Transport and Dielectric Properties of Poly(ethylene terephthalate) as Determined via Electrochemical Techniques

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SYNOPSIS

The electrochemical impedance spectroscopy (EIS) technique was used to evaluate the water transport (diffusion and equilibrium water uptake) and the dielectric properties of free-standing poly(ethylene terephthalate) (PET) membranes at 40°C. Permeability and diffusion coefficients were also obtained using the Payne cup method and the MacBain quartz spring balance to assess the reliability of the EIS method when compared to other techniques. In addition, an electromigration (dc) technique was used to estimate the NaCl diffusion coefficient across PET films. Results obtained indicate that PET is highly permeable to water and much less permeable to salt. The water diffusion coefficient, D, varies from 2.11×10^{-9} to 9.97×10^{-9} cm^2 s^{-1} for thicknesses between 22 and 205 μm, whereas the equilibrium water uptake, W, varies from 0.54 to 0.95 wt % for the same given range of thicknesses. The average calculated dielectric constant of the free-standing PET films is 3.6. An estimate of the NaCl diffusion coefficient, D_s, is 9.34×10^{-14} cm^2 s^{-1}. Transport properties results obtained via the electrochemical technique are in reasonable agreement with those obtained with the classical gravimetric method. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Water-transport properties of polymers have traditionally been performed via gravimetric techniques. These techniques can incorporate experimental errors and difficulties especially when thin films and high water vapor activity must be investigated. This paper reports an experimental investigation on the use of the electrochemical impedance spectroscopy (EIS) technique as an alternative method to the gravimetric one for evaluating transport and dielectric properties of free-standing poly(ethylene terephthalate) (PET) films. Impedance measurements can be performed quickly and reliably, and polymeric film properties such as diffusivity, solubility, or equilibrium water content and dielectric constant can be obtained simultaneously. In addition to the EIS technique that is based on an ac electrical stimulus, the electromigration (dc) technique was also used to estimate the salt (NaCl) transport across PET films. Uptake of salt and water constitute a serious reliability problem for polymers used in microelectronics and can result in reduced performance and lifetime of electronic devices.[1-4]

EXPERIMENTAL

Materials

PET films of 22, 75, and 205 μm thickness were furnished by Texas Instruments, Attleboro, MA. Sodium chloride solutions were prepared from reagent-grade material and dissolved in high-purity distilled water (18 MΩ cm resistivity).

Apparatus

A schematic of the electrochemical cell (a two-compartment quartz cell) used for the electrical (dc and

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ac) measurements is shown in Figure 1. The PET film was mounted in the sample holder and sealed with Viton O-rings. The membrane surface area was 7.54 cm². Each compartment of the cell (120 cm³) was equipped with a magnetic stirrer, platinum electrode (positioned 10 cm from the membrane), and heating mats. Temperature control allowed adjustment of the solution temperature from room temperature to approximately 60°C. A temperature of 40°C was, however, used in all the experiments described below. Each compartment of the cell was filled with either distilled water or an aqueous solution of NaCl.

For the water-transport measurements, the free-standing PET film was placed in the cell, the electrolyte poured in, and the capacitance of the membrane was determined as a function of the time. A Solartron 1286/1250 Impedance System was used. The two-electrode setup of the Solartron 1286 electrochemical interface was used, and the applied voltage over the membrane was set to 0 V (dc bias). An ac excitation wave of 5 mV amplitude was superimposed on the dc component. The impedance response of the membrane was determined by a Solartron 1250 transfer function analyzer. The excitation frequency was varied between 10 KHz and 25 Hz, and 10 steps per frequency decade were taken. The unit was set to auto integration of the impedance to an accuracy of 10%, and the maximum number of integration cycles was set at 50 to strike a

good balance between integration speed and accuracy. After each frequency sweep between the frequency limits as described above, the data were saved to disk, after correcting for the surface area of the specimen. The time elapsed since the immersion of the membrane was also saved at the beginning and the end of each sweep.

From the data as saved above, the capacitance at every frequency, f, was calculated as $C_t = 1/(2\pi f S Im)$, where Im is the imaginary part of the impedance, and S the membrane surface area. The data were examined for any data in error due to faulty integration, and the average capacitance value for the sweep was determined. The elapsed time was calculated as the average between the time at the start and the end of the sweep. In this way, each sweep yielded a data pair in the form (t, C_t), where t is the elapsed time since immersion of the membrane, and C_t the capacitance at time t. Combining the data pairs of all the sweeps yielded the C_t vs. t curve.

