چکیده:

ارزیابی فیلم های پلیمری متصل و آزاد

نفوذپذیری پوشش یک PVC متصل به سوکت فلزی همانند یک فیلم آزاد توسط طیف سنج امپدانس الکتروشیمیایی ارزیابی شده است و نتیجه آن با تست های گراویمتری مقایسه شده است .

طیف امپدانس گونه ی کاربردی متصل و آزاد رفتار های متفاتی داشتند.

غلظت بیرونی محلول تعیین کننده ای برای پوشش خاذن است و برای جذب آب فیلم می باشد.

نتایج تفاوت های مهمی را بین این ۲ روش نشان داد.

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E.I.S. evaluation of attached and free polymer films

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Abstract

Permeability of a PVC coating attached to a metal substrate and as a free film was assessed by electrochemical impedance spectroscopy. The results were compared with those from gravimetric tests. The impedance spectra of applied and free films have distinct behaviour. The concentration of the outer solution is determinant for the coating capacitance and for the water uptake of the film. The results revealed important differences between the two techniques. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Organic coatings; PVC coatings; Electrochemical impedance

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1. Introduction

PVC polymers can be blended and mixed with plasticizers in various proportions, producing a significant number of blends with different degrees of hardness/softness. These blends can be used in numerous applications such as mem-branes, tubes or coil coatings. In coil-coated steel, the dura-bility of the materials depends greatly on the adhesion be-tween coating and substrate. When in contact with water, however, the coating absorbs water, swells and often the adhesion is lost or decreased.

It has been reported that the swelling of coatings on rigid substrates when in contact with solution lead to a raise of the internal tensions [1], which can lead to loss of adhesion. For PVC applied on a substrate, wrinkle formation was observed during immersion [2], possibly as a consequence of these internal tensions.

Estimation of the volume fraction of water in organic coatings is often made by electrochemical impedance spectroscopy (EIS) and based upon the evolution of the coating capacitance, according to the Brasher–Kingsbury equation [3]:

$$D \quad \frac{\log.C_t = C_0 \ \ /}{\log.80/} \ ; \tag{1}$$

in which C_t is the coating capacitance at an instant t and C_0 the capacitance of the “dry” coating, usually obtained by extrapolation to the instant of immersion. This equation is based upon a number of assumptions, namely a low concentration of water in the coating and a uniform water distribution across the coating. Of these two assumptions, the first usually limits the validity of the equation to the initial stages of absorption, whereas the second can never be satis-fied in a process of transient mass transfer. In spite of that, a work by Lindqvist [4] revealed a fairly good agreement of the Brasher–Kingsbury equation with gravimetric tests made on several types of coatings. It seems however that the degree of deviation depended greatly on the composition of the coating [4].

Assessment of the degradation of a coating has been made also by measuring the coating resistance. Walter [5] reported changes of capacitance and resistance during immersion in sodium chloride solution, attributed the paint film degrada-tion to the sodium chloride solutions and concluded that this degradation could be assessed by the drop in paint film re-sistance.

Most determinations based on impedance measurements are made on coated steel. However, a few studies using free films can be found in the literature [4,5]. Although not very conclusive, these studies are based on the assumption that the behaviour of a coated substrate could be partially inferred from the properties of the coating studied as a freestanding film. This work applies that idea to free and attached films of PVC coil coating.

2. Experimental work

2.1. Materials and cells

The study was made using plasticized PVC (commercially known as PVC “plastisol”), industrially used coil coating for steel. The polymer film was studied either as a free film

