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Effect of UV Light on Different Structural and Transport Parameters of Cellophane Membranes

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ABSTRACT

A comparative study of UV light influence on structural and transport parameters of cellophane membranes was made. Changes in the chemical structure and electrical behavior of cellophane membranes were considered by determining the hydraulic permeability, salt diffusion coefficient, and resistance values, as well as some geometrical parameters, for an untreated membrane and two differently UV-treated cellophane membranes. Differences in the characteristic parameters for the three samples showed that radiation mainly affected the membrane structure, while only small changes in membrane electrical behavior were determined.

INTRODUCTION

Electrolyte transport across cellulosic membranes such as cellulose acetate (CA), cellophane, or their derivatives has received a great deal of interest over the years (1–6). The influence of both chemical treatment and temperature on membrane structure and some characteristic parameters has also been reported (7–11). As a result of both treatments, slight changes in membrane porosity and electrochemical parameters were found (8–11), showing that chemical treatment has a clearer influence that thermal treatment.

In this work the effect of ultraviolet light (UV) on the transport parameters of a commercial cellophane membrane was studied. UV light can affect membrane structure in two different ways: 1) by providing cross-linking of the polymer chains and 2) by creating free radicals in the polymer. In order to detect both types of possible changes, hydrostatic and salt permeabilities as well as dielectric parameters have been measured for an untreated and two differently treated cellophane membrane samples (different UV light exposure time). From these experiments some characteristic parameters, such as the average hydrodynamic pore radii, the membrane resistance, and the salt diffusion coefficient (NaCl solutions), in the membranes could be determined, as well as the effect of treatment on geometrical or structural parameters (membrane thickness, degree of swelling, and fractional void volume). Structural and hydrodynamic results should also show the effect of UV light on membrane structure. Changes in the salt diffusion coefficient and resistance values are discussed as they relate of the expected chemical changes caused by UV radiation.

EXPERIMENTAL

Material

Cellophane sheets were supplied by Cellophane Española S.A. Membranes samples were cut to 4 cm width and 16 cm length. A set of four samples was exposed to UV light in an air-circulating artificial aging chamber which was provided with eight fluorescent lamps (40 W, 317 nm main radiation) at 40°C, in the way described in Ref. 12. Two different times of exposure to UV light were considered: 48 and 92 hours. Untreated samples were named CfU(1), samples exposed at UV light for 48 and 92 hours were designed CfT(2) and CfT(3), respectively. IR spectroscopy did not show any new vibration bands nor intensity changes as a result of UV light treatment. This means that there is no detectable creation of new functional groups in the material, which remains almost unaltered after UV light exposure.

Several geometrical parameters were determined for each membrane sample: dry and wet membrane thickness (δ^d and δ^w, respectively), fractional void volume (ϵ), and wet membrane density (ρ^w). Their values are shown in Table 1. The high swelling degree presented for these membranes agrees with that indicated for other commercial cellophane membranes (50 to 58% for Du Pont, or 45 to 50% for Avisco). Some geometrical differences resulting from the effect of UV light can be seen for the different parameters indicated above; the wet membrane thickness shows the clearest difference. These results are attributed to an increase of linking

TABLE 1
Geometrical Parameters: Dry (δ^d) and Wet (δ^w) Membrane Thickness, Fractional Void Volume (ϵ), and Wet Membrane Density (ρ^w) Determined for the Three Different Cellophane Membrane Samples

Membrane	CfU(1)	CfT(2)	CfT(3)
δ^d (m)	$(30 \pm 2) \times 10^{-6}$	$(29 \pm 1) \times 10^{-6}$	$(28 \pm 1) \times 10^{-6}$
δ^w (m)	$(61 \pm 3) \times 10^{-6}$	$(56 \pm 2) \times 10^{-6}$	$(52 \pm 2) \times 10^{-6}$
ϵ (%)	(0.55 ± 0.03)	(0.54 ± 0.03)	(0.51 ± 0.03)
ρ^w (g/cm^3)	(1.15 ± 0.04)	(1.13 ± 0.03)	(1.11 ± 0.03)

among the polymer chains after UV light exposure, most probably brought about by covalent bonds established through radicals.