Water permeability coefficients were also obtained by using the well-known Payne cup method to check for the accuracy of the ac technique. In addition, the water diffusion coefficient and the equilibrium water uptake, $\%W$, were determined by the MacBain quartz spring balance. The design and operation of the MacBain quartz spring balance used in this paper have been described in the literature.[5] With this system, a direct gravimetric measure of
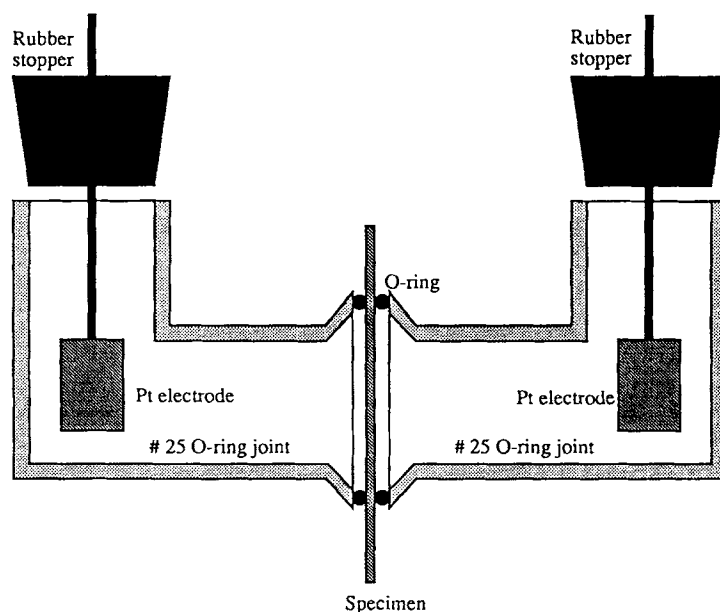
Figure 1   Schematic of the two-compartment quartz cell for water and ion diffusion coefficient determination, based on a modified #25 O-ring joint.

the penetrant uptake by the polymer as a function of time can be determined by observing changes in spring extension. In the MacBain balance cell, the polymer was hung at the base of the spring and a glass reference fiber was hung parallel to the spring to compensate for small shifts in the spring support position. The absorption cell was maintained at the constant temperature of 40°C by circulating deionized water from a bath through a fluid jacket surrounding the cell. The system, excluding the absorption cell, was pressurized with water vapor at the desired absorption pressure when the stopcock to the absorption cell was opened. At time zero, the water vapor was admitted into the absorption cell, and the spring extension was measured as a function of time.

The salt (NaCl) diffusion coefficient was determined via the electromigration (dc) technique as described in the literature.[6] The diffusion coefficients for the NaCl in the polymer may then be determined by analysis of the current breakthrough curve. After filling the diffusion cell with the electrolyte, $0.5 M$ NaCl, the PET film was mounted in the sample holder and a voltage of 10 V was applied across the two platinum electrodes. The current that flowed in the resulting completed circuit was monitored as a function of time by a Keithley model 617 programmable electrometer able to measure currents as low as 1 pA.

Theoretical Background

This paper reports an investigation on water transport in polymers determined by the technique of EIS and compares the results to those obtained via the gravimetric method; therefore, a short description of the theory on which these two methods are based will be given. This description will show that the capacitance method of evaluating water transport in polymers can be properly applied only under well-defined conditions as described below.

Gravimetric Method

Sorption and transport of small molecules in a polymer is a complex nonsteady state process.[7] To obtain the diffusion coefficient of the penetrant into the polymer, Fick's second law of diffusion must be solved. Crank[8] reported different solutions of Fick's second law depending on the initial and boundary conditions. The case of interest in this paper is that of a free film of thickness L, exposed to a uniform and constant concentration of diffusant with a zero initial concentration of the diffusant in the film. If

M_t denotes the total amount of diffusing substance that has entered the film at time t, and M_∞, the corresponding quantity after infinite time, then

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{n=\infty} \frac{8}{(2n+1)^2\pi^2} e^{-D(2n+1)^2\pi^2 t/L^2} \quad (1)$$

In deriving eq. (1), the diffusion coefficient, D, is assumed to be constant.

