Assessment of Water Uptake in Coil Coatings by Capacitance Measurements

A.S. Castela and A.M. Simões
Instituto Superior Técnico, Chem. Eng. Department, 1049-001 Lisboa Portugal
Phone: 351-218417234; E-mail: pcsimoes@alfa.ist.utl.pt

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 equation has revealed an improvement in the agreement with respect to the gravimetry.

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].

Capacitance determination by Electrochemical Impedance can also be used for the study of water absorption. 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 by:

$$C = \frac{\varepsilon \varepsilon_0 A}{d} \qquad (1)$$

where □$_0$ is the dielectric constant of free space, (8.854×10^{-14} F/cm), A the surface area of the coating and d the coating thickness. Since the relative dielectric constant of polymers is typically in the range 3-8, and for pure water it is 78.3 at 25ºC, then the uptake of water shall lead to a rise in the dielectric constant, resulting in a higher capacitance.

According to a formula proposed by Hartshorn, Megson & Rushton [7] for a coating composed of three phases – solid, water and air – the mixed dielectric constant would be given by:

$$\varepsilon_x = \varepsilon_s^{\phi_s} \varepsilon_w^{\phi_w} \varepsilon_a^{\phi_a} \qquad (2)$$

where □ represents the volume fraction of each of the components, and the subscripts s, w and a correspond to the solid phase, the water and the air, 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 equation (2) gives the Brasher and Kingsbury equation [8]:

$$\phi = \frac{\log\left({C_t}/{C_0} \right)}{\log(\varepsilon_w)} \tag{3}$$

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.

Equation (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 Brasher-Kingsbury 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 film composition is constant throughout the thickness.*
d) *The coating is homogeneous, and therefore its electric parameters are considered constant in all the extension of the coating.*
e) *The electrical behaviour of the film can be described by a circuit of RC networks arranged in series.*
f) *For the working conditions the high frequency approximation can be applied.*

For uniform composition and properties of the film, the complex circuit of RC networks in series degenerates in the simple circuit [12,13] of one resistance and one capacitance, R_f and C_f, in parallel between them and in series with the solution resistance $R_{\square}$, as described in Figure 1.

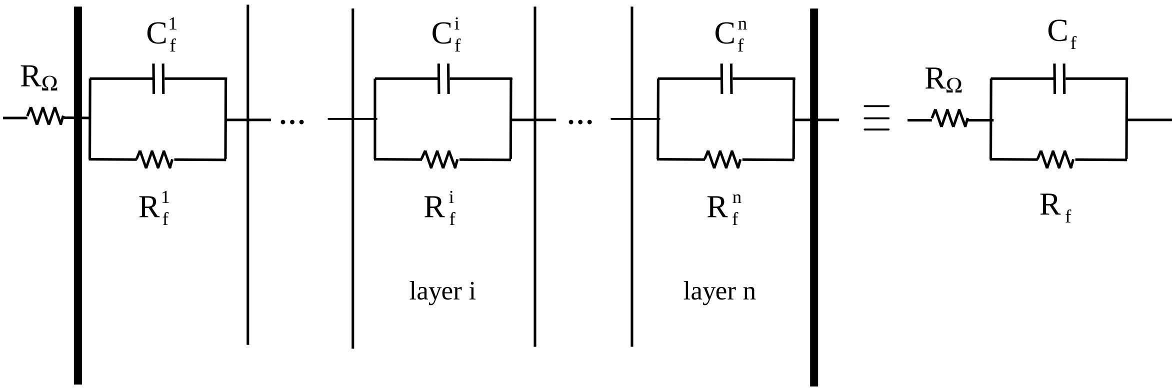

Fig. 1 – Equivalent circuit for an intact coating

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

$$Z_{imag} = -\frac{1}{\omega C_f} \tag{4}$$

A system that can be described by the previous assumptions corresponds to a mixture of independent components. In this case we shall assume that 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:

$$\varepsilon = \varepsilon_s \phi_s + \varepsilon_w \phi_w + \varepsilon_a \phi_a \tag{5}$$

which is equivalent to assuming that in each layer the regions of coating, water and air are in parallel.

By substituting in equation (4), the following expression can be derived:

$$Z_{imag} = \frac{-d}{\omega \varepsilon_0 \left(\varepsilon_s \phi_s + \varepsilon_a \phi_\mathrm{a} + \varepsilon_w \phi_w\right)} \tag{6}$$

Since for a ternary system the volume fractions are related by $\phi_s = 1 - \phi_w - \phi_a$, then:

$$C = \left(C_a - C_s\right)\phi_a + \left(C_w - C_s\right)\phi_w + C_s \tag{7}$$

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.

$$C_0 = \left(C_a - C_s\right)\phi_{a,0} + \left(C_w - C_s\right)\phi_{w,0} + C_s \tag{8}$$

with $\phi_{a,0}$ and $\phi_{w,0}$ representing the volume fractions at immersion time for air and solution respectively.

