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Evaluating Barrier Properties Of Organic Coatings by Water Permeation And Electrochemical Methods

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INTRODUCTION

Organic coatings protect metals against corrosion by various mechanisms, which can be summarized as follows: (a) suppression of the anodic and/or cathodic reaction, (b) the introduction of a high electrical resistance into the circuit of the corrosion cell, and (c) a barrier to aggressive species (oxygen, water, and ions).

Measurement of ionic resistance by the polarization method has been used successfully for many years as a method to characterize paints and varnishes. Briefly, good performance is recognized if a high dc resistance is observed when the coating is exposed to an electrolyte solution. In these studies, it was stated that coatings frequently contain areas of low ionic resistance named d-type areas and areas of high ionic resistance named l-type areas. The predominance of either kind of these areas determines the total ionic resistance of a coating.

Today, electrochemical impedance spectroscopy (EIS) is preferred to evaluate the performance of organic coatings because it allows for a more complete characterization. For instance, the uptake of ions into the coatings has been related to the increase in d.c. resistance of the coatings, while the uptake of water has been related to the increasing capacitance of the coatings. Also, EIS has been used to estimate the degree of delamination.

According to Szarek, coatings can be classified into four groups. The first group is made up of those coatings that act like dielectrics and barrier materials. Failure of these materials to protect the substrate arises from the penetration of conductive solutions into the coating by diffusion. The second group of coatings includes those possessing conductive pathways, which usually allow immediate contact between metal and electrolyte solution. Commercial paints usually produce coatings with pores and fissures that originated during the evaporation of solvents and atmospheric exposure. All of these discontinuities have to be considered as potential conductive paths when in contact with an electrolyte solution. The third group includes those very porous, fissured, or well-conducting coatings, including those of advanced degradation, where the capacitive effect of the coating may be disregarded. The fourth group is constituted by some hydrocarbon-based oils and protective coatings, whose hydrophobic nature, as well as lack of pores and fissures, gives them the char-
thin layers of films should give rise to a highly impermeable coating due to the lowering of pathways of a given layer by the subsequent layer, i.e., there would be an increase in the tortuosity of transport pathways in the coatings.

In view of that discussion, the purpose of this work is to further investigate the present knowledge about the performance of organic coatings, from a combined study of water transport, d.c. resistance measurements, and EIS measurements carried out in epoxy-polyamide varnish films. The effect of thickness on the behavior of these materials is investigated from the point of view of a multilayered model, where a single film of high thickness would be equivalent to the one constitution by the superposition of several thin films.

**EXPERIMENTAL**

**Materials**

The epoxy resin studied was the diglycidyl ether of bisphenol A, as we verified by the FTIR spectra of the material received from Tintas Renner S.A. Cure was carried out by the addition of an equivalent weight of a polyamide curing agent (Versamid 115). The system was diluted to 78% w/w in a mixture 1:1.1 of xylene/acetone in order to obtain a varnish with a viscosity adequate to be applied by an extension bar.

**Sample Preparation**

Free films used in studies of transport properties and d.c. resistance measurements were prepared by casting the epoxy-polyamide varnish with a variable extension bar onto glass plates. Attached films used in d.c. resistance and EIS measurements were prepared by casting the varnish onto nongalvanized carbon steel plates, which were then electroplated. After curing, the films were cured at room temperature in a closed chamber for four days and then further cured for 24 hr in an oven at 80°C. An almost complete crosslinking of the material was obtained with this rigorous treatment, as we verified from solvent extraction measurements.

Free films were desiccated from the glass plates after immersion in distilled water for about three days, dried between two sheets of absorbent paper, and then kept on a desiccator containing silica gel.

**Water Permeation**

Water permeation was performed with the weighed-cell technique, in which the Wt/m is measured on open aluminum cups, thus functioning as a partition element between the interior and exterior of the cup. In “wet cup experiments,” pure water or NaCl solution with a known activity is put into the cup and the resulting set (cup, water/solution, and film) is placed upside down in a chamber under dry atmosphere, which is achieved by placing a pot containing a strong desiccant (P₂O₅) inside the chamber. Under these conditions, a water activity difference (or equivalently, a water vapor pressure difference) is established between the inside and outside of the cup, so that water is forced to permeate the film from inside to outside. By periodically weighing the cup, the amount of mass is obtained over time, which allows for the determination of water flow through the film. In “dry cup experiments,” desiccant P₂O₅ is put into the cup, which, after being capped with the film, is placed upright in a chamber whose humidity is controlled by placing a pot containing pure water or NaCl solution with a known activity. Under these conditions, water is forced to permeate the film from outside to inside. In this case, water flow through the film is measured by following the mass gain over time.

**Water Sorption**

Water sorption was measured by soaking discs of films with 20 mm diameters in pure water or NaCl solutions with variable activities over a period of week. Although a day is sufficient for the films to take up a maximum quantity of water as was verified from previous tests, we kept them immersed for a week in order to wash out impurities like entrapped solvents inside the films.

After that, the films were dried between two filter papers, weighed, and then dried in an oven at 80°C for 24 hr. By weighing the films again, the water uptake could be obtained by the formula:

\[ W = \frac{W_2 - W_1}{W_1} \]

where \( W \) is the film thickness, \( W_1 \) the initial film thickness, and \( W_2 \) the film thickness after the drying.

**D.C. Resistance**

D.C. resistance was measured by the polarization method. Free films were “sandwiched” between two halves of a cell, both of which were filled with NaCl solution, and the cell was placed into an electrochemical cell. The effect of the cell was used to maintain electrical contact with the solution. A potential of 0.6 volts was applied to the electrodes and the resistance was obtained by measuring the current.

