However, the amounts of water in the coatings determined from EIS are very often different from those obtained by gravimetry with free films. In some cases, gravimetry was found to be non-adequate because of leaching processes [32,34–36] in the paint but very often, gravimetry was considered as the reference method for free films. Researches were then performed in order to precise the origin of such differences between EIS and gravimetry and/or to better understand water uptake mechanisms [37–43], and new approaches or models were proposed [44–56], based on non-fickian water absorption or gradients of properties within the coating thickness. If these different approaches lead to interesting results, no unified explanation was proposed to clarify the overestimation of water uptake by the B&K equation and no comparison between pigmented and unpigmented coatings were presented.

In this work, we propose to revisit the B&K equation and to compare water uptake values obtained by EIS to those measured by gravimetry. A model epoxy system is chosen in order to avoid leaching processes or specific interaction between water and organic additives. The polymer system is studied as pigmented and unpigmented free films and coatings in order to evaluate the influence of pigments. The different initial hypothesis from Brasher and Kingsbury's work are discussed and the effect of swelling is considered.

2. Experimental

2.1. Preparation of free films and coatings

The epoxy resin was prepared from DiGlycidylEther of Bisphenol A (DGEBA from Aldrich, D.E.R.™ 332) cured with methylpentanediamine (DAMP from Aldrich, 99% Assay). All materials were used as received without further purification. A stoichiometric amount of DGEBA was added to the amine hardener, mixed at room temperature and degassed under vacuum. For pigmented free films, titanium dioxide (DUPONT TS-6200) was inserted into the mixture at a rate of 20 wt.%. The size of the particles were about 0.39 μm. After stirring at room temperature, the pigmented and unpigmented systems were degassed under vacuum for 10 minutes.

In order to create free films, the mixture was transferred to a mould, which consisted of two Teflon sheets which were separated by a spacer of about 120 μm thick. For coated steel panels, the mixture was deposited onto steel Q-Panels and inserted in the mould used for free films. A controlled curing protocol was used to create a homogeneous fully cured network, as presented elsewhere [57]. The cured specimens were stored in a desiccator containing silica gel desiccant to prevent moisture absorption before immersion. The dry thickness was about 100 ± 6 μm for free films and coatings (measured by an Elcometer 311 Gauge Thickness). Each measure is repeated at least two times to verify the repeatability and the accuracy of the method.

2.2. Gravimetric measurements

For the free films, the water uptake $\chi_m(t)$ was measured by gravimetry using a balance PRECISIA (10^{-5}g precision) using the protocol describes elsewhere [23,58]. For each measure, three samples were used. The mass water uptake $\chi_m(t)$ absorbed by free films was calculated as:

$$\chi_m(t) = \frac{m(t) - m_0}{m_0} = \frac{m_{water}}{m_{polymer}} = \chi_V(t).\frac{\rho_{water}}{\rho_{polymer}} \quad (3)$$

where m(t) is the mass of the wet specimen at time t, m_0 is the mass of the dry specimen.

From the mass water uptake $\chi_m(t)$, the equivalent volume water uptake $\chi_v(t)$ in free films without titanium dioxide was calculated according Equation (3) using the densities at 30 °C of water $\rho_w = 995.6\ kg.m^{-3}$ and of the polymer $\rho_{polymer} = 1182.9\ kg.m^{-3}$. For free films with 20%wt TiO_2 (mass ratio $f_{TiO2} = 0.2$), the equivalent volume water uptake $\chi_v(t)$ was obtained from $\chi_m(t)$ using:

$$\chi_m(t) = \frac{m(t) - m_0}{m_0} = \frac{m_{water}}{m_{polymer}} = \chi_V(t).\frac{\rho_{film}}{\rho_{TiO_2}}.\left[\left(\frac{f_{TiO_2}.\rho_{polymer}}{\rho_{TiO_2}}\right) - f_{TiO_2} + 1\right] \quad (4)$$

where $\rho_{film} = 1396.1\ kg.m^{-3}$ and $\rho_{TiO2} = 4000\ kg.m^{-3}$.

For desorption measurements, the same calculations were made in order to obtain the water uptake values. Sorption and desorption curves were plotted as function of the reduced time $\tau = \sqrt{t}/e$ where t is the immersion time and e is the film thickness.

2.3. Measure of the glass transition Tg

Differential Scanning Calorimetry (DSC) analyses were performed with a DSC Q100 TA Instruments under nitrogen purge. The free films (about 10 mg) were put in hermetic stainless steel caps to avoid water evaporation and were heated from 20 to 200 °C with a heating rate of $10\ °C.min^{-1}$ under a nitrogen flow of $50\ mL.min^{-1}$. The glass transition temperature, Tg, was taken at the half height of the change in heat capacity (middle of transition).

2.4. EIS measurements

The free films (with or without pigments) were aged between two glass cells (Fig. 1), filled with the NaCl 3 wt.% solution, the whole setup being placed in an oven at 30 °C. The water uptake was followed in situ with a two graphite rods as electrodes and the exposed surface was $5.73\ cm^2$.

The ageing of coated steel Q-panels was realized with a O-ring seal impedance glass cell filled by the saline solution (NaCl 3 wt.%). The contact surface was about $16\ cm^2$ and the ageing was performed at 30 °C during 6 weeks. The water uptake was followed

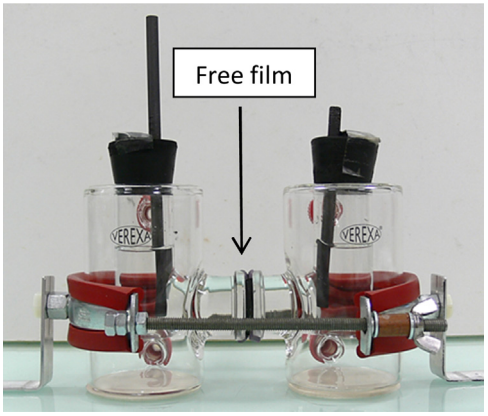

Fig. 1. EIS cell used with pigmented and unpigmented free films, where free films are placed between the two half cells.