Experimental Setup

Hydraulic Permeability

The experimental arrangement for measuring the hydraulic permeability was described elsewhere (13). A constant pressure method was used (14): the position of the air/water interface (y) in a capillary tube at one side of the cell was read at different times while keeping the water level in a vertical capillary tube at the other side of the cell constant. A series of measurements was made for each membrane at a constant temperature of 25°C. The pressure difference ranged between 20 and 45 cm of water for each series. All measurements were carried out with stirring to ensure the uniformity of the water temperature in each half-cell.

Salt Diffusion

Diffusion measurements were carried out in a cell system similar to that indicated in Ref. 15. The membrane was initially separating a concentrated constant solution (side 1) and a dilute concentration solution (side 2). Changes in the solution on side 2 were recorded versus time by means of a conductivity cell. Four different concentration gradients were considered (ΔC = 0.005, 0.01, 0.05, and 0.1 M) for the three cellophane membranes in order to see any influence of the concentration level on the salt diffusion values.

Electrical Impedance

The cell system is the same than that used in the diffusion experiments. A frequency response analyzer FRA (Solartron 1255), controlled by a computer and connected with the solutions in each half-cell via platinum electrodes, was used for impedance measurements. The experimental data were corrected by software for the influence of connecting cables and other parasitic capacitances as indicated in Ref. 16. The measurements were carried out using 100 different frequencies, which ranged between 10Hz and 10MHz, with different NaCl solutions for concentration ranging between 10^{-3} and 5×10^{-2} N.

RESULTS AND DISCUSSION

Plots of the position of the air/water interface (y) in the horizontal capillary tube versus time at different pressure gradients across the CfU(1) membrane are shown in Fig. 1. Similar plots were obtained with the two other membranes. From the slope of these straight lines, the volume flux through the membrane, J_v, can be obtained:

$$J_v = (1/S_{\mathrm{memb}})(dV/dt) = (S_{\mathrm{cap}}/S_{\mathrm{memb}})(dy/dt) \qquad (1)$$

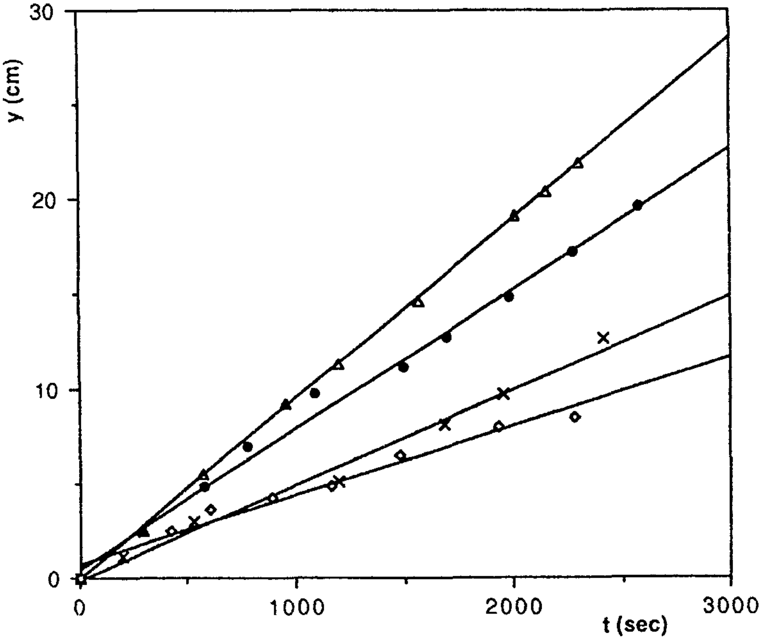

FIG. 1 Variation of the water/air meniscus position versus time for the CfU(1) membrane at different applied pressures: (△) 4500 Pa, (●) 3900 Pa, (×) 3000 Pa, (◇) 2400 Pa.

where S_{cap} and S_{memb} are the areas of the capillary tube and the membrane.