**Electrochemical Impedence Spectroscopy**

EIS measurement was performed on the coated films. PVC cylinders with 21 mm internal diameters and 30 mm height were bound with adhesive onto the cured films. This setup consisted the measurement cell, with the steel plate acting as a working electrode. A platinum strip was used as a counter electrode and a calomel electrode was used as a reference electrode. The cells were filled with a NaCl solution from 3M and then EIS measurements were performed over time. A potential of -0.2 V was applied from EBGIG Instruments and a frequency response analyzer from Solartron Instruments coupled with EIS measurement, the rest potential was measured and the value found was used as an imposed signal amplitude. The signal frequency range chosen was 1 MHz to 100 mHz, but in many cases the measurement was interrupted before the end because the response signal was prone to great error at low frequency.

**RESULTS AND DISCUSSION**

**Permeation**

Figure 1 shows a plot of mass flow vs inverse of the thickness of the film. The upper curve represents data from experiments performed under normal water activity difference, the difference between the water activity inside the cup and water activity outside the cup, \( \Delta a_w \) equal to unity. The lower curves represent data from experiments performed under \( \Delta a_w = 0.5 \). Open symbols represent data from dry cup experiments, closed symbols represent data from wet cup experiments. It can be seen that when \( \Delta a_w = 1 \) the same curve is obtained for dry and wet cup experiments, yet when \( \Delta a_w = 0.5 \) the curve for the dry cup experiment is shifted above the one of the dry cup experiment. The explanation for this result is given next.

Generally, the measured mass flow \( \frac{\Delta m}{\Delta t} \) of a liquid penetrating through polymer films is the sum of two flows: the Fickian (or diffusive) flow \( \bar{J}_D \) and the viscous flow \( \bar{J}_V \). The first, dependent upon the film thickness, corresponds to the activated penetrating transport through the polymer matrix and the second, independent of the film thickness, to transport through frozen holes. We call frozen holes the free volume associated with the discontinuous distribution of microvoids in a gel-like liquid (or glass) after solvent evaporation. In the case of crosslinked polymers like epoxy resins, these hole can also be microgouges of low crosslinking density. We assume that these holes are sufficiently large enough to promote capillary penetrating condensation, and so the viscous flow should be controlled only by the penetrating evaporation at the outgoing surface of the film. Normally, it is reasonable to expect the number of microvoids to rapidly decrease with increasing film thickness, but, depending on the solvent evaporation rate, in
thin layers of films should give rise to a highly impermeable coating due to the narrow voids of pathways of a given layer by the subsequent layer, i.e., there would be an increase in the tortuosity of transport pathways in the coatings.

In view of that discussion, the purpose of this work is to further investigate the present knowledge about the performance of organo-coatings, from a combined study of water transport, d.c. resistance measurements, and EIS measurements carried out in epoxy-polyamide varnish films. The effect of thickness on the behavior of these materials is investigated from the point of view of a multilayered model, where a single film of high thickness would be equivalent to the construction by the superposition of several thin films.

EXPERIMENTAL

Materials

The epoxy resin studied was the diglycidyl ether of bisphenol A, as we verified by the FTIR spectra of the material received from Tintas Renner S.A. Cure was carried out by the addition of an equivalent weight of a polycrylate curing agent (Versamid 115). The system was diluted to 70% w/w in a mixture 1:1.1 of xylene/isopropanol in order to obtain a varnish with a viscosity adequate enough to be applied by an extension bar.

Sample Preparation

Free films used in studies of transport properties and d.c. resistance measurements were prepared by casting the epoxy-polyamide varnish with a variable extension ratio onto glass plates. Attached films used in d.c. resistance and EIS measurements were prepared by casting the varnish onto nongalvanized carbon steel plates, which were then electroplated. After casting, the films were cured at room temperature in a closed chamber for four days and then further cured for 24 hr in an oven at 80°C. An almost complete crosslinking of the material was obtained with this rigorous treatment, as we verified from solvent extraction measurements. Free films were desiccated from the glass plates after immersion in distilled water for about three days, dried between two sheets of absorbent paper, and then kept on a desiccator containing silica gel.

Water Permeation

Water permeation was performed with the weighed-cell technique, in which the weight of water passing through a film in an open aluminium cup, thus functioning as a partition element between the interior and exterior of the cup. In "wet cup experiments," pure water or NaCl solution, with a known activity is put into the cup and the resulting set (cup, water/solution, and film) is placed upside down in a chamber under dry atmosphere, which is achieved by placing a pot containing a strong desiccant (P₂O₅) inside the chamber. Under these conditions, a water activity difference (or equivalently, a water vapor pressure difference) is established between the inside and outside of the cup, so that water is forced to permeate the film, from inside to outside. By periodically weighing the cup, the amount of mass is obtained over time, which allows for the determination of water flow through the film. In "dry cup experiments," desiccant P₂O₅ is put into the cup, which, after being capped with the film, is placed upright in a chamber whose humidity is controlled by placing a pot containing pure water or NaCl solution with a known activity. Under these conditions, water is forced to permeate the film from outside to inside. In this case, water flow through the film is measured by following the mass gain over time.

Water Sorption

Water sorption was measured by soaking discs of film, with 37 mm in diameter, in pure water or NaCl solutions with variable activities over a period of a week. Although a day is sufficient for the films to take up a maximum quantity of water as was verified from previous tests, we kept them immersed for a week in order to wash out impurities like entrapped solvents inside the film.