Equation (1) gives a unique curve when plotted as M_t/M_∞ vs. $\tau^{1/2}$, where $\tau = Dt/L^2$ is dimensionless time. For relatively small values of τ, corresponding to $M_t/M_\infty < 0.6$, eq. (1) reduces to

$$\frac{M_t}{M_\infty} = \frac{4t^{1/2}}{\pi^{1/2}L} D^{1/2} \quad (2)$$

Equation (2) shows that as the time goes to zero the amount of substance absorbed depends on the square root of time, i.e.:

$$M_t = At^n \quad (3)$$

where $A = (4M_\infty D^{1/2})/(\pi^{1/2}L)$ and $n = \frac{1}{2}$. Equation (2) is generally used to evaluate the diffusion coefficient, D, from the values of $M_t(t)$ provided that the equilibrium water uptake, M_∞, is known.[9-14]

Equation (1) describes the uptake of solute into polymers when Fick's law is obeyed. The transport phenomenon of such diffusants is called "Fickian diffusion."[9] It is well known, however, that there are cases in which the transport of diffusants in polymers is not described by eqs. (1) and (2). When the diffusant swells the polymer, the solute uptake occurs with kinetics quite different from that described by eq. (1). These processes are called "non-Fickian diffusion processes."[9] It is possible to show, however, that for a "non-Fickian process" the relationship between the amount of substance absorbed for small time and the time, t, is similar to eq. (3), i.e.:

$$M_t = Kt^n \quad (3a)$$

where $n \neq \frac{1}{2}$, and $K \neq A$ in this case. For $n = 1$, eq. (3a) describes the well-known Case II transport. The main physical feature of this case is that the sorption process is controlled by the velocity of the sharp boundary separating the outer swollen shell (essentially at equilibrium penetrant concentration) from the unpenetrated glassy part. In Case II, K is directly related to this velocity. The range $\frac{1}{2} < n < 1$ corresponds to intermediate cases between Fickian and

Case II transport. Different theories have appeared in the literature describing these intermediate cases (see Ref. 9 and literature cited therein). Finally, some penetrant–polymer systems exhibit a dramatic increase in the sorption rate in the last part of the sorption curve. Because of this anomalous behavior, these cases are currently called "Supercase II." Leaving aside the "Supercase II," eq. (3a) furnishes a method for evaluating if the process is Fickian or not. Taking logs of eq. (3a) gives

$$\text{Log } M_t = \text{Log } K + n \text{ Log } t \tag{4}$$

The exponent n in eq. (3a) can, thus, be evaluated by plotting on a Log–Log plot the total amount of substance, M_t, vs. the time, t. In this plot, the slope gives the exponent n from which the phenomenology of the transport process can be derived. It must be pointed out that it is not always possible to describe the kinetics of a complex sorption mechanism by means of eq. (3a). Conclusions reported above can, therefore, be applied only to polymer–penetrant systems obeying eq. (3a).

Capacitance Method

The use of the EIS to evaluate the transport properties of polymeric films is based on the assumption that a polymeric material under an applied electrical stimulus behaves like an equivalent circuit of resistors and capacitors.[15] The most common equivalent circuit used in the literature to describe electrical properties of polymeric materials is shown in Figure 2.[15] Exposure to water or salt solutions alters the electrical characteristics (resistivity and capacitance) due to the uptake of both the solvent and salt into the polymer, as schematically shown in Figure 2. It is assumed, furthermore, that water uptake affects the film capacitance, whereas salt uptake affects the film resistivity. On the basis of these assumptions, an electrical ac stimulus allows investigation with the immersion time.

Changes in electrical properties during the exposure of polymer film to aqueous environments are based on a modification of an original formula given by Hartshorn et al.[16] The application of this formula to a polymer containing water requires the assumptions that (i) the change in capacitance is due entirely to the permeation of water into the film, (ii) the permittivity of the absorbed water is constant and equal to 80, (iii) the swelling of the polymer film can be ignored, and (iv) the distribution of water in the film is random and uniform. Under these assumptions, this formula gives

(a)

(b)
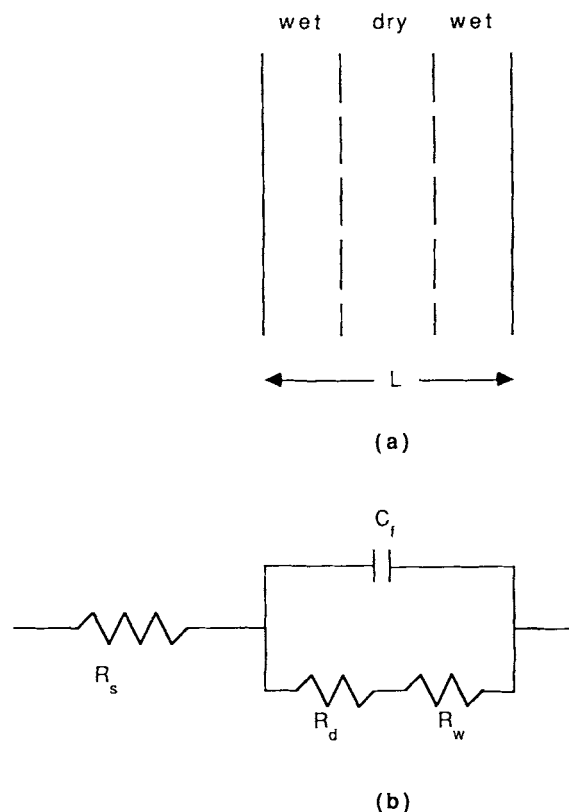
Figure 2 Schematic representation of (a) the water (or salt) advancing front into a PET sheet of thickness L and (b) the correspondent equivalent electrical circuit. R_s represents the resistance of the external solution; R_d and R_w represent the electrical resistance of the unpenetrated (dry) and penetrated (wet) part of the film, respectively, whereas C_t is the film capacitance.

