Assessment of water uptake in coil coatings by capacitance measurements

A.S. Castela, A.M. Simões∗
Chemical Engineering Department, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

Received 13 September 2001; received in revised form 26 July 2002; accepted 15 October 2002

Abstract
A model for the estimation of water uptake in polymeric coatings is presented, based upon a linear combination of the individual capacitances of the polymeric phase, the water and the air contained in the coating. Experimental comparison of the model with the Brasher–Kingsbury (BK) equation has revealed an improvement in the agreement with respect to the gravimetry.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Water uptake; Organic coatings; Electrochemical impedance

1. Introduction
The barrier effect of organic coatings is a key factor in the corrosion protection provided to the substrate. Under atmospheric exposure, water, oxygen and aggressive ions are the species responsible for the onset of the corrosion processes. Water penetration promotes corrosion, but it also induces internal stresses in the coating. It can either induce contractive internal stresses due to the extraction of soluble components, or expansive stresses, with swelling [1]. The most direct way to determine the water content in a coating is by weight measurements [2–4] either as weight gain during absorption or as weight loss during drying. Other possible techniques include differential scanning calorimetry, which detects only the clustered water [5], or FTIR [6].

For systems in immersion, the water content can be determined by electrochemical impedance. The principle is based on the known fact that the presence of water increases the capacitance of the coating. If the coating is treated as a parallel plate capacitor, then its capacitance is related with the relative dielectric constant $\varepsilon$ by

$$C = \frac{\varepsilon \varepsilon_0 A}{d}$$

where $\varepsilon_0$ is the dielectric constant of free space ($8.854 \times 10^{-12} \text{F/cm}$), $A$ the surface area of the coating and $d$ is the coating thickness. Since the relative dielectric constant of polymers is typically in the range of 3–8, and for pure water is 78.3 at 25°C, then the uptake of water will lead to a rise in the dielectric constant, resulting in a higher capacitance.

According to a formula proposed by Hartshorn et al. [7] for a coating composed of three phases—solid, water and air—the mixed dielectric constant would be given by

$$\varepsilon_x = \varepsilon_s \phi_s + \varepsilon_w \phi_w + \varepsilon_a \phi_a \quad (2)$$

where $\varepsilon$ and $\phi$ represent the dielectric constant and the volume fraction of each component, and the subscripts $s$, $w$ and $a$ correspond to the solid, water and the air phase, respectively.

For systems in immersion, the water content can be determined by electrochemical impedance. The principle is based on the known fact that the presence of water increases the capacitance of the coating. If the coating is treated as a parallel plate capacitor, then its capacitance is related with the relative dielectric constant $\varepsilon$ by

$$C = \frac{\varepsilon \varepsilon_0 A}{d}$$

where $\varepsilon_0$ is the dielectric constant of free space ($8.854 \times 10^{-12} \text{F/cm}$), $A$ the surface area of the coating and $d$ is the coating thickness. Since the relative dielectric constant of polymers is typically in the range of 3–8, and for pure water is 78.3 at 25°C, then the uptake of water will lead to a rise in the dielectric constant, resulting in a higher capacitance.

According to a formula proposed by Hartshorn et al. [7] for a coating composed of three phases—solid, water and air—the mixed dielectric constant would be given by

$$\varepsilon_x = \varepsilon_s \phi_s + \varepsilon_w \phi_w + \varepsilon_a \phi_a \quad (2)$$

where $\varepsilon$ and $\phi$ represent the dielectric constant and the volume fraction of each component, and the subscripts $s$, $w$ and $a$ correspond to the solid, water and the air phase, respectively.

By taking the dielectric constant of air as $\varepsilon_a \approx 1$ and taking into consideration that for low water content $\phi_s = 1 - \phi_w = \phi_a \approx 1$, re-arrangement of Eq. (2) gives the Brasher–Kingsbury (BK) equation [8]

$$\phi_w = \frac{\log(C_t / C_0)}{\log(\varepsilon_w)}$$

where $C_t$ and $C_0$ are the values of capacitance at an instant $t$ and for the dry coating, respectively. $C_0$ is usually obtained by extrapolating the coating capacitance to $t = 0$.

Eq. (3) assumes that the increase of the coating capacitance is only due to the ingress of water, that there is no swelling of the film and that the distribution of water in the film is uniform and with a low volume fraction. The subject has been treated in the literature by several authors, who have determined either the water content [3,4,9] or the diffusivity of water. Lindqvist [3] made experimental comparison of several equations for the mixed dielectric constant, and concluded that the best approach to gravimetric data was given by the BK equation. The degree of agreement depends on several factors, namely the type of coating [3] and the temperature [10,11]. However, in many cases the values estimated by capacitance measurements are excessively high.
These discrepancies may be due to a number of factors, such as the presence of pigments in the coating, the penetration of ions, polymer relaxation or simply the equation of mixture. In this paper a new model for the estimation of the water content is presented, based upon a different equation of mixture.

