A new model for estimation of water uptake of an organic coating by EIS: The tortuosity pore model

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ABSTRACT

In this work, a new and more intricate model of estimate water uptake inside an organic coating by impedance measurements is proposed, the tortuosity pore model (TPM). In this model, the organic coating (film) is considered to be a ternary system, composed of liquid (solution), solid (coating matrix) and gas (air) phases. Moreover, the pores tortuosity inside the coating is taken into consideration. Comparison between this new model and the other models found in the literature will be presented, showing that this new model presents for water uptake better correlation with the values obtained by gravimetry.

1. Introduction

The organic coatings are widely used to protect metals against corrosion, conferring a physical barrier that makes difficult the diffusion of aggressive ions and avoiding its contact with the metal substrate. The amount of water/solution into the organic coating (film) is a very important property, contributing to the assessment of the anticorrosive protection of organic coatings.

The most used model for water uptake estimation of a film by the EIS technique is based in the Brasher and Kingsbury’s (BK) Eq. (1) [1]:

\[
\phi_{\text{water}} = \log(C_{\text{film}}) \log(\epsilon_{\text{water}})
\]

in which \(C_{\text{film}}\) and \(C_{0}\) represent the capacitance of the film and the capacitance of the “dry” film coating, respectively, \(\epsilon_{\text{water}}\) is the dielectric constant of water and \(\phi_{\text{water}}\) is the water content, expressed as volume fraction of the coating. In this model, the dielectric constant of the film is given by the Hartshont, Magson and Rushton’s formula [2] applied to a paint containing voids filled with air and water (Eq. (2)):

\[
\epsilon_{\text{film}} = \epsilon_{\text{coat}} \times \epsilon_{\text{water}} \times \phi_{\text{air}}
\]

where \(\epsilon_{\text{film}}, \epsilon_{\text{coat}}, \epsilon_{\text{air}}\) and \(\epsilon_{\text{water}}\) are the dielectric constants of the film and of the phases present in the film, respectively and \(\phi_{\text{coat}}, \phi_{\text{air}}\) and \(\phi_{\text{water}}\) the volume fractions of the same phases. In this paper, the solid part of the organic coating plus the existence pores and voids is considered as the film, whereas organic coating is only the former component.

Lindqvist [3] compared the Brasher and Kingsbury’s equation with five mixture formulas derived from the theory of the dielectric properties of heterogeneous materials. However, to estimate the amount of water absorbed by a paint film on metal, the empirical equation given by Brasher and Kingsbury gives better agreement with gravimetry than the mixture equations. Those equations are all based on the theoretical model of an inner component of spheres randomly distributed in an outer continuous media, which is too simplistic to be applied to water in paint films [3].

Bellucci and Nicodemo [4] proposed two models, one for thin films (discrete model—DM) and another one used for thicker films (continuous model—CM), for the determination of the ratio \(\phi/\phi_{\infty}\), where \(\phi\) represents the mass uptake of water in volume fraction and \(\phi_{\infty}\) the equilibrium volume fraction. In the DM model it is assumed that the organic film behaves electrically like a capacitor in parallel with a resistance, while for the CM model, the film is divided in thin layers and it is assumed to behave like a finite series of RC circuits with each layer corresponding to an RC circuit. In these models, it was not determined the absolute amount of water into the films, only the diffusion coefficients were determined.

A series of publications come out with water uptake estimations, taking into consideration the swelling of the film [5] and the non-Fickian behaviour of the water uptake process into the film...
The dielectric changes in the film are measured using constant phase elements [8] and also using the concept of dielectric relaxation and the capacitance with Cole–Cole depression [7]. Other authors [9–12] refer that water absorption by the coating leads to solid phase structural changes and, consequently, modification of their mechanical and electric properties will occur. Duval et al. [12] proposed a method for the estimation of this altered dielectric constant considering the glass transition temperature.

More recently Castella et al. [13–15] presented a model assuming that the film is composed by 3 phases, solid (coat), liquid (sol) and gaseous (air), insoluble among them, their electrical properties and ionic forces are constant throughout the thickness and the water uptake model and electrical properties of the film can be described as a finite series of RC circuits throughout the film thickness. With these assumptions, the dielectric constant of the film can be given by the average of the dielectric properties for each component expressed in the following equation [15]:

\[ \varepsilon_{film} = \varepsilon_{coat} \times \phi_{coat} + \varepsilon_{air} \times \phi_{air} + \varepsilon_{sol} \times \phi_{sol} \]  

(3)

with \( \phi_{air} \), \( \phi_{coat} \) and \( \phi_{sol} \) being the volume fractions of the air, coating and solution, respectively, and \( \varepsilon_{sol} \) corresponds to the dielectric constant of the solution.