After that, the films were dried between two filter papers, weighed, and then dried in an oven at 80°C for 24 hr. By weighing the films again, the water uptake could be calculated, i.e., 20% of dry film. Further drying for another 24 hr did not produce any change in the weight of the films.

D.C. Resistance

D.C. resistance was measured by the polarization method. Free films were "sandwiched" between two halves of a cell, both of which were filled with NaCl solution with 37 mm in diameter immersed into each compartment of the cell. The surface of the cell was used to maintain electrical contact with the solution. A potential of 0.6 volts was applied to the electrodes and the resistance was obtained by measuring the current.

Electrochemical Impedance Spectroscopy

EIS measurements were performed on the attached films. PVC cylinders with 21 mm internal diameters and 30 mm in height were bound with adhesive onto the cured films. This set constituted the measurement cell, with the steel plate acting as a working electrode. A platinum strip wire was used as a counter electrode and a calomel electrode was used as a reference electrode. The cells were filled with a NaCl solution from 3M and then EIS measurements were performed over time. A potential of 0.1 V/mV was applied from EGG8 Instruments and a frequency response analyzer from Solartron Instruments. A spectrum EIS measurement, the rest potential was measured and the value found was used at an imposed signal amplitude. The signal frequency range chosen was 1 MHz to 100 mHz, but in many cases the measurement was interrupted before the end because the response signal was prone to great error at low frequency.

RESULTS AND DISCUSSION

Permeation

Figure 1 shows a plot of mass flow into the inverse of the thickness of the film. The upper curve represents data from experiments performed under internal to external water activity difference, the difference between the water activity inside the cup and water activity outside the cup), equal to unity. The lower curves represent a change of water activity difference, with an activity inside the cup, equal to 0.5. Open symbols represent data from dry cup experiments, closed symbols represent data from wet cup experiments. It can be seen that when NaCl = 0.5 the same curve is obtained for dry and wet cup experiments, yet when NaCl = 0.5 the curve for the dry cup experiment is below the curve for the wet cup experiment. The explanation for this result is given next.

Generally, the measured mass flow (J) of a liquid penetrating through polymer films is the sum of two flows: the Fickian (or diffusive) flow (i) and the viscous flow (i). The first, dependent upon the film thickness, corresponds to the activated penetrating transport through the polymer matrix and the second, independent of the film thickness, to transport through frozen holes. We call frozen holes the free volume associated with the discontinuous distribution of microvoids in a gel-like liquid (or glass) after solvent evaporation. In the case of crosslinked polymers such as epoxy resins, the holes can also be microvoids of low crosslinking density. We assume that these holes are sufficiently large enough to promote capillary penetrating condensation, and so the viscous flow should contribute only by the penetrating evaporation at the outgoing surface of the film. Normally, it is reasonable to expect the number of microvoids to rapidly decrease with increasing film thickness, but, depending on the solvent evaporation rate, in
many instances these voids could be created as a consequence of solvent retention.

On the other hand, in the case of thin films (generally less than 20 μm thickness), these holes can be described as pinholes, which are constituted by rough defects in films like bubbles, pores, and fissures that could be produced by the deficient application of films, mechanical/thermal stresses, and presence of solid impurities. The paint formulations whose pigments are poorly wetted by the resin can lead to debonding at the interface, which will produce pores in paint films. Discovci et al.10 referred to these defects, as micropores, and showed that they are responsible for electrolyte penetration through films of epoxy resin. By exposure of films to 3% sodium chloride, they found that, although the quantity of electrolyte inside micropores can be only one-tenth of that inside the polymer net, ionic conduction through the film depends only on conduction through macropores. Lineoissier et al.10 from measurements of water diffusion in polystyrene films, found a non-Fickian behavior, characterized by a fast transport with no time lag. They credited this rapid non-Fickian transport to the presence of defects in the bulk of this material, as they verified by transmission electron microscopy.

At the present, we believe that in thin films, pinholes and frozen holes can coexist, so that the measurement of transport properties in these films can lead to parameters not characteristic of the polymer itself, but of parameters related to the transport through rough defects, which are characteristic to the processing. Hence, if one wishes to obtain intrinsic properties of the polymer, measurements should be carried out in thick films, where defects are expected to be almost completely eliminated.

If Fick's first law is obeyed, when the film thickness tends to infinity, the J value should extrapolate to zero. But if the polymer matrix that contains a fraction of frozen holes, the J value, extrapolated to infinite film thickness, is not zero and would correspond to the flow through these frozen holes. Defining this flow as $J^F$, it is given by:

$$J^F = \frac{I^F}{A_s}$$

(1)

where $I^F$, $A_s$ and $A_p$ are the penetrating evaporation rate at the experimental temperature, the area corresponding to the fraction of frozen holes, and the geometric area of permeation, respectively. At this point it is important to indicate that once the gel in the liquid is formed, after solvent evaporation, the frozen microvoids are distributed throughout the bulk sample, and so $A_p$ can be considered independent of film thickness.

Let us consider the following equations:

$$J^P = J^F + J^T$$

(2)

$$J^T = -\frac{D_p \Delta P_p}{L}$$

(3)

where equation (2) and equation (3) define the experimental penetrating flow and Fick's first law, respective
dively, and $D_p$, $\Delta P_p$ are the mean permeability coefficient, the internal to external penetrating vapor pressure difference (i.e. $\Delta P_p = P_g - P_a$) and the thickness of the sample, respectively. It can be noted that the difference flow $J^P$, since $J^T$ corresponds to the transport through frozen holes and is independent of the film thickness, making $J^P$ dependent.