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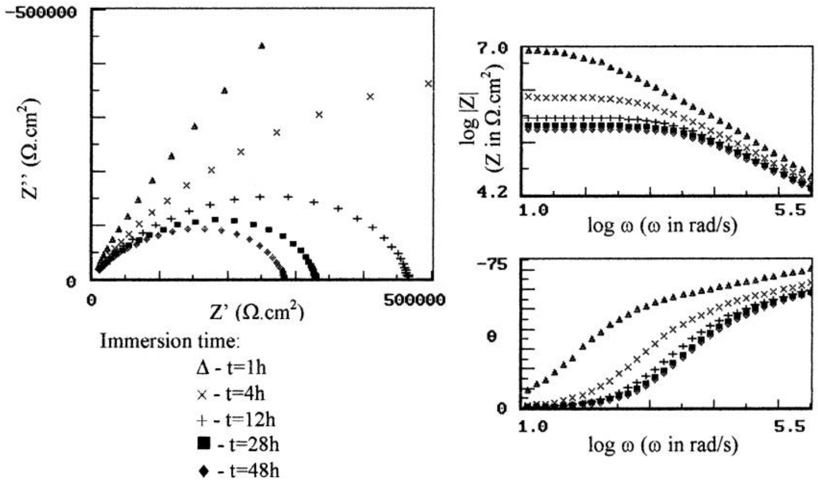

Fig. 1. Impedance spectra of free film at various immersion times (3% NaCl).

(140 _m) or applied (200 _m) over an acrylic primer (5 _m) on galvanized steel substrate (20 _m zinc layer).

The electrochemical measurements on the attached films were made using a three-electrode cell in which the sample was placed horizontally. A perspex cylinder was glued to the sample and filled with solution. The exposed area was 66 cm^2. A stainless steel (AISI 316) counter electrode and a saturated calomel electrode (SCE) completed the arrangement. The total volume of electrolyte was 500 cm^3.

For the free films a two-compartment cylindrical cell was used, the separation being made at a hole with an area of 2 cm^2. The free film, consisting only of the PVC without any primer, was held vertically between two perspex holders, closing this hole. A four-electrode arrangement was used, the electric current flowing between two identical electrodes (AISI 316 stainless steel) placed on opposite sides of the film. One SCE was placed in each compartment for correct potential measurement. The electrolyte was NaCl in aqueous solutions, the concentrations being the same in the same in the two compartments.

All measurements were made at ambient temperature (20 C), in NaCl aqueous solutions with concentrations of 0.3–3 wt.%.

2.2. Impedance measurements

The impedance measurements were made using a Solartron 1255 frequency response analyzer and a Solartron 1256 electrochemical interface. For the painted panels, a sine wave of 30 mV (rms) was applied across the cell. The same amplitude was tried on the two-compartment cell for the measurements across the film, but since film breakdown occurred in a few cases, a 10 mV amplitude was chosen.

2.3. Gravimetric tests

Free films with an area of 2.5 2.5 cm^2 were dried in a dessicator and then immersed in NaCl solution. At chosen times each film was taken from the solution, the excess water was quickly removed with filter paper, and the weighing made with a Sartorius MC5 microbalance (1 _g resolution).

3. Results

At the beginning of the immersion period, the impedance measurements made on free films in a frequency range of 50 kHz–2 Hz revealed a fully capacitive behavior. After a 1 h of immersion a resistive behavior was already visible at the low frequencies (Fig. 1). This resistance regularly decreased during immersion, whereas the capacitance increased. These changes were very pronounced in the first hours of immersion and later became less significant, especially after the first day of immersion.

A simple way to interpret these spectra is to determine the capacitance and the resistance at a fixed frequency. Walter [5] made a study in which the changes in the film were followed by measuring the 1 kHz capacitance. With the present data, and because the phase angle is always below 90 , the frequency at which the measurements are made can be of influence on the capacitance calculated directly from the imaginary part of impedance. This influence can be observed in Fig. 2, where the single frequency capacitance, determined as C D 1/2 fZ^{00}, is plotted as a function of the frequency, f. The 1 kHz capacitance is within the range of the nF cm^{-2}, with a phase angle of 40 . As the frequency increases, the phase angle also increases and the capacitance tends towards a more stable value. The higher frequencies were therefore considered more reliable for the capacitance measurements, and the frequency of 50 kHz was chosen in this study.