In this study [14] two equations were established for estimation of the water uptake using results obtained by EIS: one for applied films on the substrate, the ideal binary equation—IEB (Eq. (4)) and another one for detached films, low frequency equation—LF (Eq. (5)):

\[ \phi_{IEB} = \frac{\left| Z_{imag} \right|_f \left( \left| Z \right|_f \right)^2 - \left| Z_{imag} \right|_0 \left( \left| Z \right|_0 \right)^2}{\omega (C_{sol} - C_0)} \]  

(4)

\[ \phi_{LF} = -\frac{\left| Z_{imag} \right|_f}{\omega (C_{sol} - C_0) \left| Z_{real} \right|_0 \omega (C_{sol} - C_0) \left| Z_{real} \right|_0} \]  

(5)

in which \( \left| Z_{real} \right|_f \), \( \left| Z_{imag} \right|_f \), \( \left| Z \right|_f \), represent the real part, the imaginary part and the modulus of impedance, respectively at the frequency \( f \) and time \( t \) and \( \left| Z_{imag} \right|_0 \), \( \left| Z_{real} \right|_0 \), \( \left| Z \right|_0 \), identical meaning for the same frequency \( f \) and the beginning of immersion (\( t=0 \)). \( \left| Z_{real} \right|_{f=0} \) is the real part of the impedance when frequency goes to zero at a given time, \( \omega = 2\pi f \) is the angular frequency and \( C_{sol} \) would be the capacitance if the whole film was made of solution.

It was concluded that this model presented better correlation values with the gravimetry method than the ones presented before.

The aim of this work is the development of a new model that could estimate more realistic water uptake values, i.e., better correlated with those obtained by gravimetry.

2. Model development

In the model, the tortuosity of micropores inside the film is taken into consideration and the tortuosity factor is defined [16] as the ratio between the distance that a species has to travel to get trough the film (\( f_p \)) and the thickness of the film (\( f_{film} \)):

\[ \xi = \frac{f_p}{f_{film}} \]  

(6)

Several assumptions were considered for the development of this model such as:

(i) The different phases are insoluble among them.
(ii) There is no swelling, compression or leaching of the film (\( \delta_{film} \) const.). According to Ref. [1] the water uptake produces internal stresses in the paint, with little or no swelling.
(iii) The film presents a constant composition throughout its thickness.
(iv) The volume fraction of the coating is constant during the water uptake process, which results from the combination of (i) and (ii).
(v) At the beginning of the immersion, the film is only composed by 2 phases, the coating and the air, i.e., there is no solution inside the film before the immersion. During the water uptake process, the film is composed by three phases: coating, air and solution.
(vi) Each phase presents constant electric properties throughout the film and during the water uptake process. The same happens with the ionic force inside the film.
(vii) The electrical properties of an organic film can be described as an RC circuit, as described in the literature [3,4,17,18]. This assumption can be a good approximation if the immersion solution is sufficiently conductive and the distance between the working and reference electrodes is higher than the film thickness, since in such conditions the solution is a “good” electrolyte and its impedance (\( \sim 100 \Omega \)) is negligible compared with the organic coating impedance (\( \sim 10^5 \Omega \)).
(viii) The film can be considered as a series of layers with very small thickness, \( \delta_{layer} \), as showed in Fig. 1. The electrical properties of the film for the dry and saturated condition can be described as a finite series of RC circuits, being C an ideal capacitor.
(ix) The electrical behaviour of each continuous phase present in a layer could be represented as an RC circuit where C is an ideal capacitor.

Considering that the properties of the film are homogeneous throughout its thickness for steady state (dry and saturated conditions), as described in assumptions (iii) and (vi), then the film can

\[ \text{Fig. 1. Equivalent circuit for the (a) the whole film and (b) film divided into layers.} \]
be divided into very small and identical layers, with thickness \(e_{layer}\), as considered in assumption (viii) and showed in Fig. 1, in which each layer contributes to the overall impedance of the film with the same impedance value.

Taken into consideration assumption (i) in which there is no dissolution among the film phases, it can be assumed that each layer can be composed of micro and nanocracks filled with solution or air distributed in the coating matrix, as described in Fig. 2. Consequently, each layer is divided into several regions, composed by pores filled with solution or air and the coating phase.

The development of this new model implies that the layer thickness is sufficiently thin in order the following conditions are verified:

(a) Microcracks in the layer (Fig. 2) are straight or oblique (with no curves).
(b) Each sector of the layer containing an oblique pore (Fig. 3a) can be divided into 4 different zones as described in Fig. 3b (zones 1, 2, 3 and 4). Considering assumption (ix) the electrical behaviour of each continuous phase in the pathway of a current line can be described as a RC circuit.

Considering the established constrains for the layer thickness and the generic pore geometry (Fig. 3a), the tortuosity factor of each pore is defined as

\[
\xi_p = \frac{h}{e_{layer}}
\]

(7)

where \(\xi_p\) is the tortuosity factor of each pore and \(h\) is the pore length.

