

Study of Electrical Properties of Polymeric Materials Using Electrochemical Impedance Spectroscopy

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ABSTRACT: Electrochemical impedance spectroscopy (EIS) has been used to determine the water absorption characteristics of polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyaromatic amide (Aramid), and amine-quinone polyurethane (AQ) free-standing polymer films. A method for calculating percent moisture uptake is presented based on capacitance measurements via EIS, which requires initial or "dry" capacitance values, C_0 . Three different methods for obtaining C_0 values were described and employed, but the most reliable values were obtained via EIS measurement using Hg contacts. C_0 values obtained by this method resulted in calculated water uptake values nearly identical to those obtained by measured weight gain. Lower capacitance values were observed for films immersed in distilled water compared to 0.1M NaCl, which indicates that water uptake is greater in NaCl than in pure water. The four polymers examined in this study can be listed in order of decreasing resistance to moisture absorption as AQ > PET > PEN > Aramid. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 553–560, 1998

Key words: electrochemical impedance spectroscopy; water uptake; moisture absorption; EIS; capacitance

INTRODUCTION

A wide variety of polymeric materials are commonly used in the manufacture of magnetic tapes for many different kinds of applications, including audio, video, data storage, and data acquisition. The ability to magnetically record data on tape is principally responsible for the widespread, rela-

tively inexpensive use of sound and video images.¹ Magnetic tapes can be thought of as two layers of materials. The top layer is relatively thin, usually 2–4 μm , consisting of a colloidal suspension of magnetic particles in a polymer binder that has been painted on the bottom layer or substrate. The substrate, frequently polyethylene terephthalate (PET), is usually much thicker, about 10 μm or more. One of the technological goals of the magnetic tape industry is to significantly increase the storage capacity per unit volume of tape. Advances in research aimed at achieving this goal fall primarily in two categories: (1) the development of smaller magnetic particles with higher magnetization, and (2) the development of thin-

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ner polymer substrates. New particles currently under consideration are frequently metallic, for example, iron, and are thus much more susceptible to corrosion than $\lambda\text{-Fe}_2\text{O}_3$. As particles become smaller, the impact of corrosion damage is magnified, because even a tiny amount of corrosion can cause loss of data from particles with average dimensions of $0.4 \times 0.04 \mu\text{m}$. Polymers used for substrates must meet stringent physical requirements. The tendency for the substrate to absorb water is one characteristic that is of interest, because the presence of water may enhance corrosion damage.

This article reports an experimental investigation on the use of electrochemical impedance spectroscopy (EIS) to determine the electrical properties of several different free-standing polymer films and how these properties change as water and ions are absorbed into the polymer films. The materials investigated were polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyaromatic amide (Aramid), and an amine–quinone polyurethane (AQ). As mentioned above, PET films are widely used in commercial tapes. PEN, Aramid, and AQ polymer films have also been proposed as possible alternatives to PET. AQ polymers are particularly interesting, because they have been reported to reduce the corrosion of iron.^{2–4} The objective of this study was to refine the conventional AC impedance method for free-standing polymer films, and to measure the moisture absorption characteristics of the above-mentioned films.

THEORETICAL BACKGROUND

Because this article reports an investigation on water uptake in free-standing polymer films as determined by EIS, a short description of the underlying theory is given. Changes in the electrical properties of organic coating systems during exposure to moisture has been investigated by various researchers including the work of Wormwell and Brasher⁵ in the early 1950s, followed by Brasher and Kingsbury⁶ and Gentles.⁷ In these publications an electrical capacitance method was first introduced to evaluate the water uptake of paint films on metal immersed in seawater. The capacitance method of evaluating water absorption into polymers is based on the assumptions that (1) the change in capacitance is due entirely to the permeation of water into the film, (2) the per-

Table I Materials Used in EIS Measurements

Polymer Films	Thickness (μm)
PEN ^a	4.5, 11, 25
PET ^b	6, 13, 16, 23
Aramid ^a	4.4
AQ ^c	20

^a Donated by Teijin, Ltd., Tokyo, Japan.

^b 16- μm film donated by Teijin, Ltd., Tokyo, Japan; the rest were purchased from Goodfellow, Inc.