Figure 2 shows the volume flux versus the transmembrane pressure difference, ΔP, for the three samples. The membrane hydraulic permeability, L_p, is determined by the slope of these straight lines:

$$J_v = L_p \Delta P$$

The hydraulic permeability value for each membrane is shown in Table 2. From these results, and assuming for the membrane matrix a network of cylindrical pores whose directions are randomly distributed, the average hydrodynamic pore radius, r_H, is given by (13):

$$r_H = (24\mu\delta Lp/\epsilon)^{1/2} \tag{2}$$

r_H values for the three membranes are also indicated in Table 2. These results show the influence of UV light on membrane structure as a small decrease in the hydrodynamic radius for both treated membranes with respect to the untreated one.

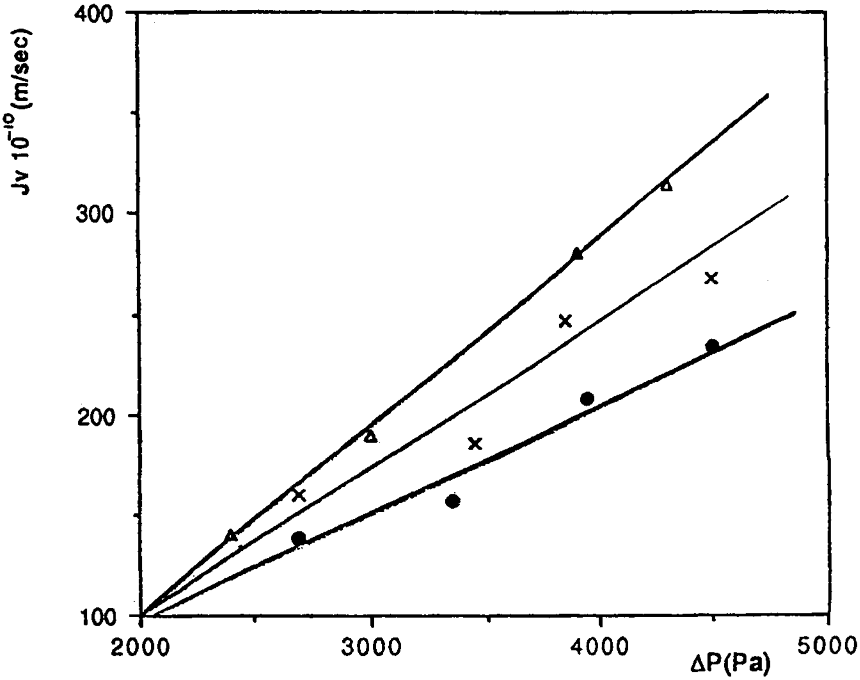

FIG. 2 Volume flux, J_v, as a function of the pressure difference, ΔP, for the different membrane samples: (△) CfU(1), (×) CfT(2), (●) CfT(3).

TABLE 2
Transport and Structural Membrane Parameters: Hydraulic Permeability (L_p), Average Hydrodynamic Pore Radius (r_H), Average Salt Permeability ($\langle P_s \rangle$), and Average Diffusion Coefficient ($\langle D_s \rangle$) for the Different Cellophane Membrane Samples

Membrane	CfU(1)	CfT(2)	CfT(3)
L_p (m³/s·Pa)	$(7.3 \pm 0.3) \times 10^{-10}$	$(5.4 \pm 0.2) \times 10^{-10}$	$(6.0 \pm 0.3) \times 10^{-10}$
r_H (m)	$(5.0 \pm 0.4) \times 10^{-9}$	$(3.8 \pm 0.3) \times 10^{-9}$	$(4.0 \pm 0.3) \times 10^{-9}$
$\langle P_s \rangle$ (m/s)	$(2.4 \pm 0.3) \times 10^{-6}$	$(2.1 \pm 0.2) \times 10^{-6}$	$(1.6 \pm 0.2) \times 10^{-6}$
$\langle D_s \rangle$ (m²/s)	$(2.7 \pm 0.4) \times 10^{-10}$	$(2.2 \pm 0.3) \times 10^{-10}$	$(1.6 \pm 0.3) \times 10^{-10}$

Variation of the conductivity (K_2) versus time in diffusion experiments for the untreated CfU(1) membrane at different NaCl concentration gradients is shown in Fig. 3. A comparison of the diffusion results for the three membranes at a given concentration difference (ΔC = 0.01 M) is presented in Fig. 4. According to Fick's first law, the salt flux (for a quasi-