The impedance, \(Z\), of the zones containing only one phase (zones 2 and 4) results from a simple RC circuit described by the following equation:

\[
Z_{zones \ 2 \ and \ 4} = \frac{\rho}{\varepsilon_\text{filler} A_{\text{filler}}} + \frac{j \varepsilon_\text{filler} \omega}{\sigma_{\text{filler}}}
\]

(8)

in which \(\rho\) and \(\varepsilon\) is the resistivity and dielectric constant of the phase, respectively, \(\omega = 2\pi f\) is the angular frequency with \(f\) being the linear frequency, \(\varepsilon_\text{filler}\) and \(A\) are the thickness and transversal area of the phase, respectively, \(\varepsilon_\text{g}\) is the dielectric permittivity of the vacuum \((8.85 \times 10^{-12} \text{ F/cm})\) and \(\sigma\) is the intensive admittance.

The main difficulty for the determination of the pore sector impedance and, consequently, of the layer impedance is the determination of the impedance for the zones 1 and 3 of the sector (Fig. 3b). The volume of each phase (coating or pore filler, being the filler the solution or air inside the pore) in the pathway of a particular current line in these zones is variable. However, for both continuous phases there is a linear variation of their thicknesses throughout the pore, from a limit situation where the current lines cross only one unique phase to the other limit situation where the current lines cross only the other continuous phase. This corresponds to the description of series and parallel RC networks which impedance is given by the following equation (Annex 1):

\[
Y_{zones \ 1 \ and \ 3} = \frac{1}{Z} \int_0^{1/Z} \left( \frac{1}{Z} \right) = \int_0^1 \frac{\varepsilon_\text{sheet}}{\Theta_{\text{coat}} X + \Theta_{\text{filler}} (1 - X)} dx
\]

\[
= \frac{\varepsilon_\text{sheet}}{\Theta_{\text{filler}} - \Theta_{\text{coat}}} \ln \left( \frac{\Theta_{\text{filler}}}{\Theta_{\text{coat}}} \right)
\]

(9)

The analytical solution of the above differential equation is apparently simple. However, the argument inside the logarithm is a complex function and the separation of the real and imaginary parts gives a complicated function. The extraction of the complex function in the argument of the logarithm can be made applying the mathematical laws for the complex numbers and also the Euler's theorem, given the following equation:

\[
Y_{zone \ 1 \ and \ 3} = \varepsilon_\text{sheet} \sqrt{\frac{\rho_{\text{filler}}}{\rho_{\text{coat}}} (1 - (B_{\text{filler}} - B_{\text{filler}}^*))}
\]

(10)

in which

\[
B_{\text{filler}} = \frac{\rho_{\text{filler}} (1 + \psi_{\text{filler}}^2) \left[ \ln - \psi_{\text{filler}} \ln \Theta_{\text{coat}} \right] - \rho_{\text{coat}} (1 + \psi_{\text{filler}}^2) \left[ \ln - \psi_{\text{filler}} \ln \Theta_{\text{coat}} \right]}{\left( \rho_{\text{filler}} - \rho_{\text{coat}} \right)^2 + \left( \rho_{\text{filler}} \psi_{\text{filler}} - \rho_{\text{coat}} \psi_{\text{coat}} \right)^2}
\]

\[
B_{\text{filler}} = \frac{\rho_{\text{filler}} (1 + \psi_{\text{filler}}^2) \left[ \ln - \psi_{\text{filler}} \ln \Theta_{\text{filler}} \right] - \rho_{\text{coat}} (1 + \psi_{\text{filler}}^2) \left[ \ln - \psi_{\text{filler}} \ln \Theta_{\text{filler}} \right]}{\left( \rho_{\text{filler}} - \rho_{\text{coat}} \right)^2 + \left( \rho_{\text{filler}} \psi_{\text{filler}} - \rho_{\text{coat}} \psi_{\text{coat}} \right)^2}
\]

(10.1)

where
\[
\left\{ \begin{align*}
A_{\text{Tg}} &= \arctg \left( \frac{\psi_{\text{coat}} - \psi_{\text{filler}}}{1 + \psi_{\text{coat}} \psi_{\text{filler}}} \right) \\
\ln n &= \ln \left( \frac{\rho_{\text{filler}}}{\rho_{\text{coat}}} \sqrt{1 + \frac{\psi_{\text{coat}}^2}{1 + \psi_{\text{filler}}^2}} \right)
\end{align*} \right.
\] (10.2)

and \( \psi = \omega \varepsilon_{\text{film}} \) for each phase present in the zone of the pore.

Since the different zones considered are in parallel with each other (Fig. 3) and the surface of the film is perpendicular to the current lines, then the total admittance of a pore sector can be obtained by the addition of the admittances of each individual zone.