^c Donated by Prof. D. Nikles, Chemistry Department, The University of Alabama.

mittivity of the absorbed water is constant and equal to 80, and (3) the swelling of the polymer can be neglected. The method of calculating the volume fraction of water absorbed by the paint film from observed capacitance values is based on a modification of an original formula given by Hartshorn, Megson, and Rushton,⁸ and assumes that the distribution of water into the film is uniform:

$$\phi = \frac{\log(C_t/C_0)}{\log(80)} \quad (1)$$

In this equation, ϕ is the volume fraction of the absorbed water, C_t is the capacitance after time of exposure, t , and C_0 is the “dry” capacitance at time $t = 0$ (i.e., at the start of the experiment). The capacitance at $t = \infty$, C_∞ , is taken as the value of the capacitance after the film is fully saturated with water, as indicated by the appearance of a plateau in a plot of water uptake versus time. The equilibrium water uptake is obtained by using the above equation with $C_t = C_\infty$. However, application of eq. (1) requires the dry film capacitance C_0 . In the literature C_0 values have been calculated from eq. (1) by extrapolating a plot of water uptake versus time back to zero time.^{9,10,12} In the present study, C_0 values were experimentally measured by two different methods and were also calculated by extrapolation.

EXPERIMENTAL

Materials and Methods

The polymer films used in this study and their respective thicknesses are shown in Table I. EIS experiments were performed on the polymer films (both dry and immersed in either pure water

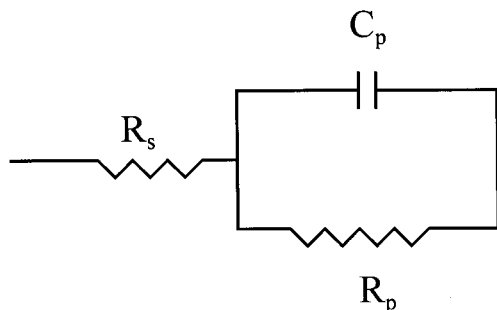


Figure 1 Equivalent circuit used for fitting EIS data.

or NaCl solution) and consisted of impedance measurements as a function of frequency. The instrumentation used included a Solartron 1255 Frequency Response Analyzer, Solartron 1286 Electrochemical Interface Potentiostat, and commercial ZPLOT, and ZVIEW software. Two different experimental setups were used to conduct the EIS studies on the above-mentioned polymer films. The first was a vice grip pressure clamp designed for making measurements of “dry” polymer films without immersion in a solution, and the second was designed for making measurements on films immersed in solution. The experimental measurements were carried out in a fairly standard manner with an applied signal of 10 mV, beginning at the maximum frequency (1×10^6 Hz) and sweeping down to the minimum frequency (0.1 Hz). The resulting data, in the form of impedance versus frequency and phase angle versus frequency, could then be fitted to the theoretical EIS response to an equivalent electrical circuit (Fig. 1), representing the physical arrangement of polymer film in the appropriate setup. In Figure 1, R_s is the solution resistance, and R_p and C_p are the resistance and capacitance of the polymer film, respectively. In most of the cases, the resistance of the coating was quite small and could be neglected. In the case of amine–quinone, however, R_p had a significant value. After obtaining the impedance and phase angle plots, the capacitance values for each polymer film were calculated for each curve by fitting the data to this equivalent circuit using commercial software. Experiments were performed on the as-received polymer films and on films immersed in mercury, in distilled water, and in 0.1M NaCl.

Measurements of Polymer Films Exposed to Electrolyte

EIS measurements were made on all polymer films as a function of time of immersion in 0.1M

NaCl (reagent grade) and high purity distilled water ($18 \text{ M}\Omega \text{ cm}$ resistivity) in a specially designed electrolyte cell, a schematic of which is shown in Figure 2. The electrolyte cell consisted of two machined Plexiglas compartments each fitted with a neoprene O-ring, two platinum electrodes, and a clamp that served to compress the O-rings onto the polymer sample. This setup is similar to one used by Kloppers et al.¹⁰ Samples of polymer film ($5 \times 5 \text{ cm}$) were placed between the two Plexiglas compartments. The area of the polymer film exposed to the electrolyte was 3.143 cm^2 . The experiment was initiated by filling the compartments with the desired electrolyte and taking impedance measurements after 10, 20, 30, 40, 50, and 120 min of immersion. The percentage water uptake was calculated from eq. (1) using the C_t values obtained from fitting experimental data. For comparison the percentage water uptake in the polymer films was also measured from simple weight gain. This was accomplished by immersing polymer film samples ($2 \times 2 \text{ cm}$) in 0.1M NaCl solution for 120 min and calculating percentage weight gain. It should be noted that the use of eq. (1) requires values for the “dry” capacitance, C_0 . Methods involved in measuring or calculating these C_0 values are described in the following section.

