Effect of pigment and temperature onto swelling and water uptake during organic coating ageing

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ABSTRACT

Free films and coatings of a model epoxy system, with or without pigment (TiO$_2$), were aged in saline solution at different temperatures (30 °C, 40 °C and 50 °C). The water uptake was evaluated using gravimetry for free film and using electrochemical impedance spectroscopy (EIS) for coatings. In parallel, the swelling of coatings was in situ monitored using scanning electrochemical microscopy (SECM).

It was shown that the temperature has no effect on the water uptake values for unpigmented systems and a slight effect onto swelling. For pigmented systems, the water uptake values slightly increase likely due to additional water absorption at the pigment/binder interphase. The swelling of pigmented coating was found to be lower than that of unpigmented coatings for all ageing temperatures. This result was explained by particular internal stresses that develop in pigmented system.

Water uptake values obtained from gravimetry and EIS, using the Brasher and Kingsbury equation, were different for all the temperatures for unpigmented and pigmented coatings. Using a modified Brasher and Kingsbury equation that considers the experimental swelling obtained by SECM, the same water uptake values were obtained for all systems and all temperatures. Finally, it appears that the coating swelling is a key parameter to evaluate water uptake in organic coatings, especially when different coatings are compared.

1. Introduction

When organic coatings are aged in humid conditions, the water can penetrate the polymer network and different processes can arise (e.g. plasticization, leaching, etc.…) that have been abundantly described in literature [1–9]. The water uptake can also lead to the swelling of organic coatings which is a disruption of the intermolecular hydrogen bonds within macromolecular chains by water molecules [10]. If the swelling becomes important, the mechanical properties of the coatings can be modified and the durability of the coated systems can be drastically decreased. Then, it seems important to better assess the swelling of organic coatings which is however not easy because of low thicknesses.

Souto and al. [11] used Scanning Electrochemical Microscopy (SECM) to evidence the swelling of organic coatings but the dimensional changes were not quantified. In our previous work [12] we proposed an experimental procedure using SECM to measure the swelling during the immersion of the coatings. The current at the tip decreases when approaching to the substrate (approach curve in the negative feedback mode) because the coating is non-conductive. This curve can be fitted [13] which allows to evaluate the touching position. When repeating these measurements during the immersion of coatings,

keeping the initial position (far away from the coating) of the tip unchanged, this touching position will be lower and lower because of swelling. It is then possible to measure directly the swelling of the coating during immersion thanks to in situ SECM measurements.

The measured swelling can also be used to correct the Brasher and Kingsbury equation [14] which was originally based on the absence of swelling. By using a modified equation [15], the water uptake values obtained by electrochemical impedance spectroscopy (EIS) are then very similar to those obtained by gravimetry.

In this work, we propose to evaluate the effect of the immersion temperature and the presence of pigments onto the swelling and the water uptake of an epoxy coating. A model epoxy-amine 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 the pigments (titanium dioxide) and the temperature onto the swelling and the water uptake.

2. Materials and methods

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 and mixed at room temperature. 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 min. For 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 coatings, the mixture was deposited onto steel Q-Panels and inserted in the mould used for free films. Before application, the Teflon sheets and Q-Panels were thoroughly rinsed with acetone. A controlled curing protocol was used to create a homogeneous fully cured network, as presented elsewhere [12]. The cured specimens (free films and coatings) were stored in a desiccator containing silica gel desiccant to prevent moisture absorption before immersion. The dry thickness was about 120 ± 6 μm for free films and coatings (measured by an Elcometer 311 Gauge Thickness).

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 [16,17]. For each measure, three samples were used. The mass water uptake $\chi_m(t)$ absorbed by free films was calculated as:

$$\chi_m(t) = \frac{m(t) - m_0}{m_0} = \frac{m_{water}}{m_{polymer}} = \chi_V(t) . \frac{\rho_{water}}{\rho_{polymer}} \tag{1}$$

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 to Eq. (1) 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:

$$\chi_m(t) = \frac{m(t) - m_0}{m_0} = \frac{m_{water}}{m_{polymer}} = \chi_V(t) . \frac{\rho_{film}}{\rho_{TiO_2}} .$$
$$\left[\left(\frac{f_{TiO_2} . \rho_{polymer}}{\rho_{TiO_2}} \right) - f_{TiO_2} + 1 \right] \tag{2}$$

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

Sorption curves at 30 °C, 40 °C and 50 °C were plotted as function of the reduced time $\tau = \frac{\sqrt{t}}{e}$ in order to remove the thickness effect [18], where t is the immersion time and e is the film thickness.

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, 40 °C and 50 °C during 6 weeks. The water uptake was followed in situ with a two electrodes cell, using a graphite counter electrode and the coated steel substrate as the working electrode, in order to avoid perturbations from the reference electrode in the high frequency domain [19].