Considering also that the pore sectors in a particular layer are in parallel, the admittance of the layer can be obtained by the addition of all the admittances throughout the entire layer. The application of the commutative law of the sum permits to associate the terms related with a particular phase, obtaining an equation of the following type:

\[
\frac{1}{Z_{\text{layer}}} = \sum \frac{1}{Z_{p,\text{sol}}} + \sum \frac{1}{Z_{p,\text{air}}} + \sum \frac{1}{Z_{i,\text{coat}}}
\] (11)

in which \( Z_{\text{layer}} \) is the impedance value of each layer in this model, \( Z_{p,\text{sol}} \) and \( Z_{p,\text{air}} \) are the impedances of a pore filled with solution and air, respectively, and \( Z_{i,\text{coat}} \) is the impedance value of each layer in this model, mathematically by Eq.(14.6):

\[
Z_{\text{film}} = n_{\text{layer}} Z_{\text{layer}}
\] (12)

These calculations lead to a very complicated equation for the impedance of the film. Since Eq. (12) is a complex function and that can be divided in real and imaginary parts, then the impedance of the film can be described by the following:

\[
\left\{ \begin{align*}
K_{\text{Re}}^\text{sol} &= \frac{2B_{\text{sol}} - 1}{\rho_{\text{sol}} - 1} - \frac{1}{\rho_{\text{coat}}} \\
K_{\text{Re}}^\text{air} &= \frac{2B_{\text{air}} - 1}{\rho_{\text{air}} - 1} - \frac{1}{\rho_{\text{coat}}} \\
K_{\text{Im}}^\text{sol} &= 2B_{\text{sol}}' - \omega \varepsilon_{\text{sol}} - \omega \varepsilon_{\text{film}} \\
K_{\text{Im}}^\text{air} &= 2B_{\text{air}}' - \omega \varepsilon_{\text{air}} - \omega \varepsilon_{\text{film}}
\end{align*} \right.
\] (13.1)

and \( F_{\text{sol}} = e_{\text{sheet layer}}/A_{\text{layer}} \sum \sqrt{\frac{2}{\gamma_{\text{p, sol}}}} - 1 \) and \( F_{\text{air}} = e_{\text{sheet layer}}/A_{\text{layer}} \sum \sqrt{\frac{2}{\gamma_{\text{p, air}}}} - 1 \) are defined as the tortuosity function for the pores filled with solution and air, respectively, and \( B_{\text{sol}}, B_{\text{air}}, B_{\text{air}}' \) and \( B_{\text{air}}' \) are Eq. (10.1) for the solution and air, respectively.

Considering the above statements a system of eight equations can be established, applying Eq. (13) to dry and saturated conditions and taking in consideration the assumptions (iv) and (v) presented before. The equations obtained are the following:

(a) Application of the impedance expression (Eq. (13)) to the saturated film and to the dry condition leads to four different equations, two of them describing the real part of impedance and the other two describing the imaginary part of the impedance.

\[
\begin{align*}
K_{\text{Re}}^\text{air} f_{\text{air}}' &= \frac{1}{\rho_{\text{air}}} \phi_{\text{air}}, t=0 + \frac{1}{\rho_{\text{coat}}} \phi_{\text{coat}}, t=0 = \frac{1}{\rho_{\text{film}}, t=0} \\
K_{\text{Im}}^\text{air} f_{\text{air}}, t=0 + \omega \varepsilon_{\text{film}}, t=0 &= \omega \varepsilon_{\text{film}}, t=0
\end{align*}
\] (14.1)

in which

\[
\begin{align*}
K_{\text{Re}}^\text{air} &= 2B_{\text{air}} - \frac{1}{\rho_{\text{air}} - 1} - \frac{1}{\rho_{\text{coat}}} \\
K_{\text{Im}}^\text{air} &= 2B_{\text{air}}' - \omega \varepsilon_{\text{air}} - \omega \varepsilon_{\text{film}} + \omega \varepsilon_{\text{film}} \\
F_{\text{air}}, t=0 &= e_{\text{sheet layer}}/A_{\text{layer}} \sum \sqrt{\frac{2}{\gamma_{\text{p, air}}}} - 1
\end{align*}
\] (14.2)

where \( B_{\text{air}}' \) and \( B_{\text{air}}' \) are the expressions described in Eq. (13.1) for air.

(b) As the sum of the volume fraction of all phases must be one, two equations are obtained, one for the dry condition (Eq. (14.5)) and the other for the saturation condition (Eq. (14.6)).

\[
\begin{align*}
\phi_{\text{air}}, t=0 + \phi_{\text{coat}}, t=0 &= 1 \\
\phi_{\text{air}}, t=0 + \phi_{\text{coat}}, t=0 + \phi_{\text{sol}}, t=0 &= 1
\end{align*}
\] (14.5)

(c) From assumption (iv) it must be assumed that the air volume fraction at the dry condition must be equal to the sum of the volume fractions of the air and solution in the saturated film, Eq. (14.7)

\[
\phi_{\text{air}}, t=0 = \phi_{\text{air}}, t=0 + \phi_{\text{sol}}, t=0
\] (14.7)
(d) Since the liquid phase substitutes partially the gaseous one, the
pore tortuosity function of the air at $t = 0$ has to be equal to the
sum of the pore tortuosity functions for the air and solution in
the saturation condition, Eq. (14.8).