Therefore:

$$J^T = \frac{D_p \Delta P_p}{L} - \frac{I^F}{A_s}$$

(4)

or rewriting equation (4):

$$\frac{D_p \Delta P_p}{L} = \frac{I^F}{A_s}$$

(5)

Therefore, if there is a component of viscous flow, then we observe from equation (4) that a plot of $I^F$ vs. $1/L$ like that shown in Figure 1, when extrapolated until $1/L = 0$, will intercept the ordinate axis at a point that corresponds to $J^T$. Following this procedure, we obtain in Figure 1 the values of $J^T$ corresponding to the three curves shown. When $\Delta P_a = 1$, the same value, 0.018 mg·h·g·cm<sup>-2</sup>, was obtained, for both wet and dry cup experiments. This result shows that when $\Delta P_a = 1$, the water condensed inside the frozen holes, in an extent that is equivalent for both wet and dry cup experiments, such that the same fraction of holes is contributing to viscous flow.

When $\Delta P_a = 0.5$, however, two different values of $J^T$ were obtained for wet and dry cup methods. Besides, the values 0.0088 mg·h·g·cm<sup>-2</sup> and 0.004 mg·h·g·cm<sup>-2</sup> were obtained, respectively, for wet cup and dry cup, are small-

er than one-half of that obtained when $\Delta P_a = 1$. This means that, when viscous activity is not present, less than one, there is less capillary condensation inside the holes, and hence, the viscous flow component is smaller. In addition, when the aqueous solution is in direct contact with the film, as is the case in the wet cup method, a higher value of $J^T$ is obtained when compared to that obtained in the dry cup method, because of higher capillary condensation in the former.

Now, using the water evaporation rate value, $J(30°C) = 1.165$ mg·h·g·cm<sup>-2</sup> from measurements in a dip without film), the geometric area of permeation $A_p = 9.07$ cm<sup>2</sup> and the value of viscous flow, $J^T = 0.018$ mg·h·g·cm<sup>-2</sup>, it was possible to determine from equation (1) the area corresponding to the fraction of frozen holes, $A_s = 0.014$ cm<sup>2</sup>. It is important to observe that this area, which corresponds to about 0.15% of geometric area of permeation, although small, is responsible for a significant fraction of mass flow through the films, as can be seen from Figure 1. The component of viscous flow $J^T$ becomes more significant as the film thickness increases.

From the previous discussion, it becomes clear that one needs to discount from experimental flow the value corresponding to viscous flow, in order to correctly apply Fick's first law to permeation through films. Figure 2 shows a master curve obtained after subtracting the viscous flow $J^T$ from the measured flow and after correcting for the difference in water activities. Data from Figure 1 are represented as $J(30°C) - J^T$ against $L^2/A_p$ in Figure 2. For the purpose of the sample, it is represented as a single line. This is what one would expect from a system that obeys Fick's first law, described by equation (3). The slope gives a permeability coefficient of 2.10<sup>-12</sup> g·s<sup>-1</sup>·cm<sup>-2</sup>·min<sup>-1</sup>·μm<sup>-1</sup>. The independence of the permeability coefficient on the water activity, which is revealed by the single slope, shows that the water does not affect the film. Such a result is not unexpected since the films were highly crosslinked after the hard thermal treatment, namely 80°C for 24 hr, as could be estimated by solvent extraction experiments described in the Samples Preparation section.

D.C. Resistance

Data from d.c. resistance measurements are reported in Figure 3 as a plot of $R$ against thickness of film. $R$ is the measured resistance and $A$ is the area of film exposed to sodium chloride of about 5.9 cm<sup>2</sup>. Each curve corresponds to a measurement performed at a given NaCl concentration, which is indicated in the graph.

D.C. resistance measurements performed under dry conditions were also included to obtain the intrinsic resistance of the material. It can be seen that intrinsic resistance does not change appreciably within the range of thicknesses studied. Hence, the change in resistance with thickness presented with other curves is caused by the differences in ionic mobility through the films.

In general, the resistances increased with thickness until the maximum thickness of about 100-150 μm and then decreased unexpectedly. The initial increase in resistance was caused by a reduction in the fraction of pinholes with increasing thickness of the film, as was discussed in the preceding section. The decrease in measured resistance for thicker films was caused by a reduction in the degree of crosslinking as a result of solvent retention. In order to verify this supposition, we made solvent extraction measurements. Using acetone as solvent, the mass extracted from films of 23, 45, 74, and 267 μm was respectively 2.5, 2.5, 3.4, and 7.4 g/100 of dry film. As can be seen, thicker films have a higher amount of soluble material, which means they were less crosslinked. As a consequence of being less crosslinked, thicker films can have a higher fraction of frozen holes,

![Figure 4](image-url)  
**Figure 4**—Some data presented in Figure 3, but with concentration as the independent variable. The product of resistance and conductivity of NaCl solution is also included.

![Figure 5](image-url)  
**Figure 5**—Water absorption against water activity. Films with thickness around 70 μm.

![Figure 6](image-url)  
**Figure 6**—Data from EIS experiments. Imaginary component of impedance (Zm) against real component of impedance (Z). Each curve corresponds to the time exposure indicated by the legend. The variable t displayed at some points reflects the frequency used at that data point.
many instances these voids could be created as a consequence of solvent retention.  