For coatings, the EIS measurements were performed with a Gamry REF600 at the free corrosion potential using a 30 mV r.m.s perturbation (11pts/decade) in the oven acting as a Faraday cage. For short immersion times, the EIS measurement was done once while for longer immersion times, two EIS measurements were realized with a delay of 15 min. From these measurements, the film capacitance (C_{HF}) was determined using the real Re(Z) and imaginary Im(Z) parts of the impedance at high frequency (f = 10 kHz) using [20]:

$$C_{HF} = \frac{-Im(Z)}{2\pi f \left(Re(Z)^2 + Im(Z)^2 \right)} \tag{3}$$

The high frequency has been chosen as 10 kHz since theoretically,

in this high frequency domain, the total impedance of the system is governed by the coating capacitance [21,22]. The time-constants associated to corrosion processes that develop at the coating/metal interface, usually observed in lower frequency domains [23,24], are then not considered. Finally, the volume water uptake was calculated using the Brasher and Kingsbury Equation [14]:

$$\chi_V = \frac{100 . \log\left(\frac{C_{HF(t)}}{C_{HF(t=0)}} \right)}{\log \varepsilon_w} \tag{4}$$

where ε_W is the water permittivity, $C_{HF}(t)$ is the measured capacitance at any time t and $C_{HF}(t=0)$ is the measured capacitance at zero time.

The swelling of coated samples was measured using SECM (Biologic M470) according to the procedure described elsewhere [12]. The coated substrates were immersed in NaCl 3 w.t.% solution with the addition of a 10 mM potassium ferrocyanide (K$_4$[Fe(CN)]$_6$) as a redox specie at 30 °C, 40 °C and 50 °C. An ultramicroelectrode of 10 μm was used as a tip. The current of the tip was measured during approaching the tip towards the substrate in the z-direction (approach curve) with a very slow velocity 0.5 μm/s. Then, the approach curve was fitted in order to evaluate the touching position using [13]:

$$I_{norm} = \frac{\frac{2.08}{RG^{0.358}}\left(L - \frac{0.145}{RG}\right) + 1.585}{\frac{2.08}{RG^{0.358}}(L + 0.0023RG) + 1.57 + \frac{\ln RG}{L} + \frac{2}{\pi RG}\ln\left(1 + \frac{\pi RG}{2L}\right)} \tag{5}$$

where $I_{norm} = \frac{I_{tip}}{I_{ss}}$ is the normalized tip current, $RG = \frac{Rg}{a}$ is the normalized outer tip radius, L = d/a is the normalized tip-coated substrate distance, I_{tip} the tip current, I_{ss} the steady state current when the tip is far from the coated substrate, *Rg* the outer tip radius, *a* the tip radius and d is the distance between the tip and the coated substrate.

3. Results and discussion

3.1. Water uptake in free films

The sorption curves obtained from gravimetry of free films with and without titanium dioxide at 30 °C, 40 °C and 50 °C are presented in Fig. 1. Each curve is the sum of all points obtained for the three identical free films. After an initial water absorption, a plateau is obtained showing water saturation for both systems. The mass water uptake is $\chi_m = 2.8\%$ for the unpigmented free films for all immersion temperatures, which is, using Eq. (1), a volume water uptake of $\chi_V = 3.4\%$. For the pigmented free films (20 wt.% TiO$_2$), the same values are obtained at 30 and 40 °C. However, these values slightly increase at 50 °C to $\chi_m = 3.1\%$ which corresponds to $\chi_V = 3.7\%$. This increase may be related to the local breakdown of the interphase between the pigment and the binder at elevated temperatures which has been evidenced in the case of particle-filled epoxy-based adhesives [25,26].

3.2. Water uptake in coatings

The sorption curves of the coatings obtained by EIS using the classical Brasher and Kingsbury (B&K) equation without and with titanium dioxide at 30, 40 and 50 °C are presented in Figs. 2 and 3 respectively. In these figures, the sorption curves (χ_V) obtained from two different coated samples (a and b) are compared to the sorption curves ($\chi_{m\_}G$ and $\chi_{V\_}G$) obtained by gravimetry for free films of the same composition and aged in the same conditions. As it was observed for free films, the volume water uptake values for both coated samples present the same features: an initial water absorption followed by a plateau showing the water saturation for both systems. It can be noted (e.g. Fig. 3, τ»120000s$^{1/2}$ cm^{-1} at 50 °C) that two values obtained with a delay of 15 min for the same panel differ from 0.1%, which is basically the minimum error that can be obtained. In addition, a 1% error on the calculation of the initial capacitance leads to 0.2% variation of the