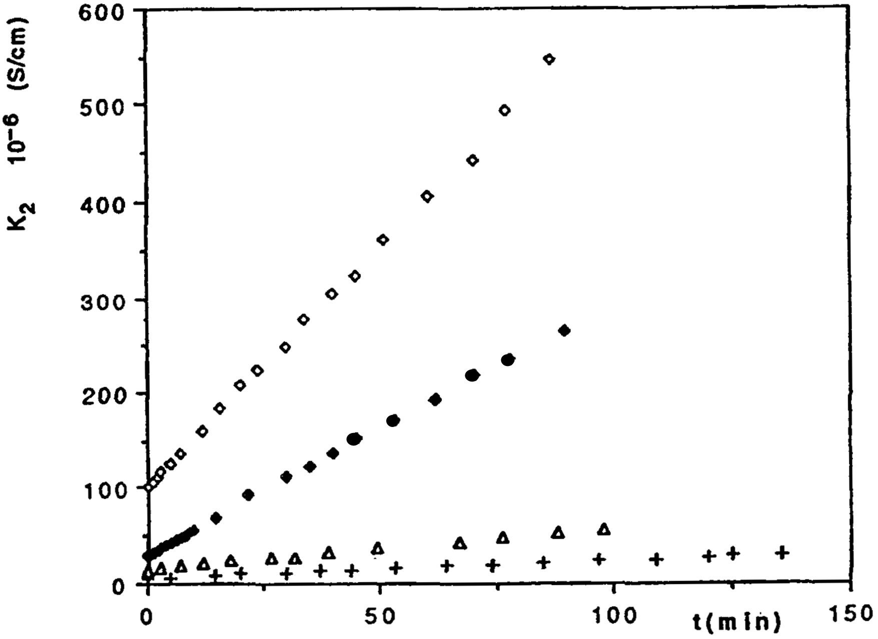

FIG. 3 Conductivity changes, K_2, versus time for the untreated CfU(1) membrane at different concentration gradients: (◇) ΔC = 0.005 M, (◆) ΔC = 0.01 M, (△) ΔC = 0.05 M, (+) ΔC = 0.1 M.

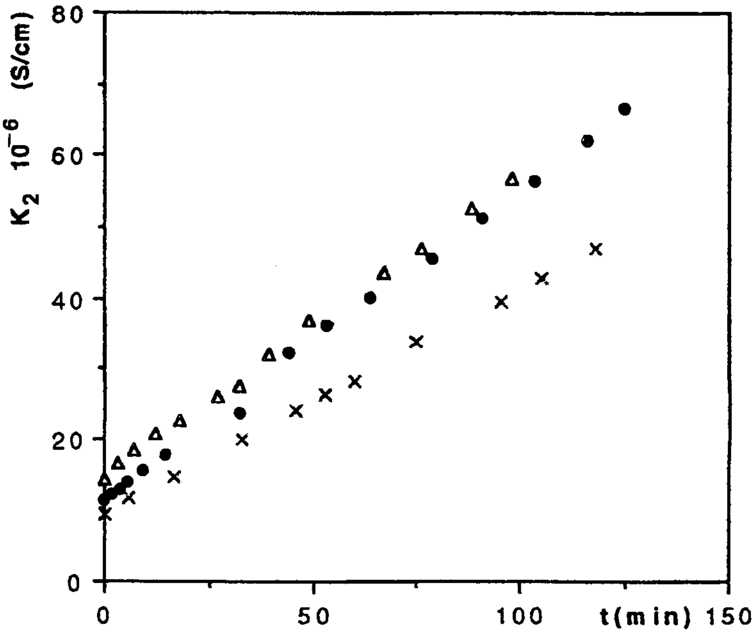

FIG. 4 A comparison of the conductivity changes, K_2, versus time for the three membrane samples at a given concentration gradient (ΔC = 0.01 M): (△) CfU(1) membrane, (●) CfT(2) membrane, (×) CfT(3) membrane.