$$\phi = \frac{\text{Log}(C_t/C_0)}{\text{Log } 80} \tag{5}$$

where ϕ is the volume fraction of absorbed water; C_t the capacitance at time t, and C_0 the capacitance at time $t = 0$, i.e., at the start of the experiment. C_0 is obtained by extrapolation of the $C_t(t)$ values as $t \rightarrow 0$, as will be described in the following. The capacitance at $t = \infty$, C_∞, is taken as the value of the capacitance after the appearance of a plateau, indicating that equilibrium has been reached and the film is fully saturated with water. The equilibrium water uptake is obtained by using eq. (5) with $C_t = C_\infty$. Equation (5) will, thus, be used as basic relationship between mass uptake, expressed as volume fraction, ϕ, and capacitance change, expressed as C_t/C_0. To use eq. (5), however, the dry film capacitance, C_0, is required. Since this value is not known *a priori*, it must be obtained from the time

behavior of the capacitance itself, as will be shown below.

For small values of t, eq. (5) yields

$$\lim_{t \to 0} \phi = \lim_{t \to 0} \frac{\mathrm{Log}(C_t/C_0)}{\mathrm{Log}\, 80} \qquad (6)$$

The value of C_0 as shown by eq. (6), thus, depends on the time dependence of ϕ for $t \to 0$. Since the volume fraction $\phi = \phi_\infty(M_t/M_\infty)$, and M_t can be expressed by eq. (3a) for small values of t, one has

$$\phi = \phi_\infty \frac{M_t}{M_\infty} = Bt^n \qquad (7)$$

where B is given by $B = K\phi_\infty/M_\infty$, and ϕ_∞ is the equilibrium volume fraction.

Equations (6) and (7) show that C_0 cannot be taken as the linear extrapolated value of $C_t(t)$ for $t \to 0$. The correct extrapolated value of C_0 depends on the value of n that, as discussed above, is related to the type of diffusive process. In other words, the type of $C_t(t)$ for $t \to 0$. The correct extrapolated value of C_0 depends on the value of n that, as discussed above, is related to the type of diffusive process. In other words, the type of diffusion (if Fickian or not) must be known *a priori* to apply the capacitance method to the polymer-diffusant system. If n is not known *a priori*, then any kind of extrapolation is arbitrary and can lead to erroneous results and interpretation of the experimental data. If the relationship between the capacitance and the volume fraction is known in an explicit formula, then the exponent n can be evaluated from the capacitance values itself. This aspect will be described below.

Assuming that eq. (5) holds true, one has

$$\frac{C_t}{C_0} = e^{\alpha\phi} \qquad (8)$$

where $\alpha = 2.3\, \mathrm{Log}\, 80$. For $t \to 0$, the volume fraction $\phi \to 0$; thus, a series expansion of eq. (8), with use of eq. (7), yields

$$\frac{C_t}{C_0} = 1 + \alpha\phi = 1 + \alpha Bt^n \qquad (9)$$

From eq. (9), the exponent n and the dry film capacitance, C_0, can be evaluated by nonlinear regression analysis applied to the experimental capacitance data.

When the diffusion phenomenon is Fickian, a close relationship for the diffusion coefficient, D,

can be derived if eq. (5) holds true. For small values of the equilibrium water uptake ($\phi_\infty \ll 1$), it is a simple matter to show that

$$\frac{\phi}{\phi_\infty} = \frac{C_t - C_0}{C_\infty - C_0} = \frac{M_t}{M_\infty} \qquad (10)$$

In this equation, C_0 is the extrapolated value of C_t for $\sqrt{t} \to 0$ and $(C_t - C_0)/(C_\infty - C_0)$ is the dimensionless film capacitance. The conclusion is drawn that all kinetic expressions in M_t/M_∞ reported above [eqs. (1) and (2)] can be easily translated into dimensionless capacitance equations by using the relationship (10). The diffusion coefficient, D, can, thus, be evaluated by using eq. (2) and the dimensionless capacitance expression as described by eq. (10).