$$\sqrt{2} \sum p_{\text{air}, t=0} - 1 = \sqrt{2} \sum p_{\text{air}, \text{sat}} - 1 + \sqrt{2} \sum p_{\text{sol}, \text{sat}} - 1$$  \hspace{1cm} (14.8)

The resolution of the eight equation’s system leads to the fol-
lowing equation for the water uptake fraction:

$$\phi_{\text{sol, sat}} = \frac{\omega \varepsilon \Gamma (\varepsilon_{\text{film, sat}} - \varepsilon_{\text{film, t=0}}) - \sum (1/\rho_{\text{film, sat}} - 1/\rho_{\text{film, t=0}})}{\omega \varepsilon \Gamma (\varepsilon_{\text{sol}} - \varepsilon_{\text{air}}) - \sum (1/\rho_{\text{sol}} - 1/\rho_{\text{air}})}$$  \hspace{1cm} (15)

in which

$$\Gamma = [2B_{\text{air}} - 1/\rho_{\text{air}} - 2B_{\text{sol}} + 1/\rho_{\text{sol}}]$$

$$\Sigma = [2B_{\text{air}} - \omega \varepsilon \Gamma_{\text{air}} - 2B_{\text{sol}} + \omega \varepsilon \Gamma_{\text{sol}}]$$

where the terms $B$ are defined through Eq. (10.1).

It must be noticed that the electric properties values (resistivity
and dielectric constant) of the components of the film, i.e., air,
solution and coating should be previously known, while the elec-
tric properties of the film (in dry and saturated conditions) are
experimental values obtained directly from impedance measure-
ments.

One of the difficulties of this model is related with the
knowledge of the electrical properties of each component of
the film. For the air it seems a good approximation to consider
$\rho_{\text{air}} = 4 \times 10^{13} \, \Omega \, \text{cm}^{-1}$ and $\varepsilon_{\text{air}} = 1$ [19], despite some level of humidity
is expected for the air when water permeates the film. For the
solution inside the pores, the electrical properties of the immer-
sion solutions were used; nevertheless this could lead to some errors [6].

Finally, the electrical parameters for the solid phase are very
difficult to estimate. For this model it was considered a limited group
of possible values with physical meaning and the worst case sce-
nario, i.e., the parameters values used are those which maximize the
water uptake (Annex 2). It was not considered changes in the coat-
ing electrical parameters induced by the water permeation [12], as
consequence of the assumptions (i) and (ii), although this intro-
duces some error in the model. However, considering dissolution of
water in the coating and lixiviation of the solid phase would turn
the model even more difficult to establish and use.

Eq. (15) is complex and its use is difficult. For practical applica-
tions a valid numerical approximation of the global equation was
made with the aim to obtain a simpler equation that facilitates the
use of the tortuosity pore model (TPM):

$$\phi_{\text{TPM}} = \frac{\varepsilon_{\text{film, sat}} - \varepsilon_{\text{film, t=0}} - \varepsilon_{\text{sol}} \rho_{\text{sol}} (1/\rho_{\text{film, sat}} - 1/\rho_{\text{film, t=0}})}{2 \varepsilon_{\text{coat}} (1/\rho_{\text{film, sat}} - 1/\rho_{\text{film, t=0}})}$$

This approximation was also obtained using the same limited range of values defined in Annex 2, assuring that a deviation of $\phi$
from the original equation (Eq. (15)) was less than 10%.

3. Model validation

3.1. Experimental procedure

3.1.1. Samples

This study was made using plasticized PVC (PVC plastisol) indus-
trially used in the coil-coating industry. The polymer film was
studied as both applied film in nickel foil and detached. In the first
case the film was applied on pure nickel foil (0.15 mm of thick-
ness, 99%, Goodfellow) with the purpose to avoid corrosion of the
substrate allowing the study of the organic film behaviour without
interference of corrosion. The applied films contained a PVC plastisol
top coat (160 $\mu$m of thickness) on an acrylic primer (40 $\mu$m
of thickness). The detached films (only PVC plastisol) presented an
average thickness of 200 $\mu$m. All the thickness measurements were
made with a micrometer (Mitutoyo series 293 with precision of
0.001 mm).

3.1.2. Electrochemical impedance spectroscopy (EIS) measurements

Two different electrochemical cells were used. For the detached
films, the measurements were made in a four-electrode cell, while
for the applied films a three electrode cell was used. As electrodes,
platinum wire was used, with two different exposed areas: smaller
area acting as reference and the larger area acting as counter elec-
drodes.

For the applied films, the electrochemical impedance measure-
ments were made using a Gamry FAS1 Femtostat + PC4 Controller
Board. A Frequency Response Analysers (Solartron 1255) coupled
to an Electrochemical Interface (Solartron 1286) was used for the
detached films, since a four electrodes systems cannot be used in
Gamry equipment. The spectra acquisition was made using two fre-
quency ranges. For the complete spectra a 65 kHz–0.5 Hz frequency
range was swept with 9 points per decade. For fast measurements at
the beginning of immersion, the 60–10 kHz frequency range was
swept with 8 points per decade. In all cases a 5 mV amplitude wave
was applied and the exposed area was 3.14 cm$^2$. The measurements
lasted for 4 weeks of immersion, at room temperature in 0.5 M and
0.05 M NaCl solutions.