On the other hand, in the case of thin films (generally less than 20 μm thickness), these holes can be described as pinholes, which are constituted by rough defects in films like bubbles, pores, and fissures that could be produced by the deficient application of films, mechanical/thermal stresses, and presence of solid impurities. Also, paint formulations whose pigments are poorly wetted by the resin can lead to debonding at the interface, which will produce pores in paint films. Discovici et al.18 referred to these defects as macropores, and showed that they are responsible for electrolyte penetration through films of epoxy resin. By exposure of films to 3% sodium chloride, they found that, although the quantity of electrolyte inside macropores can be one-tenth of that inside the polymer net, ion conduction through the film depends only on conduction through macropores. Linossier et al.19 from measurements of water diffusion in polystyrene films, found a non-Fickian behavior, characterized by a fast transport with no time lag. They credited this rapid non-Fickian transport to the presence of defects in the bulk of this material, as they verified by transmission electron microscopy.

At the present, we believe that in thin films, pinholes and frozen holes can coexist, so that the measurement of transport properties in these films can lead to parameters not characteristic of the polymer itself, but of parameters related to the transport through rough defects, which are characteristic to the processing. Hence, if one wishes to obtain intrinsic properties of the polymer, measurement should be carried out in thick films, where defects are expected to be almost completely eliminated.

If Fick’s first law is obeyed, when the film thickness tends to infinity, the Fickian value should extrapolate to zero. However, if the polymer matrix that contains a fraction of frozen holes, the Fickian value, extrapolated to infinite film thickness, is not zero and would correspond to the flow through these frozen holes. Defining this flow as $J_t$, we have:

$$J_t = \frac{1}{\eta}$$

where $J_t$, $\eta$, and $\eta$ are the penetrating evaporation rate at the experimental temperature, the area corresponding to the fraction of frozen holes, and the geometric thickness of the sample, respectively. This point it is important to indicate that once the gel in the liquid is formed, after solvent evaporation, the frozen microwords are distributed throughout the bulk sample, and so $\eta$ can be considered independent of film thickness. Let us consider the following equations:

$$I_{ev} = I_{t} - I_{f}$$

$$I_{t} = -\frac{\Delta P}{\eta} \frac{L}{L}$$

where equation (2) and equation (3) define the experimental penetrating flow and Fick’s first law, respectively. and $\frac{\Delta P}{\eta} \frac{L}{L}$ are the mean permeability coefficient, the internal to external penetrating vapor pressure difference (i.e., $\Delta P_L = P_L - P_E$) and the thickness of the sample, respectively. It is then possible to write the difference flow $I_{t}$, since $I_{t}$ corresponds to the transport through frozen holes and is independent of the film thickness, making $I_{t}$ grow.

Therefore:

$$I_t = I_{ev} - I_f$$

or rewriting equation (4):

$$\frac{\Delta P}{\eta} \frac{L}{L} = I_{ev}$$

Therefore, if there is a component of viscous flow, then we observe from equation (4) that a plot of $I_{ev}$ vs. 1/L like that shown in Figure 1, when extrapolated until 1/L = 0, will intercept the ordinate axis at a point that corresponds to $I_f$. Following this procedure, we obtain in Figure 1 the values of $I_f$ corresponding to the three curves shown. When $\Delta t = 1$, the same value, 0.018 mg/m² h, was obtained, for both wet and dry cup experiments. This result shows that when $\Delta t = 1$, the water condensed inside the frozen holes, in an extent that is equivalent for both wet and dry cup experiments, such that the same fraction of holes is contributing to viscous flow.

When $\Delta t = 0.5$, however, two different values of $I_f$ were obtained for wet and dry cup methods. Besides, the values 0.008 mg/m² h and 0.004 mg/m² h were obtained, respectively, for wet cup and dry cup, are small.

Figure 4—Some data presented in Figure 3, but with concentration as the independent variable. The product of resistance and conductivity of NaCl solution is also included.

er than one-half of that obtained when $\Delta t = 1$. This means that, when water activity is less than one, there is less capillary condensation inside the holes, and hence, the viscous flow component is smaller. In addition, when the aqueous solution is in direct contact with the film, as is the case in the wet cup method, a higher value of $I_f$ is obtained when compared to that obtained in the dry cup method, because of higher capillary condensation in the former.

Now, using the water evaporation rate value, $J_0$ (30°C) = 11.65 mg/h·m²·cm (from measurements in a dip without film), the geometric area of permeation $\eta_0$ = 9.07 cm², and the value of viscous flow, $I_f$ = 0.018 mg/h·m²·cm²; it was possible to determine from equation (1) the area corresponding to the fraction of frozen holes, $A_f = 0.014$ cm². It is important to observe that this area, which corresponds to about 0.15% of geometric area of permeation, although small, is responsible for a significant fraction of mass flow through the films, as can be seen from Figure 1. The component of viscous flow $I_f$ becomes more significant as the film thickness increases.

From the previous discussion, it becomes clear that one needs to discount from experimental flow the value corresponding to viscous flow, in order to correctly apply Fick’s first law to permeation through films. Figure 2 shows a master curve obtained after subtracting the viscous flow $I_f$ from the measured flow and after correcting for the difference in water activities. Data from Figure 1 are represented as $I_{ev} - I_f$ against $\Delta P / L$ in Figure 2. As you can see (in the example), it is possible to draw a single line. This is what one would expect from a system that obeys Fick’s first law, described by equation (3). The slope gives a permeability coefficient of 2.10 × 10⁻⁴ g·cm⁻³·cm⁻²·s⁻¹·cm⁻²·mmHg⁻¹. The independence of the permeability coefficient on the water activity, which is revealed by the single slope, shows that the water does not affect the film. Such a result is not unexpected since the films were highly crosslinked after the hard thermal treatment, namely 80°C for 24 h, as could be estimated by solvent extraction experiments described in the Samples Preparation section.

D.C. Resistance

Data from d.c. resistance measurements are reported in Figure 3 as a plot of $R$ against thickness of film. $R$ is the measured resistance and A is the area of film exposed to water, about 5.9 cm². Each curve corresponds to a measurement performed at a given NaCl concentration, which is indicated in the graph.