When the equilibrium volume fraction, ϕ_∞, is not small, then the relationship to use is eq. (5). The following general relationship between the capacitance and the mass uptake is obtained in this case:

$$\frac{\phi}{\phi_\infty} = \frac{\mathrm{Log}\, C_t - \mathrm{Log}\, C_0}{\mathrm{Log}\, C_\infty - \mathrm{Log}\, C_0} = \frac{M_t}{M_\infty} \qquad (11)$$

Equation (11) shows that the dry film capacitance can be evaluated as the limiting value of $\mathrm{Log}\, C_t$ for $\sqrt{t} \to 0$, whereas the diffusion coefficient can be determined by using eq. (2) in conjunction with eq. (11).

RESULTS AND DISCUSSION

The C_t vs. $\sqrt{t}$ curves for the three specimens investigated are shown in Figures 3–5. The data pairs in the form (t, C_t) obtained as described above were subsequently analyzed in terms of eqs. (2) and (10), i.e.:

$$\frac{C - C_0}{C_\infty - C_0} = \frac{4t^{1/2}}{\pi^{1/2}L}D^{1/2} \qquad (12)$$

It is immediately obvious that a plot of the dimensionless quantity on the left-hand side of eq. (12) vs. the square root of the time elapsed since immersion gives the diffusion coefficient of water in the membrane. It is important to note that for the thinnest sample provided, with a thickness L, of 22 μm, the water uptake is so rapid that the time required to carry out a frequency sweep as described above is a significant portion of the time to saturation. This has two effects: (i) The capacitance may
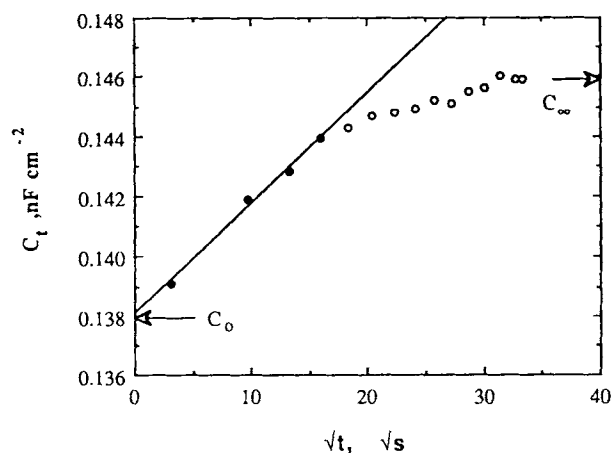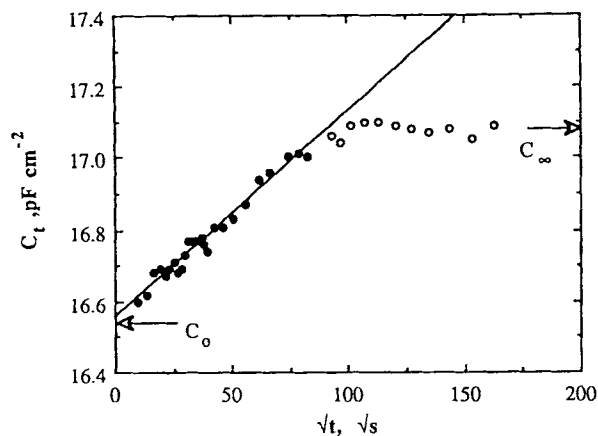
Figure 3   Film capacitance C_t, in nF cm^{-2}, vs. $\sqrt{t}$, in $\sqrt{s}$, at temperature of 40°C for a 22 μm-thick PET film. The dry film capacitance, C_0, and the equilibrium film capacitance, C_∞, are reported with an arrow on the left-hand and right-hand scales, respectively.

change significantly while the sweep is carried out, and (ii) fewer data points can be measured to define the transient, because the sample saturates rapidly due to the small thickness. These effects may lead to inaccuracies in subsequent calculations for the 22 μm sample.