For the determination of electrical parameters of the film, it
was assumed that the film behaves like an RC circuit with an ideal
capacitor at a single frequency (50 kHz). At this frequency the elec-
trolyte resistance (100 $\Omega$) is much smaller than the film resistance
(10$^7$ $\Omega$), consequently the solution interference is negligible. The
dielectric constant ($\varepsilon_{\text{film}}$) and the resistivity ($\rho_{\text{film}}$) of the film can be
determined by the following expressions:

$$\varepsilon_{\text{film}} = \frac{|Z_{\text{imag}}|}{|Z|} \times \frac{1}{\varepsilon_0} \times \frac{\varepsilon_{\text{film}}}{A_{\text{film}} E_0}$$  \hspace{1cm} (17)

$$\rho_{\text{film}} = \frac{|Z_{\text{real}}|^2}{|Z|^2} \times \frac{A_{\text{film}}}{\varepsilon_{\text{film}}}$$  \hspace{1cm} (18)

where $Z_{\text{real}}$, $Z_{\text{imag}}$ and $|Z|$ are the real part, imaginary part and
modulus of the impedance of the film, $\varepsilon_{\text{film}}$ and $A_{\text{film}}$ the thickness and
area of the film and $f$ the frequency at which the measurements are
made (50 kHz) and $\varepsilon_0$ the dielectric permittivity of the vacuum
(8.85 x 10$^{-12}$ F/cm).

For the determination of electrical properties of the film in dry
conditions, the impedance measurements were performed imme-
diately since the beginning of immersion at a single frequency
(50 kHz) during a short period of time. The impedance values used
were obtained from linear extrapolation of the impedance values
at the initial time of immersion ($t = 0$).

3.1.3. Gravimetric measurements

The gravimetric measurements were made using a Sartorius
MC5 microbalance with 1 $\mu$g resolution. The samples areas were
2.25 cm$^2$ and they were kept in desiccators for 1 week before
immersion in 0.5 M or 0.05 M NaCl solutions. The samples were
immersed during 4 weeks and the immersion solution tempera-
ture was kept at 22 ± 1 $^\circ$C. When removed from the solutions, the
samples were quickly dried with filter paper and the loss of weight

Fig. 4. Bode diagrams for detached and applied PVC plastisol films immersed in 0.5 M NaCl solutions.

during the drying of the film is monitored until complete dryness. The water absorption by the gravimetric method is calculated by the following equation:

\[
\varphi_{\text{grav}} = \frac{M_{\text{sat}} - M_{\text{film}}}{V_{\text{film}}} \times \frac{1}{d_{\text{water}}} \quad (19)
\]

where \( M_{\text{sat}} \) and \( M_{\text{film}} \) represent the weight of the film in saturation and after drying (dry weight), respectively, \( d_{\text{water}} \) the specific gravity of water and \( V_{\text{film}} \) the film volume for each sample. The water absorption calculated by this method was referred to the final dry weight, due to the leaching that occurs in this type of films. The weight of the coating in the saturation was obtained by linear extrapolation of the weight loss curve for the first instant of drying. The dry weight was determined after the sample dry in a desiccator for 4 weeks.

4. Results and discussion

Fig. 4 depicts the Bode diagram for the detached and applied PVC film immersed in 0.5 M of NaCl solution. It can be observed that the spectra change with time, with the impedance decreasing as water uptake penetrates into the film.

Nevertheless the spectrum does not correspond to an ideal capacitive-resistive response (assumption (vii)) in the high frequency region it was considered such that to estimate the electrical properties for this type of film. The same was made in previous models [1,4,13,14], since the consideration of non-ideal circuits would make the models even more complex to use.

Fig. 5 depicts values estimated for the water uptake of the detached film using the Brasher and Kingsbury’s equation—BK (Eq. (1)), the low frequency equation—LF (Eq. (5)) and the tortuosity pore model—TPM (Eq. (16)). These results are compared with the ones obtained by gravimetry, considered as the reference technique. In this case it can be observed that, for the more concentrated solution (0.5 M NaCl), the TPM presented estimated water uptake values better correlated with the gravimetric technique, while for the more diluted solution (0.05 M NaCl) the TPM gives values slightly higher than the ones obtained using the LF equation. This fact is due to the approximation that is made in the LF equation [14]. In this case of Eq. (5), a low frequency approximation was used in the deduction of the equation and that could be responsible for the slightly better results observed when compared with the TPM for diluted solutions. For longer immersion times the RC circuit becomes non-ideal and the values obtained for the lower frequency impedances are higher than for the ideal circuit, leading to lower water uptake values.