Subtracting (7)-(8) it gives:

$$C\text{-}C_0 = \left(C_a - C_s\right)\left(\phi_a - \phi_{a,0}\right) + \left(C_w - C_s\right)\left(\phi_w - \phi_{w,0}\right) \tag{9}$$

The relation between the fractions of the components can be expressed as follows:

$$\phi_s + \phi_w + \phi_a = \phi_{s,0} + \phi_{w,0} + \phi_{a,0} = 1 \tag{10}$$

From the previous relations we can obtain:

$$\left(\phi_a - \phi_{a,0}\right) = \left(\phi_{w,0} - \phi_w\right) + \left(\phi_{s,0} - \phi_s\right) \tag{11}$$

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

$$\left(C_a - C_s\right)\left(\phi_{w,0} - \phi_w\right) + \left(C_a - C_s\right)\left(\phi_{s,0} - \phi_s\right) + \left(C_w - C_s\right)\left(\phi_w - \phi_{w,0}\right) = C\text{-}C_0 \tag{12}$$

$$\left(C_a - C_s\right)\left(\phi_{s,0} - \phi_s\right) + \left(C_w - C_a\right)\left(\phi_w - \phi_{w,0}\right) = C\text{-}C_0 \tag{13}$$

Based on the assumptions *a)* and d*)* it can be stated that $\phi_{s,0} = \phi_s$. Assuming that initially the film is dry, then the final equation is obtained for the water content in a ternary system consisting of coating, water and air:

$$\phi_w = \frac{C - C_0}{C_w - C_a} \tag{14}$$

In this equation, *C* is the measured capacitance (calculated from the imaginary part of impedance) and C_0 is obtained from extrapolation of C_t to $t = 0$. C_W and C_a can be calculated from equation (1), taking $\varepsilon_w \approx 78.3$ and $\varepsilon_a \approx 1$.

A simplification of equation (14) can be obtained by considering that $C_w >> C_a$:

$$\phi_w = \frac{C - C_0}{C_w} \tag{15}$$

These two correlations, (14) and (15), 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: PVC (200 m, including acrylic primer), PVDF (27 m, including polyester primer) and polyester (27 m, including polyester primer), with various pigments.

Gravimetry

Weighting was made using a Sartorius MC5 microbalance. Although the resolution was 1 g, a minimum variation of 10 g was used in the measurements. The total weight of Ni-coated samples was in the range 700 to 800 mg (area of 3.5cm^2). After 7 days of immersion the films were quickly dried with blotting paper, passed in a cold air blow for ≈5 seconds, and weighted. 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 moment was determined as:

$$\phi_w = \frac{M - M_0}{V}\frac{1}{\rho_w} \tag{14}$$

where *M* and M_0 are the mass of the sample at any instant t and after drying. □$_W$ is the density of water (taken as 1g/cm^3) and *V* is the volume of the coating, calculated as the product of the area by the thickness (after verification by SEM of cross-cut samples). The weight of the dry sample was determined weighing and drying the samples in a desicator at ambient temperature until constant weight was obtained.

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 a 3 wt% NaCl solution, 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 30mV. 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.

3.1. Results

3.1.1. 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 desicator.

Typical drying curves are presented in Figure 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.

3.1.2. EIS

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:

- Ternary system equation (TS) – eq. (14); Simplified equation (SE) – eq. (15)
- For comparison, the Brasher and Kingsbury equation (BK) – eq. (3) – is also presented.

The water uptake at saturation for PVDF with various pigments and compositions is presented in Figure 2. The largest discrepancy is given by the BK equation. The gravimetry gave values of $\square_s$ below 1% under the working conditions, whereas the BK equation gave $\square_s$>2% in all cases. The $\square_s$ 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 equation (15) gave practically the same results as the complete equation, which is not surprising considering the difference in the dielectric constants of water and air.