Measurements of C_0 for “Dry” Polymer Films

EIS measurements were made on all films in the as-received condition, which was assumed to be “dry,” no attempt was made to remove moisture that may have been absorbed from ambient air. Measurements were made with a vice grip pres-

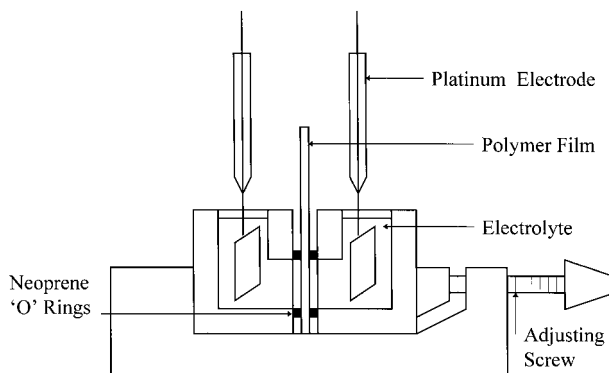


Figure 2 Schematic of the electrolyte cell used for EIS measurements of polymers immersed in either an electrolyte or mercury.

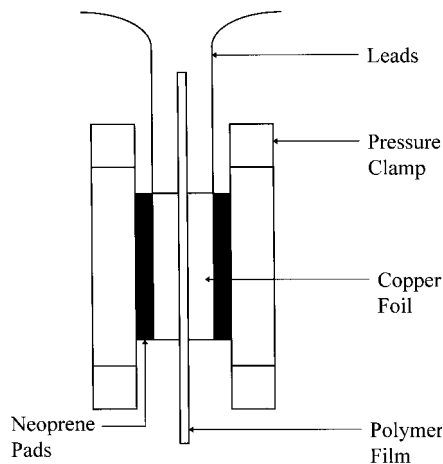


Figure 3 Schematic of the apparatus used for making EIS measurements of dry polymer films. A common, adjustable vice grip pressure clamp was used to press the copper contacts onto the polymers.

sure clamp, as shown in Figure 3. The arrangement consisted of a vice grip, neoprene pads, Cu foils (1×1 cm), Cu wire, and polymer film samples (2×2 cm), and is quite similar to that described in a previous study on coated metals.¹¹ Polymer film samples were centered between the two Cu foils such that the soldered wiring was on the outside of each foil, thus allowing for a proper electrical connection between the Cu foils and the film. The pressure adjusting screw was then tightened to ensure good contact between the Cu foils and the film sample. The area of the polymer film tested by this arrangement was the same as the area of the Cu foils, 1 cm^2 .

Because the calculation of water uptake given by eq. (1) depends upon the value of the dry film capacitance, C_0 , an accurate value for C_0 is necessary. Toward this end C_0 was measured or calculated by three different approaches. The first was the vice grip pressure clamp shown in Figure 3, which yields impedance and phase angle plots that can be fitted to an equivalent electrical circuit to obtain a value for the dry film capacitance or C_0 . The second utilized the electrolyte cell shown in Figure 2, except the electrolyte was replaced with liquid Hg. The third approach involved extrapolation of the experimental C_t data back to time zero.

RESULTS AND DISCUSSION

Typical EIS data in the form of impedance and phase angle plots are shown in Figure 4 for the

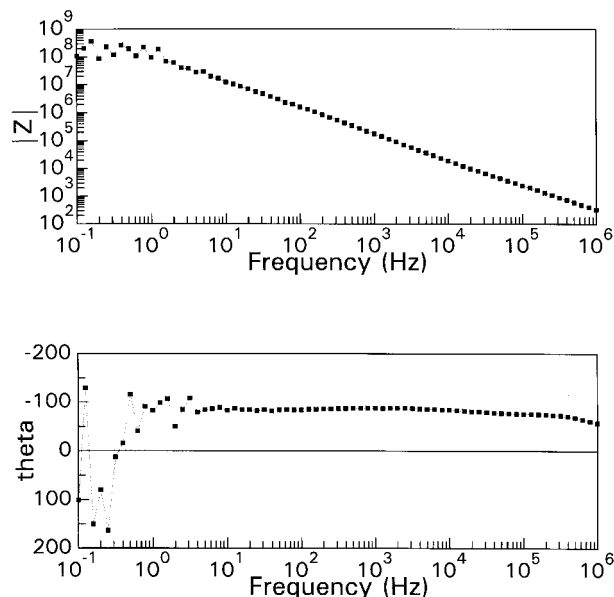


Figure 4 Impedance and phase angle plots for $25 \mu\text{m}$ PEN after 120 min immersion in $0.1M$ NaCl.