Results from gravimetric data are shown in Figure 6 as wt % mass uptake vs. $\sqrt{t}$ for the 75 and 205 μm PET films, respectively. It was not possible to carry out gravimetric measurements with the 22 μm-thick film due to the high value of D and the small film thickness. From the values of the equilibrium mass
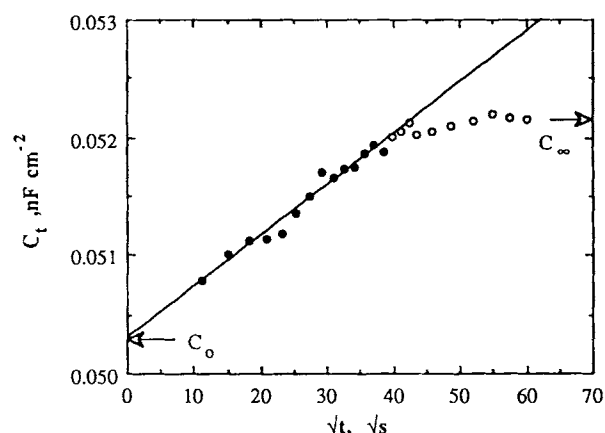
**Figure 4**   Film capacitance C_t, in nF cm^{-2}, vs. $\sqrt{t}$, in $\sqrt{s}$, at temperature of 40°C for a 75 μm-thick PET film. The dry film capacitance, C_0, and the equilibrium film capacitance, C_∞, are reported with an arrow on the left-hand and right-hand scales, respectively.


Figure 5   Film capacitance C_t, in pF cm^{-2}, vs. $\sqrt{t}$, in $\sqrt{s}$, at temperature of 40°C for a 205 μm-thick PET film. The dry film capacitance, C_0, and the equilibrium film capacitance, C_∞, are reported with an arrow on the left-hand and right-hand scales, respectively.

uptake (M_∞), the diffusion coefficient D was evaluated by using eq. (2) in the appropriate linear range. The calculated diffusivities vary from 7.76 $\times 10^{-9}$ to 1.31 $\times 10^{-8}$ cm^2 s^{-1} and increase with film thickness. Once the diffusion coefficient for each thickness is known, the dimensionless variable $\tau = tD/L^2$ can be calculated for each time t. If the diffusion phenomenon is Fickian, then all experimental data must lie on a unique curve as described by eq. (1). These results are shown in Figure 7.

As can be seen from Figure 7, the diffusivity curves of PET films for two different values of the film thickness compare satisfactorily with the theoretical curve, demonstrating that the experimental findings are well described by eq. (1). These results
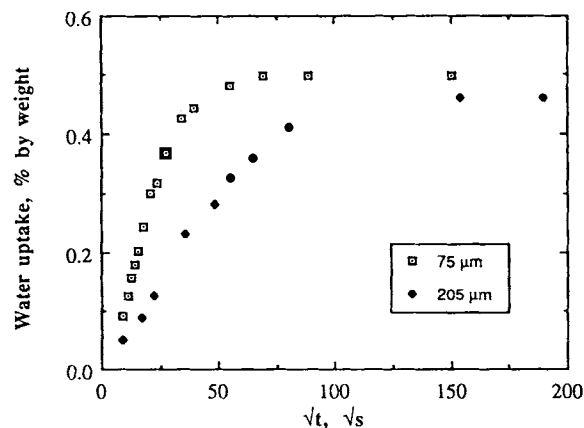
Figure 6   Water uptake in % by weight vs. the square root of the time for the 75 and 205 μm-thick PET films at 40°C and at a water activity of 0.92.
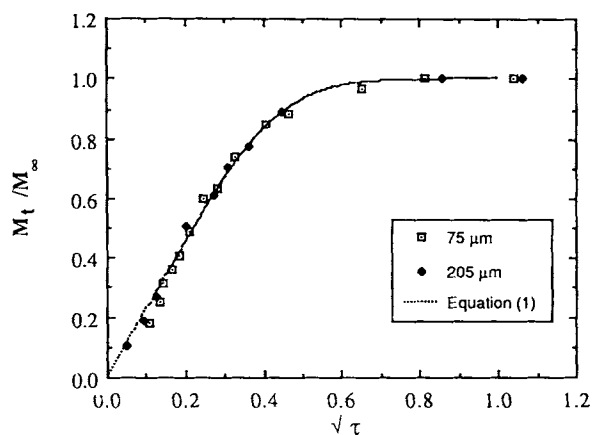
Figure 7 Dimensionless water uptake vs. the square root of the dimensionless time, τ, for the PET films investigated in this paper. The dotted line was determined using eq. (1).

support the view that water transport in PET is Fickian in nature.

The equilibrium water uptake, W, is equal to 0.46 and 0.5 wt % for the 75 and 205 μm-thick films, respectively. The water uptake, $\%W$, was converted to the solubility coefficient, S, in $[cm^3 \, (STP)]/(cm^3 \, cmHg)$ via the density of the polymer, 1.33 g cm^{-3}. The latter two values were obtained exposing the 75 and the 205 μm-thick films at a water activity equal to 0.92, because the MacBain balance technique does not allow experiments at unitary water activity. The values of D and $\%W$ for the 205 μm-thick film obtained with this technique compare well with the data obtained with the impedance technique at close to unitary water activity, as shown below. The good agreement between the diffusion coefficient as determined by gravimetry with the values as determined by the ac method indicates that in the activity range investigated (0.92–1) D is constant with the concentration of water (water uptake) into the film.