In Fig. 6 is represented the water uptake estimation for the applied film obtained in the same conditions as before, with the difference that the LF equation is replaced with the ideal binary equation—EIB equation (Eq. (4)), which presents better results when used for applied films [14]. It was observed that, for both the immersion solutions, the TPM gives water uptake values better correlated with the gravimetry ones, when compared to the other two models. It must be stressed that this new model, like the other
5. Conclusions

A new model to estimate water uptake inside non-conductive films was established taking into consideration the film tortuosity. For practical applications the original equation resulting from the model was simplified in order to obtain a handsome equation that makes its use simpler.

Although for the use of the TPM model it is necessary to know the electrical properties of the solid phase, \( \varepsilon_{\text{coat}} \) and \( \rho_{\text{coat}} \), this can be overcome establishing the limits for the values of the resistivity and the dielectric constant of the coatings.

For the PVC plastisol films, the water uptake estimated by the tortuosity pore model generally correlates better with the values obtained by the gravimetric method. In case of detached films immersed in diluted solutions, the values obtained with the TPM model are slightly higher than those obtained with the LF equation, possibly due to the fact that for longer immersion times the RC circuit becomes non-ideal.

Differences between water uptake values in diluted and concentrated solutions for detached films are smaller for the TPM model, suggesting that a further refinement of the model can lead to results in accordance with the gravimetry.

Although the results obtained are promising, further work is being carried out in order to improve the present model and make its practical use easier.

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Annex 1. : Determination of the impedance for zones 1 and 3

Accordingly the geometry of the pore in zone 1 (Fig. A1.1) the following trigonometric relations can be derived:

\[
\begin{align*}
\xi_{\text{filler}} &= h \cos \alpha \\
X &= h \sin \alpha \\
\end{align*}
\]

and, consequently

\[
\xi_{\text{pore}} = \frac{X}{\xi_{\text{filler}}} = \frac{1}{\cos \alpha}
\]

Using the Pythagoras theorem applied to the triangle marked in the same figure the following equations can be obtained:

\[
\begin{align*}
\xi_{\text{filler}} &= \frac{X}{\sqrt{\varepsilon_{\text{filler}}^2 - 1}} \\
\xi_{\text{layer}} &= \frac{X_{\text{pore}}}{\sqrt{\varepsilon_{\text{pore}}^2 - 1}} \\
\end{align*}
\]

The impedance equation for each current line in zone 1 can be described as a two RC circuits in series (Eq. (8)), each one established for an isolated phase (coating and filler). Since the transversal area of each current lines can be considered constant and given by \( \xi_{\text{sheet}} \Delta X \), in which \( \xi_{\text{sheet}} \) is considered the lateral thickness of the layer (Fig. 3a). The impedance for each current line is obtained by the following equation:

\[
Z = \frac{\rho_{\text{coat}} \varepsilon_{\text{coat}}}{\sqrt{\varepsilon_{\text{filler}}^2 - 1}} \Delta X + \frac{\rho_{\text{filler}} \xi_{\text{filler}}}{\sqrt{\varepsilon_{\text{pore}}^2 - 1}} \Delta X
\]

This equation can be manipulated using Eq. (A1.2) and considering \( \varepsilon_{\text{coat}} = \xi_{\text{layer}} - \xi_{\text{filler}} \). The resulting equation is given by:

\[
Z = \Theta_{\text{coat}} \frac{X}{\xi_{\text{sheet}} \sqrt{\varepsilon_{\text{pore}}^2 - 1}} \Delta X + \Theta_{\text{filler}} \frac{1 - X}{\xi_{\text{sheet}} \sqrt{\varepsilon_{\text{pore}}^2 - 1}} \Delta X
\]

in which \( \Theta = \rho [1 + (\omega \varepsilon_0 \rho)] = \rho - \omega \varepsilon_0 \rho^2 j / [1 + (\omega \varepsilon_0 \rho)^2] \) is the intensive admittance for an ideal RC circuit (see Eq. (8)), \( X \) is an non-dimensional integration variable given by \( x = X/X_{\text{pore}} \) and, consequently, \( \Delta X \) is given by \( x = \Delta X/X_{\text{pore}} \).
Since all the current lines in zone 1 are in parallel between them, then the total admittance of zone 1 is the sum of the admittances corresponding to all current lines. Considering that for each current line the area is infinitely small ($\Delta x \to 0 = \Delta g x - dx$), then the total admittance of zone 1 can be obtained by the following integral:

$$Y = \int_0^{1/Z} d \left( \frac{1}{Z} \right)$$

$$= \varepsilon_{\text{sheet}} \sqrt{\frac{2}{p}} \frac{1}{\varepsilon_{\text{coat}} - \varepsilon_{\text{filler}}} \int_{x=0}^{1} \left( \frac{\Theta_{\text{coat}} - \Theta_{\text{filler}}}{\Theta_{\text{coat}} - \Theta_{\text{filler}}} \right) \frac{1}{\Theta_{\text{coat}} + \Theta_{\text{filler}}} dx \quad (A1.5)$$

For zone 3 an identical equation will be found.