$25 \mu\text{m}$ PEN film after 120-min exposure to a $0.1M$ NaCl electrolyte. Fitting of these experimental data to the theoretical EIS response from the equivalent electrical circuit shown in Figure 1 provides a value for the capacitance of the polymer film. A plot of the capacitance values, C_t , as a function of the time of immersion in $0.1M$ NaCl is shown in Figure 5. Figure 6 includes the data from Figure 5 and also shows similar data collected for other films. As expected, film capacitance increases with immersion time, and then

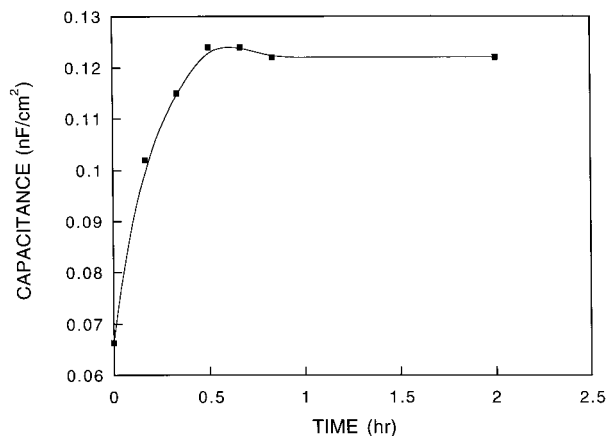


Figure 5 A plot of capacitance, calculated from EIS data, as a function of time of immersion in $0.1M$ NaCl for $25 \mu\text{m}$ PEN.

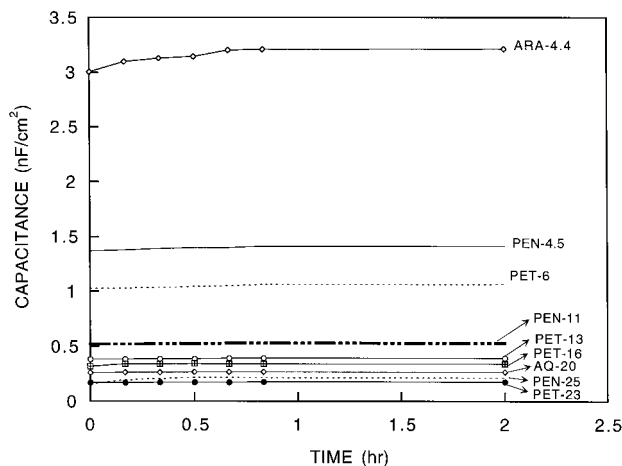


Figure 6 A comparison of the capacitance versus time data for all of the polymer films tested.

levels off after nearly an hour. Similar results have been observed by other investigators.^{9,10,12} These results are consistent with the gradual absorption of water molecules and ions from the solution until a saturation or equilibrium state is achieved. Because water has a high dielectric constant, this results in a corresponding increase in the dielectric constant of the polymer film thereby increasing the capacitance values. The capacitance value at which the film achieves saturation may be taken as a characteristic of the polymer film, as shown in Figure 6.

Calculation of the percentage or volume fraction of water uptake according to eq. (1) requires knowledge of the initial or "dry" capacitances, C_0 , of the individual polymer films. As mentioned previously, these values were obtained by three different approaches, the vice grip pressure clamp (Fig. 3), the electrolyte cell with Hg (Fig. 2), and extrapolation of the C_t data to time zero (Fig. 5). Results for all three are given in Table II, which

show that the capacitance measurements for the first two methods are fairly consistent, but the data obtained from the third varies significantly from the first two. To determine the most appropriate values for C_0 , the percent water uptake for each of the polymer films was obtained from weight gain experiments, and results are given in Table III. Percent water uptake was also calculated from eq. (1) using the C_0 measurements with Hg in the electrolyte cell, and results are also given in Table III. The data in Table III show close agreement in water uptake data between the C_0 measurements with Hg in the electrolyte cell and the weight gain measurements. Water uptake was also calculated using the other two approaches for obtaining C_0 , but showed significant deviations from the weight gain measurements. As a result, the "dry" capacitance measurements obtained with the electrolyte cell with Hg, C_0 (Hg), are taken to be the most appropriate values. Using the C_0 (Hg) values in Table II and eq. (1), percent water uptake for all the polymer films was calculated as a function of immersion time, and results are shown in Figure 7.