Experimental findings obtained with the capacitance method (Figs. 3–5) can be arranged in the same way as those obtained with the gravimetric method. Figure 8 shows the plot of the dimensionless film capacitance as a function of the square root of the dimensionless immersion time, τ, for the PET films investigated. The diffusivity curves were "normalized" by the thickness and are compared with the theoretical curve. The calculated diffusivity varies in the range 2.11×10^{-9} to 9.97×10^{-9} cm^2 s^{-1}, whereas the water uptake in the PET varies from 0.54 to 0.95 wt %.

The experimental results reported in Figures 7 and 8 overlap each other, showing, hence, that both

the capacitance and the gravimetric method well describe the Fickian behavior of PET samples. Data obtained with the ac technique exhibit more scattering for high values of τ compared to the results from the gravimetric experiments. The capacitance method, however, allows one to evaluate the diffusion coefficient of thinner films as the data obtained with the 22 μm-thick film indicate. This result is possible because (i) capacitance measurements can be taken continuously without perturbing the system investigated, and (ii) the time of acquisition of the experimental data is short compared to the time scale of the process due to the high value of the frequency of the applied ac signal used. Table I summarizes the diffusion coefficient, D, in cm^2 s^{-1} and the equilibrium water uptake, W, in wt %, obtained with the two methods.

Assuming that the PET behaves like a pure capacitor, the permittivity ε can be calculated by the following equation:

$$C_0 = \varepsilon\varepsilon_0/L \qquad (13)$$

where C_0 is the dry film capacitance in F cm^{-2}; ε_0, the absolute permittivity (8.854×10^{-14} F cm^{-2}); and L the film thickness in cm. Figure 9 shows the capacitance C_0 as a function of $1/L$ for the PET films investigated in this paper. The experimental points lie on a straight line that extrapolates to the origin of the axis in agreement with eq. (13). The estimated relative permittivity is equal to 3.60. Thus, transport and dielectric properties of PET were determined simultaneously by the EIS technique.

The salt (NaCl) diffusion coefficient across PET
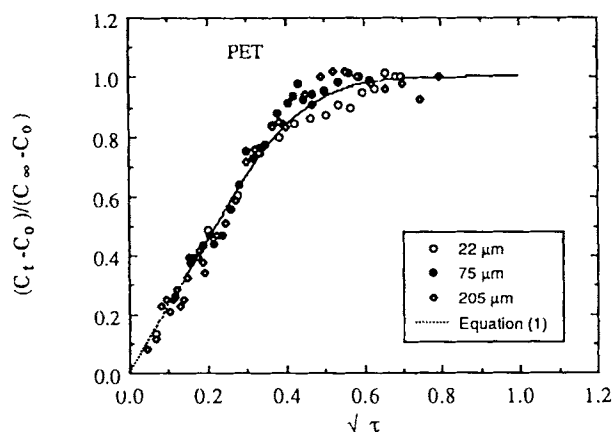
Figure 8 Dimensionless film capacitance, $(C_t - C_0)/(C_\infty - C_0)$, vs. the square root of the dimensionless time, τ, for the PET films investigated in this paper. The dotted line was determined using eq. (1).

Table I Water Diffusion Coefficient, D, in $cm^2 s^{-1}$, Water Uptake, W, in % by Weight, Water Solubility, S, in $[cm^3(STP)]/(cm^3 cmHg)$, Water Permeability, P, in $[cm^3(STP) cm]/(cm^2 s cmHg)$, and $D \times S$, in $[cm^3(STP) cm]/(cm^2 s cmHg)$ as a Function of Film Thickness at the Temperature of 40°C (Subscripts "g" and "c" Indicate Gravimetric and Capacitance Method, Respectively)

L (μm)	W_g	$D_g \times 10^9$	W_c	$D_c \times 10^9$	$P \times 10^8$	$D_c \times S \times 10^8$
22			0.95	2.11	3.10	1.3
75	0.50	7.76	0.83	5.91	3.30	3.3
205	0.46	13.10	0.54	9.97	4.21	3.6

was estimated by applying the electromigration technique.[6] This technique is based on the fact that the salt concentration profile into the polymer divide, roughly, the film in two parts: a wet and dry part, as schematically shown in Figure 2(a). It is furthermore assumed that the resistance of the dry part, R_d, is much higher than the resistance of the wet part, R_w. Under this hypothesis, the total film resistance is, thus, determined by the value of R_d until the two advancing fronts meet at $x = L/2$. The time Θ at which the salt advancing front met at $x = L/2$ is given by

$$\Theta = \frac{(L/2)^2}{6D_s} \qquad (14)$$

where D_s is the salt diffusion coefficient. At the time Θ, therefore, a sharp variation in the film resistance, or in the current flowing across the film, must be observed. From the values of Θ and L, it is a simple matter of fact to estimate, via eq. (14), the salt diffusion coefficient. Tests carried out on the 22 μm-thick specimen indicated that no breakthrough of