D.C. resistance measurements performed under dry conditions were also included to obtain the intrinsic resistance of the material. It can be seen that intrinsic resistance does not change appreciably within the range of thicknesses studied. Hence, the change in resistance with thickness presented by other curves is caused by the differences in ionic mobility through the films.

In general, the resistance increased with thickness until a maximum of about 100-150 μm and then decreased unexpectedly. The initial increase in resistance was caused by a reduction in the fraction of pinholes with increasing thickness of the films, as was discussed in the preceding section. The decrease in measured resistance for thicker films could be caused by a reduction in the degree of swelling as a result of solvent retention. In order to verify this supposition, we made solvent extraction measurements. Using acetone as solvent, the mass extracted from films with 23, 45, 74, and 267 μm was respectively 2.5, 2.5, 3.4, and 7.4 g/100 of dry film. As can be seen, thicker films have a higher possibility of soluble material, which means they were less crosslinked. As a consequence of being less crosslinked, thicker films can have a higher fraction of frozen holes.
which, as we have seen, allow for capillary condensation of water. Ions of sodium and chloride could then be transported through these holes, producing conductive pathways in the films. In another experiment, we measured sorption of pure water in films with 23.45, 74, and 267 μm. The uptake of water was respectively 0.2, 3.1, 5.5, and 5.4 g/100 g of dry film. As we can see, thicker films absorb more water as a result of being less crosslinked. On the other hand, thinner, more crosslinked films absorb less water but have a low ionic resistance because of their high fraction of pinholes. Finally, in the range 100-180 μm the epoxy film is expected to have the optimum balance between high crosslinking and low fraction of pinholes.

Figure 4 presents the same experimental data as shown in Figure 3 but with NaCl concentration as the independent variable. The thickness of films is indicated in the legend. The product of the film resistance and conductivity of the NaCl solution was also plotted. As can be seen, the resistance, in general, decreases with concentration. This behavior was termed by Mayne et al. as concentration type direct (D) because the resistance of the film follows that of external solution. The fall in the resistance with the concentration is high for thinner films, whereas pinholes in thicker films, which are filled up with solution, more conductive pathways through the films. In this case, conductivity decreases as concentration increases due to electrolyte concentration imitated pathways, which is expected to follow that of external solution.

The area total of these pinholes can be estimated from the plot of R vs. concentration in Figure 4, according to the procedure used by Ruivo-Filho and Costa. One can calculate the polymer film stability in NaCl solution as a proportionality, whose electrodes are separated by a distance L and have an area equivalent to that occupied by pinholes, Aπ. This hypothetical cell will have a cell constant given by Rπ = L/Δn. From Figure 3, by extrapolating Rπ values for high concentration regions, where they are nearly constant, one obtains the theoretical cell constant L/Δn, which can be used to estimate the area of pinholes from the thickness of the film. These values are given in Table 1. It can be seen that these areas are much too small when compared to geometric areas of the films, about 5.9 cm². Nevertheless, in the case of 26 and 40 μm films, even that small fraction area of pinholes is sufficient enough to produce a pronounced decrease in resistance with concentration, as can be seen in Figure 4. This result is in line with that obtained by Muscovi et al. described in the Permeation Results section.

On the other hand, the area of pathways calculated for the remaining thickness is excessively small and is expected to be unrealistic. In fact, pinholes in these thick films are expected to be absent, as we have discussed in the figure 2. Actual transport through them can take place only through frozen holes. Although water can condense inside these frozen holes, ionic mobile sites are probably much lower than that in the external solution. In this case, the values of Aπ calculated by the conductivity cell model are underestimated. Indeed, as we have seen, the estimated value for Aπ from permeation experiments is 0.014 cm² or 1.4 × 10⁻⁶ cm², which is much higher than those calculated by the conductivity cell model.

Electrochemical Impedance Spectroscopy

Figure 6 shows the Nyquist representation of the data obtained from a film with 60 μm in thickness. This is a typical behavior which is expected from a metal-coating electrolyte system. In the first hours of exposure to solution, the Nyquist diagram is characterized by a single semicircular shape. Acceleration after 10-12 hours exposure, the plot takes a semicircular shape because the uptake of solution into pinholes creates conductive pathways through the film. The Nyquist system behaves like an association of capacitors and resistors. Figure 7 shows an equivalent circuit often used to represent a metal-coating electrolyte solution system. 10 Rπ is the contact resistance and Cπ is the coating capacitance. Using an appropriate circuit to fit the data to this model, Rπ and Cπ could be calculated as a function of exposure time. A plot of (Rπ, Aπ, and Cπ, vs. exposure time is shown in Figure 8. As can be seen, initially, in the first 50 h, the resistance diminishes almost three decades, corresponding to the water imbibition period. However, after about 100 h, the resistance increases again because reactions start at the interfacial metal-polymer. On the other hand, the coating capacitance increases as a result of solution uptake until an equilibrium value is reached. Similar behavior was observed for a film with 35 μm.

On the other hand, Nyquist representation of films with 26 and 40 μm is almost linear when they were exposed to solution, showing only a slight decrease in slope, even after two months of exposure. This is in accordance with the d.c. resistance measurements, where it was shown that in this range of thicknesses the films present maximum ionic resistance (see Figure 3). Hence, in this range of thicknesses, the permeation of ions through films is highly hindered because pinholes are scarcely present, as one can see from the results in Table 1. In Figure 9, Rπ and Cπ for films with 9 μm were obtained as a function of exposure time, using the model shown in Figure 7. The uptake of a small amount of solution is observed. A slight decrease in d.c. resistance and slight increase in capacitance. Similar behavior was observed for a film with 138 μm.