An examination of the data in Figure 7 can be based on either a comparison of polymer type or a comparison of thickness for a single polymer type. Considering polymer type, the four polymers examined in this study can be listed in order of increasing resistance to moisture absorption AQ > PET > PEN > Aramid, where AQ is the most resistant and Aramid the least resistant. Considering polymer thickness, it is interesting that the percent water uptake decreases as thickness increases. The dependence of water uptake on thickness may result from the structural properties (e.g., porosity, mechanical strength) of the polymer chains, which could serve to limit the expansion that necessarily accompanies the absorption

Table II Measurements of Initial "Dry" Film Capacitance, C_0 , by Three Different Methods

	C_0 (nF/cm ²)								
	PEN 4.5 μ m	PEN 11 μ m	PEN 25 μ m	PET 6 μ m	PET 13 μ m	PET 16 μ m	PET 23 μ m	ARA 4.4 μ m	AQP 20 μ m
Vice grip pressure clamp	0.501	0.223	0.091	0.403	0.187	0.146	0.097	0.690	0.172
Electrolyte cell with Hg	0.535	0.230	0.102	0.445	0.192	0.173	0.113	0.815	0.193
Extrapolation of C_t to time zero	0.443	0.185	0.07	0.346	0.112	0.091	0.074	0.726	0.154

Table III Percent Water Uptake for Different Films After 2-h Exposure to 0.1M NaCl

	Water Uptake (%)								
	PEN 4.5 μm	PEN 11 μm	PEN 25 μm	PET 6 μm	PET 13 μm	PET 16 μm	PET 23 μm	ARA 4.4 μm	AQP 20 μm
Calculated from EIS and C_0 (Hg)	21.7	16.3	12.9	19.9	16.4	15.4	10.2	31.3	7.32
Calculated from weight gain	21.4	15.3	12.2	18.8	15.2	14.4	9.49	27.4	6.01

One set of data are obtained from EIS measurements using the electrolyte cell and C_0 values measured with the same apparatus using mercury. The other set of data were calculated from weight gain experiments.

of moisture. For example, it is widely known in the magnetic tape industry that when tape is physically restrained, as is the case for tape wound in reels where only the edges are exposed, it does not expand or absorb as much moisture as when exposed on all sides.

The inverse dependence of the C_0 (Hg) measurements on thickness is shown in Figure 8 for the PET and PEN polymer films. Assuming that the dry, free-standing films behave in a purely capacitive manner, the dielectric constant, ϵ , can be calculated from the following equation for a parallel plate capacitor:

$$C_0 = \frac{\epsilon\epsilon_0}{L} \quad (2)$$

where C_0 is the dry film capacitance in nF/cm^2 , ϵ_0 is the absolute permittivity of free space ($8.854 \times 10^{-14} \text{ F}/\text{cm}$), and L is the film thickness (cm).

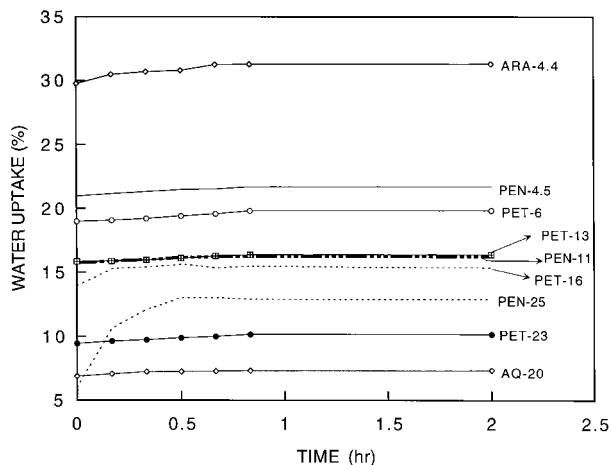


Figure 7 Water uptake (%) calculated from the data in Figure 6 and eq. (1).