Figure 9 Dry film capacitance, C_0, as a function of the reciprocal of the PET film thickness at the temperature of 40°C.

ions occurs even after applying an electric field of 10 V for 600 h. As the diffusion coefficient can be calculated only from the current transient after breakthrough,[6] we can only estimate the maximum diffusion coefficient from eq. (14), taking Θ as $600 \times 3600 = 2.16 \times 10^6$ s and with L being equal to 22×10^{-4} cm in this case. An estimate of the salt diffusion coefficient is, therefore, $9.34 \times 10^{-14} cm^2 s^{-1}$. Note that this result is an extremely conservative estimation, since it neglects the effect of the electric field. The actual diffusion coefficient may be much lower than this value.

A similar 550 h test on the 75 μm-thick sample also showed no breakthrough, and again no diffusion coefficient can be calculated, since no transient response was observed. Estimating the diffusion coefficient from eq. (14) as before, now with L equaling 75×10^{-4} cm, gives $D = 1.18 \times 10^{-12} cm^2 s^{-1}$. Again, this is an extremely conservative estimate. A test on the 205 μm-thick sample also showed that no current transient could be measured, even after a test of 800 h.

The values of D, the water diffusion coefficient in $cm^2 s^{-1}$, and $\%W$, as determined for the three specimens, are summarized in Table I. The value of 2.11×10^{-9} for the water diffusion coefficient in the thinnest sample is most likely in error due to the reasons described above. The wt % water taken up, $\%W$, is between 0.54 and 0.95, with the larger value calculated for the thinner sample, most likely due to the same limitations in the experimental technique as described before. The reported values of the diffusion coefficient, D, and $\%W$, allow the evaluation of the permeability coefficient, P, via the equation $P = D \times S$, where S is the solubility coefficient in $[cm^3 (STP)]/(cm^3 cmHg)$. The permeabilities data were compared with those as determined with the Payne cup method (weight loss measurements). Table I shows that the values of $D \times S$ from the impedance measurements and the value of P from the weight loss measurements are in reasonable agreement. This result indicates that
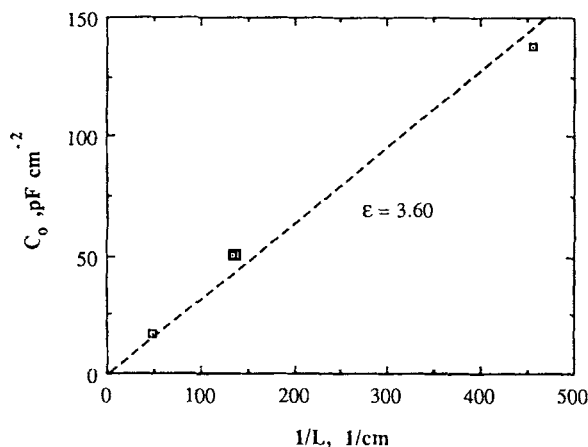
the values of the parameters, P, D, and S, are accurate as determined.

CONCLUSIONS

The results presented in this paper showed that the capacitance and the gravimetric methods of evaluating transport properties of water across freestanding PET films are in reasonable agreement. When applicable, the capacitance method can be preferred to the gravimetric method because the transport properties can be evaluated without perturbing the system under study. In addition, with the capacitance method, thin polymeric films can be tested even for relatively high water diffusion coefficients (on the order of 10^{-9} cm^2 s^{-1}). To use the capacitance method, the following assumptions should be fulfilled:

(i) A model for the effect of water on the capacitance change of the polymeric material should be available.

(ii) The mechanism of diffusion (exponent n) must be determined (if not known) in order to apply the correct procedure to obtain the dry film capacitance, C_0. From the value of C_0, the equilibrium water uptake and the polymer dielectric constant can, then, be easily evaluated. The diffusion coefficient, D, however, can be determined by simple equations only for $n = \frac{1}{2}$ ("Fickian diffusion"). For $n \neq \frac{1}{2}$, more complex transport theories must be applied in order to determine D via the EIS technique. This aspect will be addressed in subsequent papers.

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