The resistance of the film was taken as the modulus of the impedance at 2 Hz. The evolution of the capacitance and of the resistance of the polymer film is plotted in Fig. 3 a for a free film immersed in 3% NaCl solution. The resistance decreased by three orders of magnitude as a consequence of immersion, from 2 10^8 to 2 10^5 • cm^2,

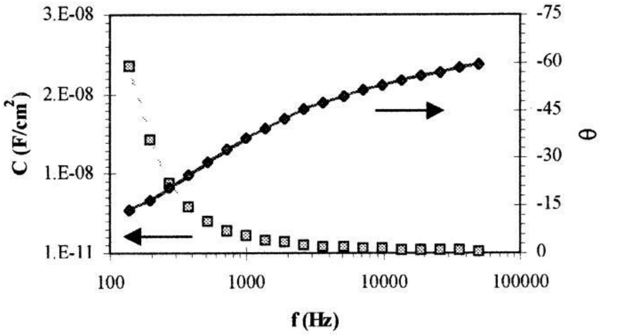

Fig. 2. Phase angle and calculated capacitance and as a function of frequency.

whereas the 50 kHz capacitance increased by one order of magnitude, from 5 10^{-11} to 3 10^{-10} F cm^{-2}. These variations were more pronounced during the first few hours of immersion, and became slower for longer exposure times. After 2 days of continuous exposure the variations in these parameters were practically negligible, suggesting a state of pseudo-equilibrium. When the resistance and the capacitance are plotted as a function of the square root of time, the variations for short exposure times become more evident (Fig. 3b) and the first part of the capacitance curve becomes practically a straight line. Extrapolation of the capacitance to the instant of immersion (t D 0) gives a value that can be associated with the properties of the dry film. In Fig. 3b, the value is C_0 D 3.8 10^{-11} F cm^{-2}, which corresponds to a relative permitivity of approximately 6, a value considered typical for a polymer film. For the resistance, extrapolation of the curve to smaller times would give an asymptotical curve, and thus a resistance value at the origin, R_0, cannot be determined. This translates the fact that at the instant of immersion, when film can still be considered dry, the impedance is too high and cannot be measured.

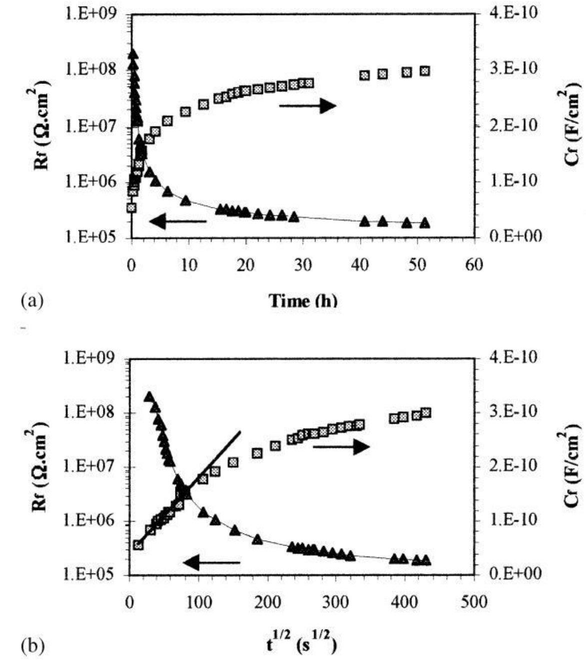

Fig. 3. Coating capacitance and resistance for a PVC free film as a function of time, during immersion in 3% NaCl, plotted in different time scales.

In another experiment, a free film was exposed to 0.3% NaCl in a first stage, and after pseudo-equilibrium was reached, the solution was changed by another one of different concentration. In this way, and using the same sample of film, impedance spectra for increasing concentrations were obtained in conditions of pseudo-equilibrium. In the tests the solution was always identical between the two cell compartments, so that there was no global concentration gradient across the cell.

Fig. 4 depicts the impedance spectra obtained in the various NaCl concentrations used: 0.3%, 1%, 2% and 3%. For each concentration, the films were allowed for stabilize for