As shown in Figure 8, the experimental data for both PEN and PET show linear behavior with intersection through the origin, in agreement with eq. (2). The dielectric constants for PEN and PET calculated from the slopes are 3.124 and 2.98, respectively. These values compare well with previously reported values.¹³ The different slopes shown in Figure 8 are a reflection of the physical properties of the polymer (i.e., dielectric constant) and as such may be used for determining C_0 values for varying thicknesses without having to make additional experimental measurements.

An interesting question to consider is whether the polymer films absorb only water, or are other species (e.g., ions) also absorbed. The theory underlying eq. (1) assumes that the increase in capacitance arises only due to the absorption of water molecules. This approach fits quite well as shown in Table III by the close agreement between weight gain experiments and percent water

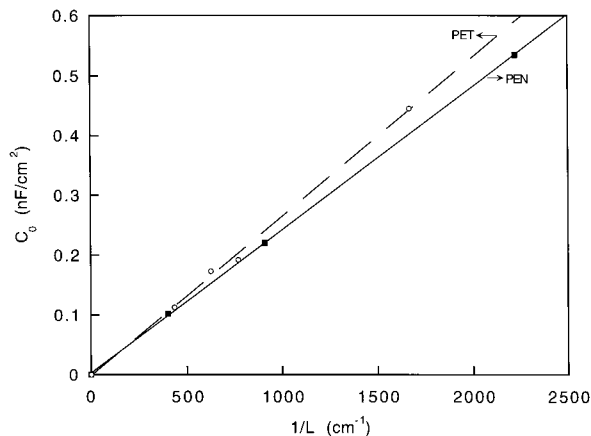


Figure 8 A plot of the dry capacitance of PET and PEN polymer films versus L^{-1} . Capacitance values were obtained using the electrolyte cell with Hg.

Table IV A Comparison of Capacitance Values Obtained After 2 h of Immersion in 0.1M NaCl Solution and Distilled Water

	Capacitance after 2-h Immersion (nF/cm ²)								
	PEN 4.5 μm	PEN 11 μm	PEN 25 μm	PET 6 μm	PET 13 μm	PET 16 μm	PET 23 μm	ARA 4.4 μm	AQP 20 μm
0.1M NaCl	1.412	0.529	0.215	1.064	0.393	0.340	0.176	3.212	0.266
H ₂ O	1.396	0.509	0.206	1.007	0.343	0.324	0.170	3.202	0.240

uptake calculated by eq. (1). For comparison, capacitance values after 2 h of immersion (i.e., the polymer is assumed to be saturated) were measured in both 0.1M NaCl and distilled water, and results are shown in Table IV. As can be seen, consistently lower capacitance values were observed for all films tested in distilled water compared to 0.1M NaCl. This indicates that water uptake, calculated as described above, is greater in NaCl than in pure water. This difference might be due to the absorption of the ionic species.

CONCLUSIONS

This investigation has demonstrated the utility of electrochemical impedance spectroscopy (EIS) for determining the electrical properties of various free-standing polymer films. Relatively simple experimental methods and techniques were developed to measure changes in capacitance as a function of polymer type, polymer thickness, and time of exposure to 0.1M NaCl and distilled water. Several conclusions can be drawn from this study. Most obvious, perhaps, is the fact that capacitance increases as water is absorbed into the polymer, and that EIS is a convenient tool for measuring even small changes in capacitance. The data presented in this study show that the change in capacitance upon immersion in an electrolyte can be fairly accurately represented by a model that assumes that the increase is due only to the change in dielectric constant brought about by the ingress of water. Use of this model depends upon knowing or obtaining initial capacitance values, C_0 , which in this study were obtained for "dry" polymers. Three different methods for obtaining C_0 values were described and employed, but the most reliable values were obtained via EIS measurement using Hg contacts. C_0 values obtained by this method resulted in calculated water up-

take values nearly identical with weight gain measurements. Furthermore, the C_0 values are linearly dependent on inverse polymer thickness, which allows C_0 to be easily calculated for other thicknesses. Lower-capacitance values were observed for films immersed in distilled water compared to 0.1M NaCl, which indicates that water uptake is greater in NaCl than in pure water. The four polymers examined in this study can be listed in order of decreasing resistance to moisture absorption as AQ > PET > PEN > Aramid. The resistance of AQ to moisture absorption may provide at least a partial explanation for the diminished corrosion of iron particles (used in magnetic tapes) that has been observed after coating with AQ polymer.²⁻⁴

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