2. Model development

2.1. Introduction

In the following exposition the system shall be described as being composed of:
- The solid phase, excluding the air and the humidity trapped inside.
- The solution contained in the coating, considered as pure water.
- The term film shall be used to nominate the system formed by the coating, the air and the solution.

It is also convenient to state the following simplifying assumptions:
- (a) The components in the film are insoluble among them.
- (b) The film does not undergo swelling due to the water absorption process.
- (c) The coating (solid phase) is homogeneous, and therefore its electric parameters are considered constant in all the extension of the coating.
- (d) The electrical behaviour of the film can be described by a circuit of RC networks arranged in series. This corresponds to the situation of steady state.
- (e) The complex circuit of RC networks in series degenerates to a simple circuit of one resistance and one capacitance, $Z_{\text{mag}} = \frac{1}{\omega C_f}$, in parallel between them and in series with the solution resistance, $R_{\Omega}$, as described in Fig. 1.

Assuming uniform composition and properties of the film, the complex circuit of RC networks in series degenerates in the simple circuit of one resistance and one capacitance, $R_f$ and $C_f$, in parallel between them and in series with the solution resistance, $R_{\Omega}$, as described in Fig. 1.

For high frequency and if the impedance is described as $Z = Z_{\text{real}} + jZ_{\text{imag}}$, the imaginary part of the RC circuit impedance is approximately the same as for the capacitance, and can be given by the following equation:

$$Z_{\text{imag}} = -\frac{1}{\omega C_f}$$

A system that can be described by the previous assumptions corresponds to a mixture of independent components. In this case the resulting dielectric constant can be given by the average of this property for each component expressed in the following equation for the dielectric constant:

$$\varepsilon = \varepsilon_s \phi_s + \varepsilon_a \phi_a + \varepsilon_w \phi_w$$

For a ternary system (TS) the volume fractions are related by

$$\phi_a = 1 - \phi_w - \phi_s$$

where $C_a$, $C_s$ and $C_w$ symbolise, respectively, the terms $\varepsilon_a \varepsilon_0 A/d$, $\varepsilon_s \varepsilon_0 A/d$ and $\varepsilon_w \varepsilon_0 A/d$, and represent the capacitance of uniform layers of air, coating and solution, respectively, each with a thickness equal to that of the film. Based on that equation, a relation can be determined for the extrapolated capacitance of the dry coating, $C_0$:

$$C_0 = (C_a - C_s)\phi_a + (C_w - C_s)\phi_w + C_s$$

with $\phi_a$ and $\phi_w$ representing the volume fractions of air and of the solution, respectively.

Subtracting (7) from (8) gives

$$C - C_0 = (C_a - C_s)(\phi_a - \phi_a^0) + (C_w - C_s)(\phi_w - \phi_w^0)$$

Fig. 1. Equivalent circuit for an intact coating.
The relation between the fractions of the components can be expressed as follows:

\[ \phi_a + \phi_w + \phi_s = \phi_{a,0} + \phi_{w,0} + \phi_{s,0} = 1 \]  \hspace{1cm} (10)

From the previous relations we can obtain

\[ \phi_a - \phi_{a,0} = (\phi_{a,0} - \phi_w) + (\phi_s - \phi_w) \]  \hspace{1cm} (11)

Using that result in expression (9) the following equation can be obtained:

\[ (C_a - C_s)(\phi_{a,0} - \phi_a) + (C_s - C_a)(\phi_w - \phi_s) + (C_w - C_s)(\phi_w - \phi_{a,0}) = C - C_a \]  \hspace{1cm} (12)

\[ (C_s - C_w)(\phi_{a,0} - \phi_a) + (C_w - C_s)(\phi_w - \phi_{a,0}) = C - C_s \]  \hspace{1cm} (13)

For low water contents, the fraction of the solid phase is high and approximately constant, and thus \( \phi_{a,0} \approx \phi_a \). Re-arrangement of Eq. (13) then gives

\[ \phi_a - \phi_{a,0} = \frac{C - C_s}{C_w - C_s} \]  \hspace{1cm} (14)

which describes the increase in the water since the instant of immersion.