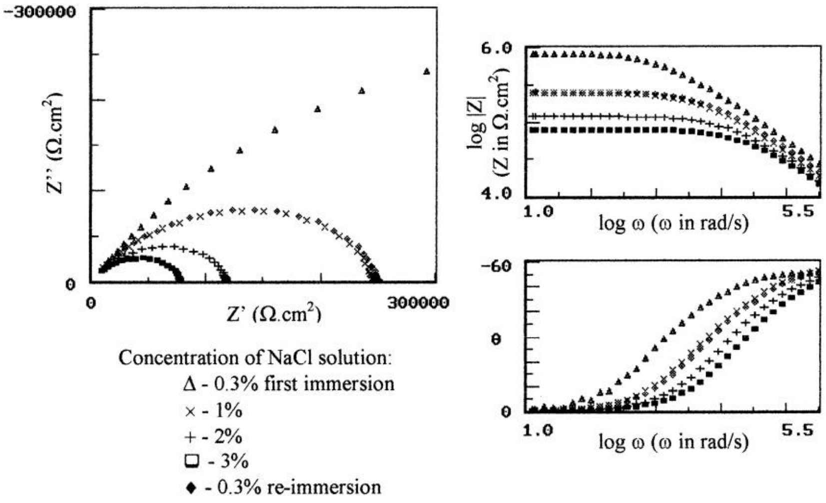

Fig. 4. Impedance spectra of a free film for different concentrations of NaCl solution.

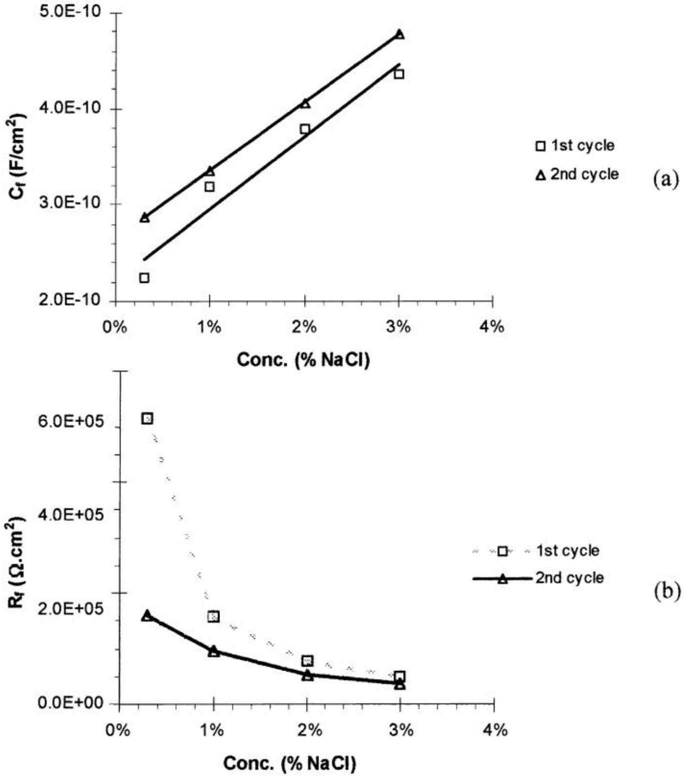

Fig. 5. (a) Film capacitance and (b) film resistance, of plastisol free film as a function of concentration of NaCl solution.

1 week. After the end of the cycle, the film was again re-immersed in the 0.3% solution until stabilization. It was observed that the impedance spectrum changed again, in the sense that it approached the one originally observed in the same solution (Fig. 4). The resistance of the film, as well as the 50 kHz capacitance, is plotted in Fig. 5 as a function of NaCl concentration. These results come from a test as described above, but in which the immersion in solutions of increasing concentration was totally repeated, i.e., two complete cycles were performed. In the first cycle, the 10-fold increase of NaCl concentration led to a decrease of resistance of two orders of magnitude. The variation was less evident in the second cycle, although it is still clear that the resistance decreased with the growing concentration of the solution. The capacitance, in contrast, increased with the concentration, following approximately a linear variation. Extrapolation to null concentration gives a value that can be interpreted as the capacitance of the film immersed in pure water. This value is $2.2\ 10^{-10}$ or $2.7\ 10^{-10}$ F cm^{-2} in the first and in the second cycle, respectively. This parameter is thus different from the capacitance of the dry film, which was estimated from Fig. 3 as $3.8\ 10^{-11}$ F cm^{-2}. Application of Eq. (1) to the film in pure water would thus lead to a fraction of water of 39%. In spite of the clear dependence of both resistance and capacitance on the concentration of the electrolyte, it was observed that the properties of the film were not completely recovered. This suggests that some irreversible change may have occurred in the polymer as a consequence of the long immersion time.