The Rπ values obtained from d.c. (free films) and a.c. (attached films) measurements are similar when the same thicknesses are compared.

CONCLUSIONS

Results revealed a high dependence of barrier properties of epoxy-polysulfide varnish films on their thickness. Thinner films have a significant fraction of pinholes, which are responsible for the loss in the barrier properties of the material. Films relatively thicker, namely 100-190 μm in thickness, when attached to a steel plate are highly impermeable to ions and do not fail in the course of two months of testing. Nonetheless, pathways in the form of frozen holes are still present in thicker films, as we verified from permeability measurements. These frozen holes can be filled with water, but ion mobility and ion concentration at these sites are
which, as we have seen, allow for capillary condensation of water. Ions of sodium and chloride could then be transported through these holes, producing conductive pathways in the films. In another experiment, we measured sorption of pure water in films with 23, 45, 74, and 267 μm. The uptake of water was respectively, 2.2, 3.1, 5.5, and 5.4 g/100 g of dry film. As we can see, thicker films absorb more water as a result of being less crosslinked. On the other hand, thinner, more crosslinked films absorb less water but have a low ionic resistance because of their high fraction of pinholes. Finally, in the range 100-180 μm the epoxy film probably prevent the optimum balance between high crosslinking and low fraction of pinholes.

Figure 4 presents the same experimental data as shown in Figure 3 but with NaCl concentration as the independent variable. The thickness of films is indicated in the legend. The product of the film resistance and conductivity of the NaCl solution was also plotted. As can be seen, the resistance, in general, decreases with concentration. This behavior was termed by Mayne et al. as conduction type direct (D) because the resistance of the film follows that of external solution. The total in the resistance with the concentration is high for thinner films because of their high fraction of pinholes, which are filled up with solution, creating conductive pathways through the films. In this case, conductivity depends on electrolyte concentration and optical properties, which is expected to follow that of external solution.

The total area of pinholes can be estimated from the plot of R vs. concentration in Figure 4, according to the procedure used by Rúvolo-Filho and Costa. One can construct a polymer film sample in NaCl solution as a conductive cell, where the electrodes are separated by a distance L and have an area equivalent to that occupied by pinholes, Ap. This theoretical cell will have a cell constant given by R = L / Ap. From Figure 3, by extrapolating R vs values for high concentration region, where they are nearly constant, one obtains the theoretical cell constant L / Ap, which can be used to estimate the area of pinholes from the thickness of the film. The calculated values are given in Table 1. It can be seen that these values are much too small when compared to geometric areas of the films, about 5.9 cm2. Nevertheless, in the case of 26 and 40 μm films, even that small fraction area of pinholes is sufficient enough to produce a pronounced decrease in resistance with concentration, as can be seen in Figure 4. This result is in line with that obtained by Mayne et al. in the Permeation Results section.

On the other hand, the area of pathways calculated for the resistance to thickness surprisingly high and is expected to be unrealistic. In fact, pinholes in these thick films are expected to be absent, as we have discussed in the previous section. Therefore, the transport through them can take place only through frozen holes. Although water can condense inside these frozen holes, ion-conducting mobile sites are probably much lower than that in the external solution. In this case, the values of Ap calculated by the conductivity model cell are underestimated. Indeed, as we have seen, the estimated value of Ap for permeation experiments is 0.014 cm2 and 1.4 x 10-2 mm2, which is much higher than those calculated by the conductivity model cell. Wu et al. used a wire beam electrode, measured ionic resistance at numerous localized areas (1 mm in diameter) in various thickness films, finding areas with high resistance (1011-1012 Ωcm) and areas with low resistance (106-107 Ωcm). From these measurements, they estimated the percentage of high resistance and low resistance areas of the film. For a phenolic varnish they found 75% of low resistance areas; for an alkyd varnish, 88% of low resistance area and for a polyester varnish, 58% of low resistance area. When computing these estimated percentages of low resistance areas, with the values in the present article, it seems that Ap areas are not related to the low resistance areas found by Wu et al. As a point of interest, it is interesting to note that in our experiments very thin films, about 16 μm in thickness, while in the present article films that are considerably thicker were studied. Hence, it is reasonable to think that the morphology of the films in the two works are distinctly different from each other.

From this result, we can assume that ion transport in thick films of this epoxy resin is highly hindered, although water transport can occur and is easily detectable. This suggests that these films have permeosensitivity, that is, they allow water transport but not ion uptake, probably due to the presence of fixed charge in the binder matrix. Therefore, the film with 175 μm, which shows the highest resistance, presents a slight tendency to conductive type direct (D), i.e., its resistance is close to that of external solution, as can be seen in Figure 4. According to Mayne et al., the increase in resistance with concentration of electrolyte is caused by a reduction in the water content of films due to a decrease in water activity in external solution. Figure 5 shows the results of water sorption measurements, where the water uptake is plotted against the activity of water in the solution of immiscible. The range of activities covered is the same as that used in d.c. resistance measurements. It can be seen that water uptake clearly decreases with a decrease in water activity (increase in NaCl concentration) in the external solution, confirming the aforementioned statement. The sorption experiments were performed in films with thicknesses around 70 μm.