In this equation, \( C \) is the measured capacitance (calculated from the imaginary part of impedance) and \( C_{a,0} \) is obtained from extrapolation of \( C_a \) to \( t = 0 \). \( C_w \) and \( C_s \) can be calculated from Eq. (1), taking \( \varepsilon = 78.3 \) and \( \varepsilon_a \approx 1 \). If the coating is initially dry, then \( \phi_{a,0} = 0 \), and

\[ \phi_a = \frac{C - C_s}{C_w - C_s} \]  \hspace{1cm} (15)

Since the dielectric constant of water is much higher than that of air, and thus \( \varepsilon_w \gg \varepsilon_s \), the following further simplification can be obtained:

\[ \phi_a = \frac{C - C_s}{C_w} \]  \hspace{1cm} (16)

These two correlations (15) and (16), are the two forms of the model, and experimental testing is presented below.

3. Experimental

Experimental testing of the model with organic-coated systems was made. In order to avoid influence from underfilm corrosion, particularly important in the gravimetry, pure nickel was chosen as substrate in all the tests. Three coatings were tested:

- Poly(vinyl chloride) (PVC): plastificed with dioctyl phthalate (DOP) whose thickness is 200 \( \mu \)m,
- Poly(vinylidene fluoride) (PVDF): blended with poly(methyl methacrylate) (PMMA) whose thickness is 27 \( \mu \)m,
- Polyester: polyester blended with melamine whose thickness is 27 \( \mu \)m.

All the coatings were produced industrially, and the thickness includes a polyester primer (acrylic primer in the PVC).

3.1. Gravimetry

Weighing was made using a Sartorius MC5 microbalance. Although the resolution was 1 \( \mu \)g, a minimum variation of 10\( \mu \)g was used in the measurements. The total weight of Ni-coated samples was in the range from 700 to 800 mg (area of 3.5 cm\(^2\)). After 7 days of immersion the films were quickly dried with blotting paper, passed in a cold air blow for \( \approx 5 \) s, and weighted. Some leaching was observed in the PVC plastisol only, with a weight loss below 1% at the end of the wetting/drying cycle. The water uptake calculated from the gravimetric data was referred to the final dry weight, to eliminate any effects of leaching in immersion. The weight at saturation was obtained by extrapolation of the drying curve to \( t = 0 \). The fraction of water at each instant was determined as

\[ \phi_w = \frac{M - M_0}{V} \frac{1}{\rho_w} \]  \hspace{1cm} (17)

where \( M \) and \( M_0 \) are the mass of the sample at any instant \( t \) and after drying. \( \rho_w \) is the density of water (taken as 1 g/cm\(^3\)) and \( V \) is the volume of the coating, calculated as the product of the area by the thickness (after inspection of cross-cut samples by scanning electron microscopy). The weight of the dry sample was determined by weighing and drying the samples in a desiccator at ambient temperature until constant weight was obtained.

3.2. Capacitance measurements

Electrochemical impedance measurements were made using a frequency response analyser (Solartron 1255) coupled to an electrochemical interface (Solartron 1286). Measurements were made at ambient temperature in sodium chloride solution prepared with distilled water, with the concentrations of 3 and 0.3 wt.%, using a three-electrode arrangement in which the exposed area was 10.18 cm\(^2\). The applied signal had a frequency of 50 kHz and amplitude of 30 mV. The electrochemical cell consisted of a PMMA cylinder glued onto the surface of the panel with epoxy resin. A three-electrode arrangement was used, with coated metal as the working electrode, together with a saturated calomel reference electrode and a Pt wire as counter electrode. All the measurements were made at the open circuit potential.

4. Results

4.1. Gravimetric data

As explained above, the water uptake was determined from the drying curves. The first part of the curve was obtained during drying in air, whereas the last points were obtained after drying to constant weight in a desiccator.
Typical drying curves are presented in Fig. 2. The curves are presented for PVDF, PVC and polyester and although not much information can be obtained from the drying kinetics—due to the limited control of the drying conditions—the shape and good definition of the lines makes the extrapolation to $t=0$ quite easy.

4.2. Electrochemical impedance

The capacitance values determined from impedance were converted into water volume fractions by applying the model presented above. Both forms of the model were used, and shall be referred as

- TS: Eq. (15); simplified equation (SE): Eq. (16).
- For comparison, the equation BK (Eq. (3)) is also presented.

The water uptake at saturation for PVDF with various pigments and compositions is presented in Fig. 3. The largest discrepancy is given by the BK equation. The gravimetry gave values of $\phi_s$ below 1% under the working conditions, whereas the BK equation gave $\phi_s > 2\%$ in all cases. The $\phi_s$ values given by the model, although still higher than the gravimetry values, correspond to 0.4–0.6 of the values from the BK equation.

Another observation is that the simplified Eq. (16) gave practically the same results as the complete equation, which is not surprising considering the difference in the dielectric constants of water and air.