3.1. *Free films vs attached films*

In Fig. 6 the impedance spectra of a coil coated sample (attached film) is shown, together with the spectrum of a free film. For the coated steel sample, the spectra were capacitive down to reasonably low frequencies, and in most cases the low frequency resistance could not be measured, since it exceeded the impedance limit of the analyzer. These features were practically constant even for long exposure times, revealing that corrosion did not occur. In the free film, in contrast, the low frequency resistance is clearly seen in the spectra and tends to decrease during the exposure.

For the attached films the 50 kHz capacitance increased during immersion in the range (2–4.5) 10^{-11} F cm^{-2} (Fig. 7). This variation was much smaller than in the free films (Fig. 3), particularly in the first days of immersion. In contrast, however, the capacitance continued to grow after that, for a period of more than 1 months. For the first 2 days of immersion, the kinetics of water uptake of the free films and attached films are basically the same in what concerns the shape of the curve (Fig. 8), although the free film presents a higher value of water uptake as expected from the previous results.

3.2. *Gravimetric tests*

Gravimetric tests were made with free films of PVC plastisol, using a microbalance. For short immersion times, the

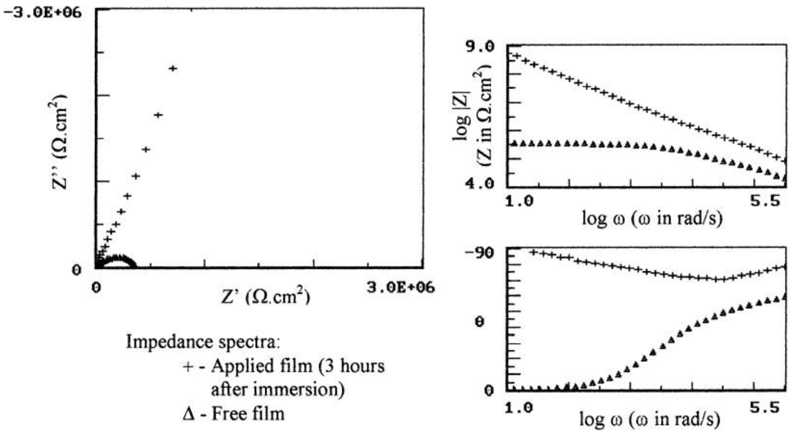

Fig. 6. Impedance spectra of a PVC plastisol film in 3% NaCl solutions.

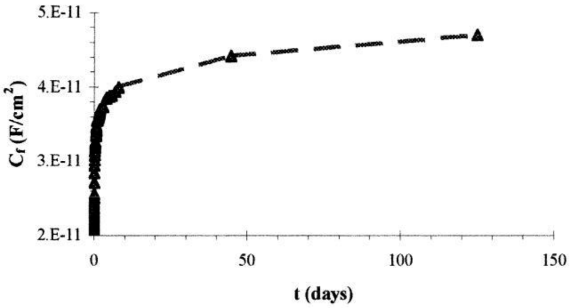

Fig. 7. Capacitance of the attached film as a function of time, during immersion in 3% NaCl.

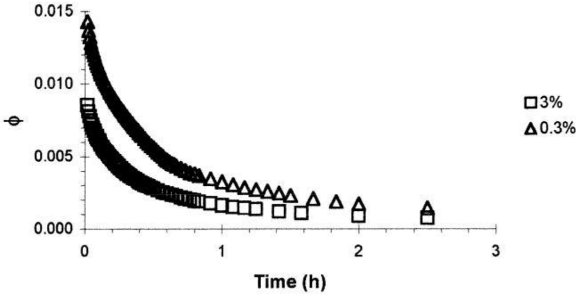

Fig. 9. Drying curves for plastisol detached film (concentration of NaCl in solution indicated in the figure).

absorption curves have essentially the same shape as the ones obtained by impedance measurements. However, for long immersions a net weight loss was observed and the attempt to determine the absorption curve has thus failed. This fact reveals a partial leaching of soluble components during prolonged immersion. The calculated total mass loss was approximately 5% with respect to the initial mass of the film.