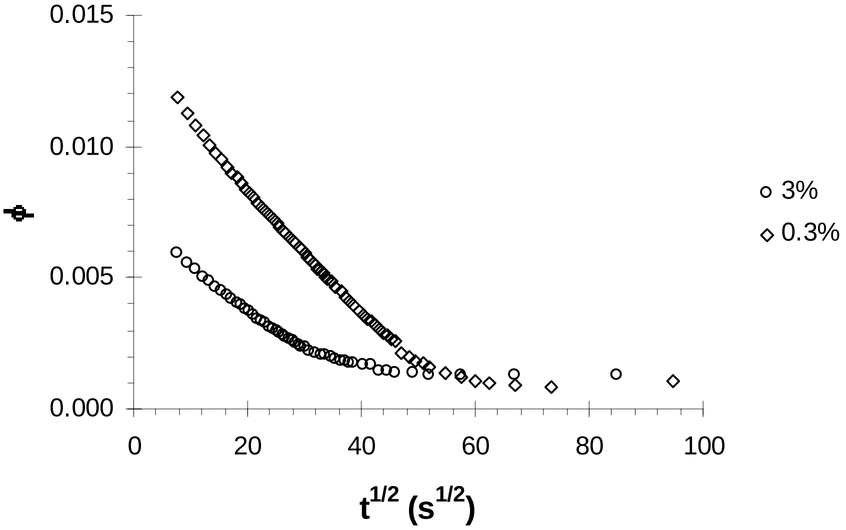

Fig. 2 – Drying curves for the various coatings.

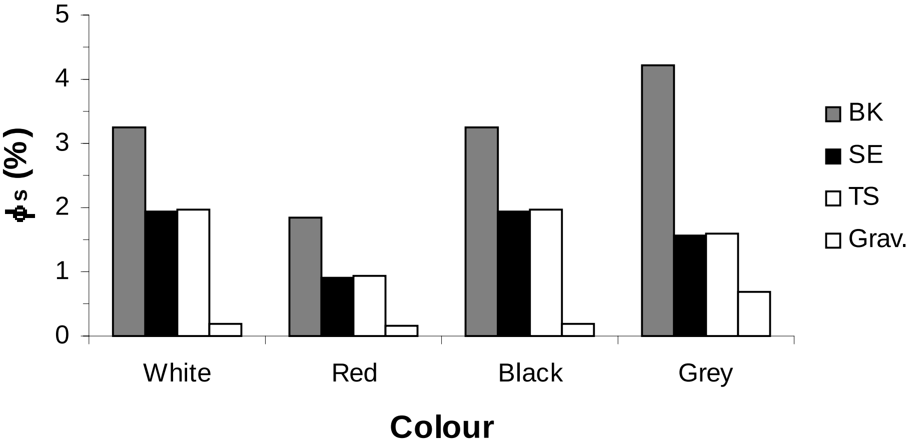

Fig. 3 – Water absorption at saturation for PVDF - BK: Brasher-Kingsbury equation; SE: Simplified equation (equation 15); TS: Ternary system (equation 14); Grav.: Gravimetry

Figure 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 inflection and reveals a 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 voids in the shape of round holes, that originate in the curing process – Figure 5. 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 Brasher - Kingsbury equation.