steady state) can be written as

$$J_s = P_s(C_1 - C_2) = P_s/\delta \Delta C^{\text{ext}} \tag{3}$$

where J_s is the diffusive salt flux, P_s is the salt permeability in the membrane, and C_1 and C_2 are the external concentrations. The molar salt flux through the membrane (dn) at any given time is given by

$$J_s = (1/S)(dn/dt) = (V_0/S)(dC_2/dt) \tag{4}$$

where V_0 is the volume of solution at the side with concentration C_2. The following expression is obtained from Eqs. (3) and (4):

$$dC_2/dt = (S/V_0)P_s/(C_1 - C_2) \tag{5}$$

By means of Eq. (5) and from the slopes of straight lines such as those indicated in Figs. 3 and 4, the values of salt permeability for the CfU(1), CfT(2), and CfT(3) cellophane membranes were obtained. P_s results do not show any clear dependence on the concentration gradient, and their average values, $\langle P_s \rangle$, are indicated in Table 2. From these results the average salt diffusion coefficient across each membrane, $\langle D_s \rangle$, was determined by means of the following relationship:

$$\langle P_s \rangle = \langle D_s \rangle \epsilon / \delta^w$$

where ϵ and δ^w are the fractional free volume and the membrane thickness, respectively, which were previously determined. The average salt diffusion coefficients for each cellophane membrane are also shown in Table 2. The salt permeability values agree with those indicated in the literature for different cellophane membranes (5). The decrease of the salt diffusion coefficient values found for both treated membranes with respect to the untreated one [20% for CfT(2) and 40% for CfT(3)] agree with the results obtained for hydraulic permeability, and indicate more clearly the influence of UV treatment on membrane structure.

Figure 5 (a and b) shows impedance plots ($-Z_{\mathrm{img}}$ vs Z_{real}) obtained by impedance spectroscopy measurements with the three cellophane samples at a given NaCl solution. Similar plots were obtained with the other concentrations studied. Analysis of the a.c. data is usually carried out by a complex plane method which involves plotting the impedance imaginary part (Z_{img}) versus the real part (Z_{real}). When plotted on a linear scale, the equation for a parallel resistance-capacitor (RC) circuit gives rise to a semicircle in the Z^* plane (similar to each of those shown in Fig. 5) which has intercepts on the Z_{real} axis at R_∞ ($\omega = \infty$) and R_0 ($\omega = 0$), where ($R_0 - R_\infty$) is the resistance of the system (17). The maximum of the semicircle equals $0.5(R_0 - R_\infty)$ and occurs at frequency ω ($\omega = 2\pi f$) such that $\omega RC = 1$, where RC is the relaxation time.

In all cases the experimental impedance values were fitted to a circuit which consists of a series association of two RC elements; one of them corresponds to the membrane (low frequencies) and the other to the electrolyte solution (high frequencies); $(R_eC_e) - (R_mC_m)$, as is also indicated in Fig. 5(a). Analysis of the impedance curves by means of a nonlinear program (18) permits us to determine directly both the resistance and capacitance values at the different concentrations studied. Quite good agreement between experimental and calculated values were obtained in all cases (error intervals lower than 8%). For the electrolytes, the calculated parameters R_e and C_e are consistent with previous values obtained for electrolyte impedance results (without any film in the cell).

The concentration dependence on R_m values for the three cellophane membranes is shown in Fig. 6. As the result of UV light treatment, a slight decrease of R_m values was obtained, which might be due to the presence of some new free radicals on the polymer chains. From this picture, and for the three cellophane samples, the strong effect of the concentration