A more reliable way to determine the permeability of the film is from the mass loss during drying of the saturated film. Fig. 9 depicts the drying curves of free films after continu-ous immersion for 2 days in NaCl solutions at ambient temperature. The results are apparently in contradiction with the impedance data. In fact, the highest mass loss was observed in the samples exposed to the lower salt concentration. Iden-tical result was observed by Walter [5]. On the other hand, there is a discrepancy in respect to the impedance data, re-lated to the absolute values of the volume fraction of water in the coating. Thus, Fig. 9 shows that the volume fraction is below 1% with the 3% NaCl solution, whereas the val-ues estimated using Eq. (1), which were nearly 10% for the attached films and 35% for the free films.

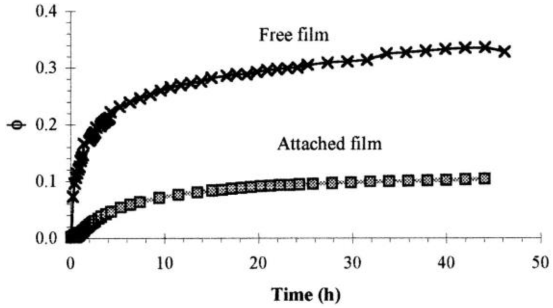

Fig. 8. Water uptake of the plastisol film as a function of time, during immersion in 3% NaCl.

3.3. *Structure of the film*

SEM imaging of the films revealed that the PVC has a highly porous structure, with internal voids of 20–50 _m (Fig. 10). It is plausible that these voids become filled with water during immersion. This structure is different from what has been observed for other polymer coatings [7–9].

4. Discussion

According to the literature [10], the conductivity of polymers in solution can be related with the conductivity of the electrolyte in two opposite ways: either the resistance

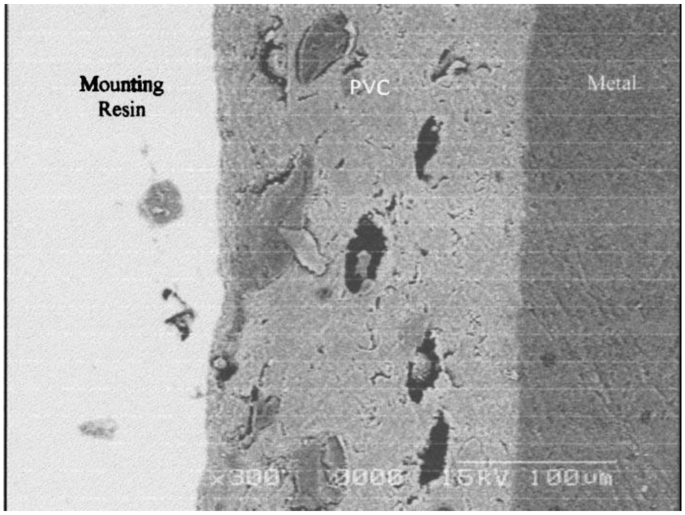

Fig. 10. SEM micrograph of applied PVC plastisol.

increases with the decrease of the resistance of the outer solution (inverse or I conduction) or the resistance decreases with that of the solution (direct or D conduction). According to Mayne [11], the changes in resistance in I films depend only on the available water in the solution, and not on the ion concentration. The behavior of D films was explained [12] either by the presence of holes, pores or capillaries filled with solution, or by a lower crosslinking density. It was also suggested that D and I areas could occur in different regions of the film. According to the above classification, the PVC films reveal D-type conductivity, since the measured conductivity of the film follow that of the solution. This was checked only with the free films, since with the attached films the resistivity could not be measured under the present operating conditions.