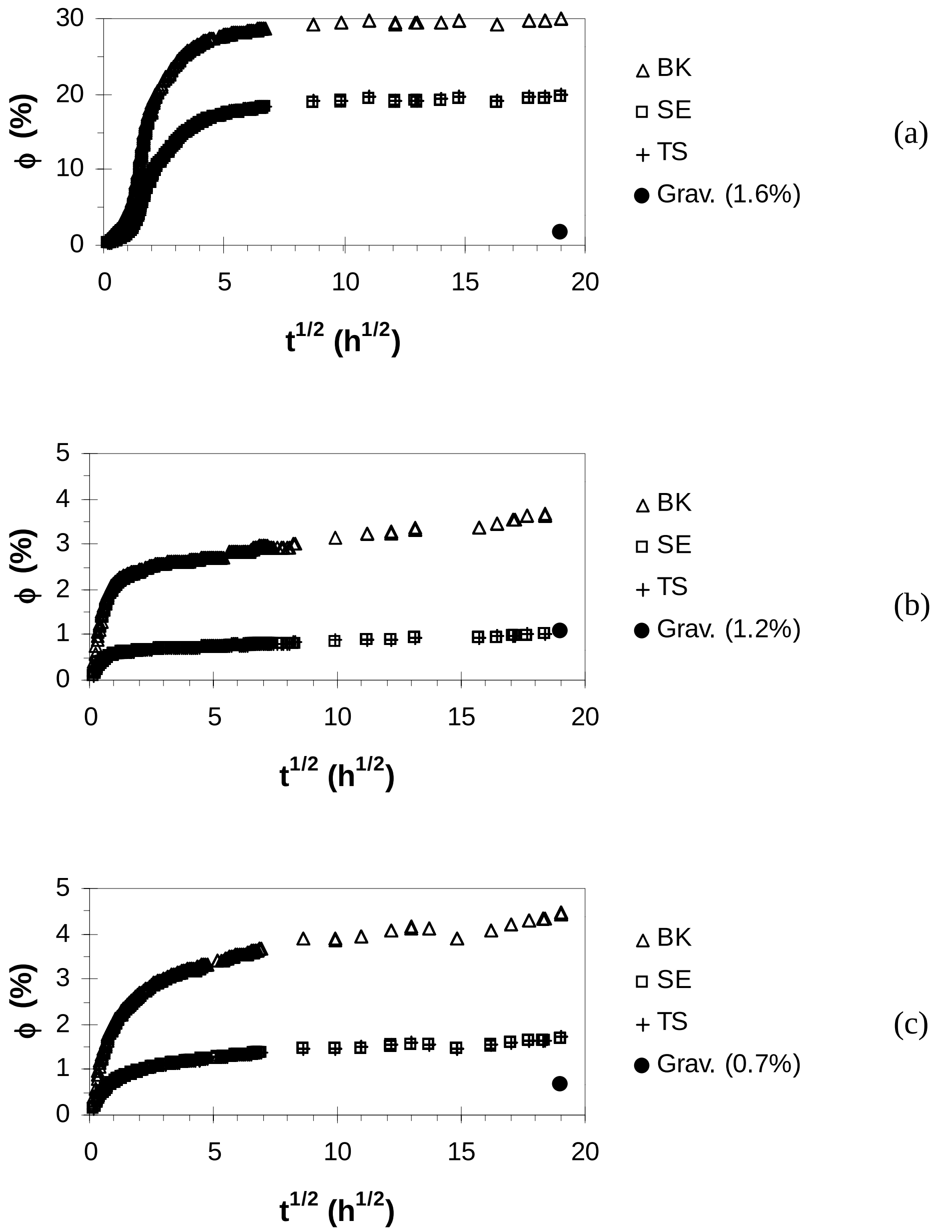

Fig. 4 – Water absorption calculated by different models and also from gravimetric data: a) PVC plastisol; b) Polyester; c) PVDF

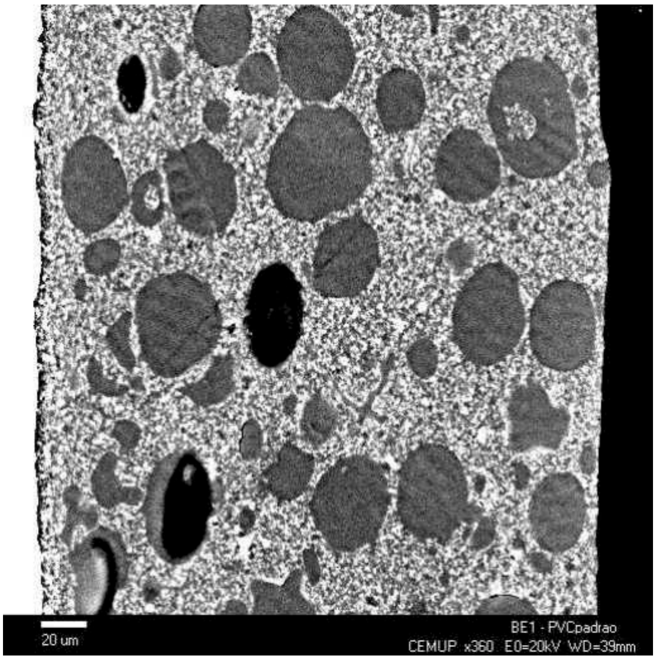

Fig. 5 – Micrograph of a cross section of the PVC plastisol

4. Discussion

The estimation of the water uptake in a coating has been often determined in the literature by means of the Brasher-Kingsbury equation. In spite of the popularity, however, not many studies have dealt with the correlation with gravimetry.

It is known that the tendency to absorb water depends on a number of factors. For example, many laboratory studies deal with clear coats, where the effect of pigments and additives does not exist. But pigments and additives usually attract water, increasing the solubility of coatings [15]. Another important parameter is the state of the coating, i.e., whether it is applied or as a free film, and it is not realistic to transfer results from freestanding to applied films [16].

The simplifying assumptions taken for this model are basically the same as in the Brasher-Kingsbury model, the main difference lying 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 a transient transport, the layers are not equivalent among them, but 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 increase as we move from outermost layers to the inside 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 the ions are smaller than that of the water. On the other hand, ions will more easily diffuse along pores after they have become filled with water.

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 electrochemical impedance [11]. 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 rate of the temperature variation and also the complexity of the coating. In commercial coatings applied on a substrate, the T_g values are sometimes 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 0ºC [18] has been determined, 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 acrilate (PMMA) used has a T_g of ~50ºC [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.

No significant differences were observed between two equations used, and therefore the simplified one is considered sufficient for the estimation of the water uptake in applied films.

A modified model has also been developed for freestanding films [19].

5. 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.

The model improves the estimation of water content made capacitance measurements with respect to previous models based upon the same type of measurements.

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