Annex 2. : Estimation of the electrical parameters of the coating phase

For the use of the TPM model in the estimation of water uptake it is necessary to know the electrical properties of the solid phase, $\varepsilon_{\text{coat}}$ and $\rho_{\text{coat}}$.

As referred before a system of 8 equations is obtained. The number of considered variables is 7 which make the system resoluble. These variables are the volume fractions of the phases at the beginning, $t=0$ (without solution) and at the saturation, sat, defined as $\phi_{\text{coat}}, \phi_{\text{air}}$, $\phi_{\text{air},t}$ and $\phi_{\text{filler},s,\text{sat}}$. The tortuosity pore functions for the air and solution at the beginning and saturation are the other three variables $F_{\text{air},t}$, $F_{\text{air},\text{sat}}$ and $F_{\text{sol},\text{sat}}$.

Considering that this model must give values for the variables that have physical meaning the following limitations were used:

(a) The coating volume fraction must be between 0.7 < $\phi_{\text{coat}}$ < 1.
(b) The water uptake cannot be negative or higher than 50% (0 < $\phi_{\text{sol},s,\text{sat}}$ < 0.5); the same was applied to the air volume fraction.
(c) Considering the geometry of the pores it can be proved that the tortuosity pore functions must be positive but lower than the respective volume fractions.

The $\varepsilon_{\text{coat}}$ and $\rho_{\text{coat}}$ values that verify these limitations are included in a narrow area (shaded area) plotted in Fig. A2.1.

Applying the impedance equation (Eq. (13)) for the dry film and considering the high frequency conditions (the film behaves like a pure capacitance), it is possible to obtain a simpler equation. The same can be made for the low frequency condition, in which the film presents a pure resistive behaviour. The conjugation of these two new equations can lead to a mathematical equation that relates the volume fraction of the coating with the dielectric constant and the resistivity of the solid phase ($\varepsilon_{\text{coat}}$ and $\rho_{\text{coat}}$):

$$\phi_{\text{coat}} = \frac{(\varepsilon_{\text{film},t} - 1)(\varepsilon_{\text{coat}} - 1)\Pi - \Lambda(1/\varepsilon_{\text{film},t} - 1/\rho_{\text{coat}})(\rho_{\text{air}} - \rho_{\text{coat}})}{(\varepsilon_{\text{coat}} - 1)^2\Pi - \Lambda(1/\varepsilon_{\text{coat}} - 1/\rho_{\text{coat}})(\rho_{\text{air}} - \rho_{\text{coat}})} \quad (A2.1)$$

in which

$$\Pi = \left[2 \ln(\rho_{\text{air}}/\rho_{\text{coat}}) - 1/\rho_{\text{air}} + 1/\rho_{\text{coat}}\right]$$

$$\Lambda = 2\varepsilon_{\text{coat}} \ln(\varepsilon_{\text{coat}}) + (\varepsilon_{\text{coat}} - 1)(-\varepsilon_{\text{coat}} - 1)$$

(A2.1')

This volume fraction of the coating must be equal to the volume fraction of the solid phase obtained in the mixture Eq. (13). This can lead to a mathematical equation that relates the dielectric constant and the resistivity of the solid phase ($\varepsilon_{\text{coat}}$ and $\rho_{\text{coat}}$) and it is represented in Fig. A2.1 by the broken line.

In spite of the broken line and the shaded area do not intercept it can be observed that they become quite near for lower $\varepsilon_{\text{coat}}$ and higher $\rho_{\text{coat}}$ values. It can be showed (Fig. A2.2) that the conjugation of low dielectric constant and high resistivity leads to the highest estimated values for water uptake obtained by this model (Eq. (15)). This showed that the worst case scenario for the estimation of this parameter is to use the smaller allowed values for $\varepsilon_{\text{coat}}$ and the larger ones for $\rho_{\text{coat}}$. It will be showed that even in this case the estimated water uptake show better correlation with the values obtained by the gravimetric technique.

For applied films of the type studied in this work the values that can be used with physical meaning are the dielectric constants that are in the interval 5–6.7, while for the resistivity parameter the values should be in the region $4 \times 10^7$ to $7 \times 10^7$ $\Omega$ cm. For the detached films the resistivity values are approximately the same, while the dielectric constant values are slightly higher (7–8.5). These values are in accordance with the expected ones, since the electrical parameters are affected by the presence of other compounds, namely inorganic ones, used in the manufacture of an organic coating, which leads to the decrease in the resistivity values since more additives correspond to more pores, conductive pathways and different pore geometries, namely the tortuosity factors. A polymer dielectric constant in the range 3–8 is commonly accepted [6, 17, 24]; however, inorganic compounds such as pigments and other additives could increase it. The difference between the dielectric constants of applied and detached films can be explained by the fact that the applied film is not only PVC plastisol, but also an acrylic primer with anticorrosive pigments, which affects the electrical parameters estimation of the coating.
References