The capacitance measured on free and on attached films had similar values at the beginning of immersion (2–5 10^{-11} F cm^{-2}), but the increase was much faster in the free films, and higher values were reached after prolonged immersion. The capacitance was approximately proportional to the concentration of NaCl (Fig. 5). According to the Brasher equation, this would mean a higher volume of water in the film at the higher salt concentrations. The gravimetric measurements, however, have shown the opposite, i.e. the film immersed in 3% NaCl had a smaller mass loss during the drying process than the one exposed to 0.3% NaCl. The trend of the gravimetric results is in agreement with the conclusions of Brasher and Nurse [13] and also with the results of Walter [5], who also found a contradiction between the capacitance and the gravimetric results concerning the influence of chloride concentration. In his interpretation, Walter assumed that the capacitance measurements were accounting not just for the water, but also for the uptake of chloride ions, and for the reorientation of the mode of distribution of water within the film. According to Mayne [11], the process of degradation of a polymer film during immersion occurs in several stages. First, water and ions penetrate into the film, but the electrolyte penetrates preferentially in the areas with lower crosslinking density. Following that, an ion exchange process takes place, by which the ions from the electrolyte become attached to the polymer network. Consequently, the resistance decreases and the protective properties of the film are diminished. The uptake of ions from solution seems to be the most appropriate factor in the description of the trends. The higher the number of ions, the higher the dielectric constant of the coating, and since the capacitance is proportional to the dielectric constant:

$$C = \frac{\varepsilon\varepsilon_0}{d}, \qquad (2)$$

the higher values of capacitance. However, it is not sure that the mass loss from gravimetry gives an accurate information on the total water uptake. It is plausible that in the presence of chloride ions in the coating, some water molecules may be bound as solvation sheets, as observed by Sussex and Scantlebury [6]. For high chloride concentrations the amount of this bound water might be significant, and drying in the desiccator might be incomplete.

The high capacitance values measured on the free films were unexpected, when compared to the attached films. Considering the process of diffusion across the polymer/solution boundary, the rate of capacitance growth in the free film should be approximately twice that of the attached film, since water can enter through both sides of the film. A higher rate for the changes in capacitance were in fact observed. However, after several days of exposure, the capacitance was still much higher in the free films, suggesting that the total amount of water at saturation were really higher in the free films. Naturally, there were physical differences between the free and the attached films. In the attached films the thickness was 200 μm and a 5 μm primer existed underneath, whereas the free films had no primer and the thickness was 140–150 μm. Since the capacitance of a dielectric is inversely proportional to its thickness, this would account for a ratio of capacitances of about 0.7 between the attached and free film, which is far less than the actual capacitance ratio. Thus, the best explanation for the different variation in capacitance seems to be the ingress of ions from the solution. As pointed out by Walter [5], the attached coatings are rigidly held on the surface of the metal and therefore are less prone to distortions as a consequence of water penetration. On the other hand, exposure for long times has shown that the capacitance of attached films usually grows very slowly even after apparent stabilization. It is possible that after the initial penetration of water in the pores of the coating, a different process occurs, that could be either the penetration of the water in the bulk of the polymer, or the slow diffusion of ions. Given the lack of rigidity of the free film and its extended surface, it seems natural that these processes occur much faster. It cannot be excluded that if the tests were sufficiently long, the capacitance of the attached films might become closer those of the free films. The practical feasibility of such a test might however be difficult due to the risk of delamination and blistering of the coating. These results are in contradiction with others obtained by D'Alkaine et al. [14] on epoxy films and Walter [5] on silicone modified polyester, where they observed a greater water uptake for attached films in comparison with free films.

For the applied films, determination of the water uptake from capacitance measurements using the Brasher equation leads to values of that were larger than those determined from gravimetry, by a factor of 10 when the values after 2 days of immersion are considered. Even if the gravimetry is not very accurate, the difference is far too high. The Brasher equation assumes a number of conditions, which generally do not hold completely. One of them is that the distribution of water in the film is homogeneous. The existence of large voids inside the coating as observed by SEM reveals that such condition can not be met in the present case. The PVC film is inhomogeneous and when these voids become filled with water and ions, the phase angle of the impedance spec-tra at high frequencies presents a tendency to lower values. This originates an enhanced capacitance, which may lead to exaggerated values of . Better correlations between gravi-metric and electrochemical data are thus required, but any correlation needs to account also for the penetration of ions in the film.

5. Conclusions

The free films of PVC plastisol have D-type conductivity, revealed by a decrease in resistivity with increasing NaCl concentration in the external solution.

The capacitance of the free-standing film determined from impedance measurements increased both with the time of continuous immersion and with the eletrolyte concentration.

The volume fractions of water estimated from impedance are much higher than those obtained from weight loss dur-ing drying. The difference can be partially explained by the penetration of ions into the film.

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