Fig. 4 depicts the time evolution of the water content in three different coatings. The water content at saturation, determined from gravimetry, is also presented. The shape of the absorption curve is Fickian, or pseudo-Fickian, except in the PVC plastisol, where a sigmoid is observed. This curve has a point of inflexion and reveals an apparent non-Fickian diffusion [14,15]. Both the sigmoidal shape of the curve and the high values of the water uptake in this coating can be explained by the film structure, with large heterogeneities in the bulk, some of which are voids in the shape of round holes as shown in Fig. 5. These structures are common for this coating and the voids result from the method of curing leading to fast evaporation of the solvent. Naturally, these voids tend to become filled with water, altering the distribution of water in the film. An interesting observation is that the new model does not alter the shape of the curves when compared to the BK equation.

5. Discussion

It is known that the tendency to absorb water depends on a number of factors. For example, many laboratory studies deal with clear coats. The presence of pigments implies the use of additives, normally surfactants, which can attract water, increasing the solubility in the coatings [15]. Some authors also claim that the permeability of coatings is reduced by the use of pigments, at least for low water content [16]. A possible explanation has to do with blocking of pores by the pigment particles. In any case the system heterogeneity becomes higher influencing the electric response and interfering with the water uptake estimation.

The assumptions taken for this model are basically the same as in the Brasher-Kingsbury (BK) model—the main difference lies in the definition of the mixed dielectric constant. Those authors assumed an empirical equation with a dispersion of water that does not correspond to a defined model, whereas in our model, the water the air and the solid
phase are described in parallel in each layer, with the layers being taken in series among them. This approximation leads to a very simple equation of mixture, provided the water content is considered as homogeneous across the film. Naturally, in transient transport, the layers are not equivalent among them, but instead the water content is higher in outer part of the film. That means that for a certain instant $t$, the capacitance decreases and the resistance increases from outermost layers to the inner part of the film. That is a limitation in transient transport, but not in equilibrium, i.e. after saturation is achieved.

Another limitation of the model is related with the effect of ions on the dielectric properties of the coating. This effect, on the contrary, influences the measurements in an advanced state of the sorption process, since the diffusivity of ions is usually smaller than that of the water. On the other hand, ions will more easily diffuse along pores after they have become filled with water.

Also the occurrence of leaching during immersion can in principle affect the estimations. This effect, however will only become important for a large dissolution of the solid phase, that would significantly decrease the fraction of solids, $\phi_s$, in Eq. (13).

Another point of interest is the temperature of the measurement, particularly in the relation between the solubility and the glass transition temperature, $T_g$. The solubility of water in an organic coating increases abruptly when the temperature increases above $T_g$ due to the fact that the polymer can more easily undergo structural relaxation when it is in a rubbery state. These changes influence the electrical properties of the coating so that it has been possible to infer from the glass to rubbery transition from measurements of

Fig. 4. Water absorption calculated by different models and also from gravimetric data: (a) PVC plastisol; (b) polyester; (c) PVDF.
Comparison of water uptake estimates from capacitance measurements has revealed that the estimates seem to be better below the transition temperature [17]. This temperature, however, is not a thermodynamic property. Its value depends on several factors, namely the complexity of the coating. In the coatings used the $T_g$ values are difficult to determine experimentally due to the existence of more than one phase and also to dissipation of heat by the substrate. The consequence of this is that often there is not a defined value of $T_g$, but rather a range of temperatures at which the transition takes place. However, for PVC plastisol a $T_g$ of approximately 0°C has been determined [18], which means that at the testing temperature the coating was in a rubbery state. The situation is not the same in the other coatings, for which at least part of the coating is in the glassy state. For example, in the PVDF coating, the acrylate PMMA used has a $T_g$ of $\sim 50^\circ$C [18]. For these coatings, the discrepancy between the model and the gravimetry is not so large, as expected, and in these cases the model proposed gives a remarkable agreement with gravimetry.

In spite of all the limitations discussed above, the model now proposed significantly improves the estimation of the water uptake with respect to the gravimetric data. Concerning the two equations used, no significant differences were observed between the estimates, and therefore the simplified one is considered sufficient for the estimation of the water uptake in applied films. Further work is now necessary in order to test the applicability of the model to other systems and the effect of the above mentioned parameters on the deviations of the model.

6. Conclusions

A model to estimate the water content in a polymeric coating based upon capacitance measurements is presented. The model describes the organic coating as a simple RC circuit, although this description is compatible with a random distribution of elements with different properties.

Acknowledgements

The experimental data used in this work were obtained under EU/ECSC contract 7210-TS/841. The concession of a Ph.D. grant to A.S. Castela by Program Praxis XXI and the financial support from POCTI (FCT, Portugal) are greatly acknowledged. Finally, the authors would like to thank Dr. Kauko Jyrkas/Rautaruukki Oy, Finland and Dr. Trevor Heatley/Corus, for useful discussions.

References