Electrochemical Impedance Spectroscopy

Figure 6 shows the Nyquist representation of the data obtained from a film with 60 μm in thickness. This is the typical behavior which is expected from a metal-coating-electrolyte system. In the first hours of exposure to solution, the film is impermeable so that the resistance of the film presents, predominantly, a capacitive behavior. Therefore, the plot corresponding to four hours of exposure is almost a straight line. After six-hour exposure, the plot takes a semicircular shape because the uptake of solution into pinholes creates conductive pathways through the film. This system behaves like an association of capacitors and resistors. Figure 7 shows an equivalent circuit often used to represent a metal-coating-electrolyte system. R1, R2, and C1 are the coating resistance and C2 is the coating capacitance. Using an appropriate circuit to fit the data to this model, R2 and C2 could be calculated as a function of exposure time, and the R2 values obtained were 2.6 x 105 Ωcm2 and 3.6 x 106 Ωcm2, respectively. The decrease in resistance and slight increase in capacitance. Similar behavior was observed for a film with 136 μm.

The R2 values obtained from d.c. (free films) and a.c. (attached films) measurements are similar when the same thicknesses are compared.

**CONCLUSIONS**

Results revealed a high dependence of barrier properties of epoxy-polymide varnish films on their thickness. Thinner films have a significant fraction of pinholes, which are responsible for the transport in the barrier properties of the material. Films relatively thicker, namely 100-190 μm in thickness, when attached to a steel plate are highly impermeable to ions and do not fail in the course of two months of testing. Nonetheless, pathways in the form of frozen holes are still present in thicker films, as we verified by permeation tests. These frozen holes can be filled with water, but ion mobility and ion concentration at these sites are

Table 1: Area Covered by Ioyes (Pinholes and Frozen Holes), Electrochemical Thickness of the Film, L

<table>
<thead>
<tr>
<th>L (μm)</th>
<th>A, cm2</th>
<th>A/p2 cm4</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>448</td>
<td>2.3 x 107</td>
</tr>
<tr>
<td>40</td>
<td>928</td>
<td>4.5 x 107</td>
</tr>
<tr>
<td>60</td>
<td>1712</td>
<td>5.7 x 107</td>
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<tr>
<td>90</td>
<td>2674</td>
<td>6.4 x 107</td>
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<tr>
<td>120</td>
<td>4840</td>
<td>9.7 x 107</td>
</tr>
<tr>
<td>179</td>
<td>8092</td>
<td>5.7 x 108</td>
</tr>
<tr>
<td>261</td>
<td>13682</td>
<td>5.1 x 108</td>
</tr>
</tbody>
</table>

Journal of Coatings Technology

Vol. 75, No. 959, April 2003
probably too small, and so the ionic resistance is high. The equivalent circuit proposed allows one to obtain R̅ values similar to the values obtained from d.c. independent measures. This fact shows that the electrochemical impedance spectroscopy can be used to characterize the ionic transport through the attached polymeric film. The same model of equivalent circuit allows us to explain the aging phenomena.

From a multilayered model it was possible to obtain a Fickian component of the water transport and the mean permeability coefficient, by subtracting the non-Fickian component of the transport from the experimental value.

ACKNOWLEDGMENTS

The authors wish to thank CNPq for their financial support of this project and LAC-COPEL for their technical support.

References


Thermal and Mechanical Properties Of UV-Cured Aliphatic Hyperbranched Polyester and Its Blends with Linear Polyurethane Acrylate

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INTRODUCTION

UV curable resins are being increasingly used in various applications, mainly in the coatings industry, graphic arts, and microelectronics. UV curing technology allows for the production of high resolution images that are required for the manufacture of integrated circuits or printing plates, as well as the achievement of fast hardening of clear or pigmented coatings, adhesives, and composites. UV curable composite contains oligomers and co-monomers, which determine the properties of a cured film.

Recently, hyperbranched polymers as partners of dendrimers have been developed.2 Both of them are made of AB, functional monomers giving a structure with numerous branching points and a large number of end-groups. These polymers may be used as oligomers for radiation curing systems because of several intriguing properties, such as low viscosity in molten state, high reactivity, and unsaturation conversion compared with traditional linear oligomers.2 Dendrimers have perfectly branched structures, while hyperbranched polymers have imperfectly branched structures that can be easily produced in large amounts by the so-called “one step” approach. Hyperbranched polymers have been considered for use as oligomers in radiation curable systems. Several studies have been published by us25 and by Hult and co-workers.67

This study deals with the synthesis of an acrylated hyperbranched aliphatic polyester based on a hyperbranched polyester and the thermal mechanical properties, thermal stability, hardness, and tensile strength of the UV-cured films both alone and in admixture with a commercial linear polyurethane acrylate.

EXPERIMENTAL

Materials and Synthesis

The hyperbranched polyester, Boltron (H20), herein designated HB20, was supplied by Perstorp AB, Sweden. Polyurethane acrylate CN972 (molar mass ~3,500 g/mol) was supplied by Sartomer Co, Exton, PA. Benzoyl-1-hydroxy-cyclohexanol (Irgacure 184) was supplied by Ciba-Geigy, Switzerland. N,N-di-methylaminoprylidine (DMAF) was supplied by Aldrich, Germany. Acryloyl chloride was synthesized in our lab by the reaction of acrylic acid with benzyl chloride. Different kinds of acrylated oligomers based on hyperbranched polymers have been synthesized; for example, an acrylated hyperbranched aliphatic polyester was synthesized by Malström,4 and acrylated hyperbranched aliphatic polyamine (ester) and poly(amide-ester) were synthesized by Shi.7-10

[Note: Key Laboratory of Fine Surface and Interface Engineering, School of Chemical Engineering, Shanghai Jiao Tong University, Shanghai, China. Partial financial support was received from National Key Laboratory Foundation of China (No. 98363065 and 20016104).]