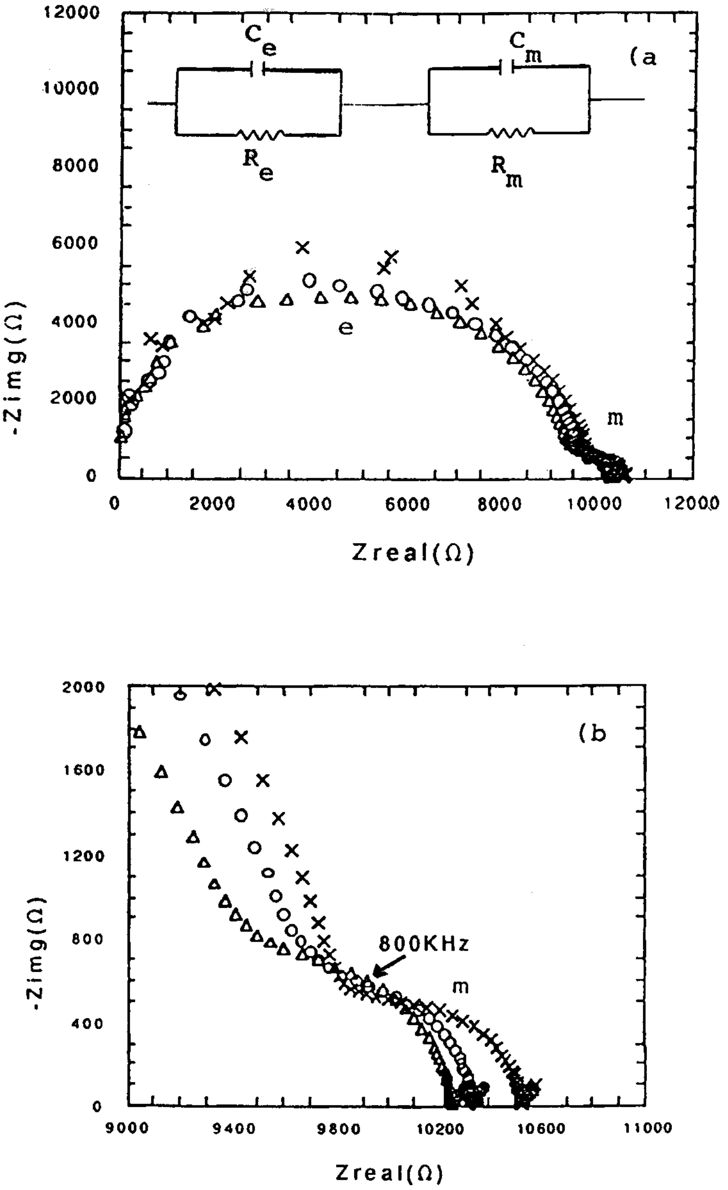

FIG. 5 Impedance curves for the three membrane samples at a given concentration (C = 0.005 M): a) equivalent circuit and the experimental points for the whole membrane/electrolyte system; b) amplification for the membrane contribution. (×) CfU(1) sample, (○) CfT(2) sample, (△) CfT(3) sample.

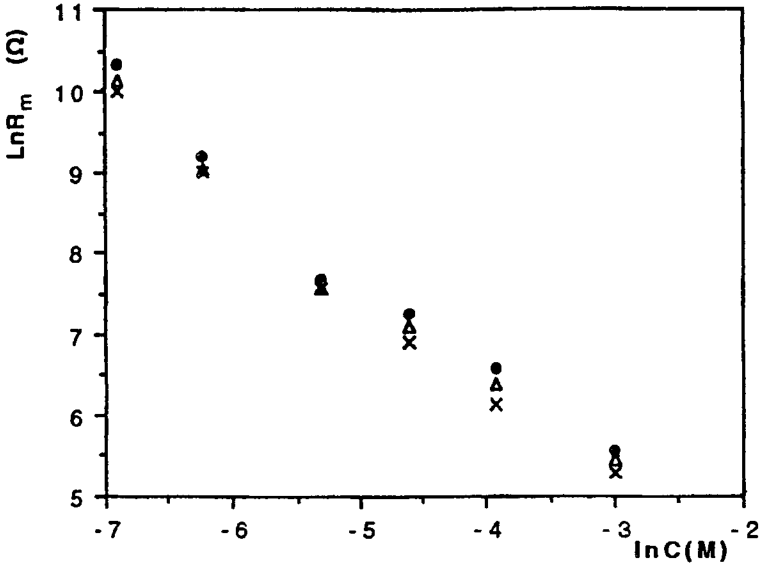

FIG. 6 Membrane resistance values versus salt concentration for the three membrane samples: (●) CfU(1) membrane, (△) CfT(2) membrane, (×) CfT(3) membrane.

on the resistance values, which is due to electrolyte invasion into the polymeric matrix (19, 20) can also be seen.

In conclusion, we can state that there are two kinds of effects by UV light on the matrix structure of cellophane membranes: 1) a change in the packing of the polymer chains, which results in a decrease of membrane swelling and the hydrodynamic and diffusion parameters; and 2) a slight decrease of the electrical resistance value as a result of some chemical changes in the polymer chains.

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