

Swelling and Diffusion Properties from Elongation of Two-Phase Polymer Membranes

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Synopsis

Experimental results were presented dealing with the water permeance and diffusion rate in two-phase membranes consisting of hydrophilic domains of polyacrylic acid chemically bound by grafting to hydrophobic matrices: these are either rigid crystalline (polypropylene) or elastomeric amorphous (EPDM). Permeance is higher in rigid matrices: this is attributed to the wide net of microfractures originated from swelling of the hydrophilic domains whose formation is only possible in the case of a rigid matrix. A calculation method was proposed, which allows the evaluation of the apparent diffusion coefficient of both water and salt, starting from dilatometric measurements of membranes contacted with water and salt water. The apparent diffusion coefficient of water in rigid membranes is of the order of $10^{-8} \text{ cm}^2 \text{ sec}^{-1}$, whereas in elastomeric membranes it appeared about 100 times lower. The apparent diffusion coefficient of salt is of the order of $10^{-12} \text{ cm}^2 \text{ sec}^{-1}$ for both rigid-matrix and elastomeric membranes when previously swollen.

INTRODUCTION

Different heterophasic membranes from hydrocarbon polymers modified by grafting with different hydrophilic monomers were previously prepared in this Laboratory. We especially studied membranes from polyacrylic acid (PAA) grafted on polypropylene (PP)¹⁻³ and from PAA grafted on EPDM elastomers, crosslinked after making the film.⁴

In this paper we report on the kinetics of elongation, due to water and salt water adsorption, of films consisting of PAA domains regularly distributed in a polyhydrocarbon matrix; they differ in the physical nature of the matrix, which is either crystalline or elastomeric.

The different mobility of hydrocarbon macromolecules is important for the determination of water transport properties within the films and the elongation rate, which is much lower in the case of films with elastomeric matrices.

The reasons for the different behavior of the two films are discussed here on the basis of their mechanical properties and an equation is given relating elongation to the diffusion rate of water, from which the diffusion coefficient can be obtained.

EXPERIMENTAL

Preparation of Membranes with Polypropylene Matrix

Grafted polymers were prepared in the homogeneous phase at a temperature above 120°C by addition of acrylic acid to a PP solution in *o*-dichlorobenzene, using benzoyl peroxide as an initiator.⁵ After grafting, the solution consisting

of solvent (90–95 wt %), grafted PP, small amounts of unreacted PP and PAA homopolymer was formed into a film¹ at 120°C by introducing a preheated glass cylinder. It was then extracted and left in the thermostat for a few minutes to allow partial evaporation, and then immersed and stored in water to allow complete precipitation and removal of PAA homopolymer which in our conditions involves the formation of some porosity. Within limits, the membrane thickness could be adjusted (from 1 to 40 μm) depending on both the solution viscosity and cylinder extraction rate.

The average size of the PAA domains determined on sections by transmission electron microscope was of about 500 Å. The frequency of the domains varied depending on the percent of grafted PAA. The membranes used had grafted PAA contents of 33 and 46 wt %, respectively.

Preparation of Membranes with an Elastomeric Matrix

The elastomer (EPDM) had the following molar composition: ethylene, 57.8%; propylene, 41.2%; and 5-ethyliden-2-norbornene, 1%. EPDM was grafted at 80°C with acrylic acid in a toluene solution, by using benzoyl peroxide as an initiator.⁴

The polymer solution was formed into a film by a Gardner blade on glass plates and the solvent was removed by evaporation.

The film was subsequently crosslinked at room temperature after swelling in *n*-butyl acetate by means of S_2Cl_2 dissolved in the same solvent^{4,6}; this was necessary to obtain good mechanical properties.

After evaporation of *n*-butyl acetate, the membranes were plunged into water for storage in order to dissolve PAA homopolymer.

The amount of grafted polyacid in the samples was 24% and 33% by weight. The average size of the PAA domains, even for such grafted polymers, was about 500 Å.

Linear Dilatometric Measurements

The length of the membrane, initially conditioned in air in a thermostated room (23°C, 50% relative humidity) kept in a vertical position between the clamps of a dynamometer⁷ and extended, but not subjected to external stresses, was measured as a function of the hydration time, starting from the moment of its contact with water at 23°C. Rectangular test pieces, 1.25 cm wide and 6 cm long, obtained by die cutting, were used. Zero stress was maintained at any moment during the elongation. The control was made with strain gauges connected to a Hottinger bridge; elongation was measured with a comparator with an accuracy of 5 μm . The membrane thickness were evaluated with $\pm 0.5 \mu\text{m}$ accuracy.

Resistance of the Limit Layer in the Water Transport Process: System Liquid-Membrane-Air

Fixed flows of anhydrous air were caused to pass continuously on one surface of the membrane (7 cm^2), with radial direction from the center to the borders. The other surface made contact with water at atmospheric pressure. The rate of permeated water was measured volumetrically in the liquid phase.

RESULTS AND DISCUSSION

Considerable water fluxes can be obtained by using membranes of PP grafted with PAA in ultrafiltration operations under pressure;¹⁻³ however, under the same conditions, membranes of EPDM grafted with PAA do not allow any flux.⁸

Membranes with an elastomeric matrix show some permeance to liquid water and to vapor at atmospheric pressure, which, however, is slightly lower than that of membranes with rigid matrix.⁸ Flux through a membrane depends on the sum of external resistances and of that offered by the membrane itself⁹; it is essentially controlled by the highest resistance. The transport properties of the two membranes may be related to the resistance of the limit layers and the membrane resistance to flux, which depends on both porosity and the diffusion coefficients.

In the case of very porous membranes, the highest resistance is from limit layer, whereas this does not happen with compact or scarcely porous membranes. For a qualitative evaluation of the importance of porosity on the basis of such a criterion, pervaporation tests were conducted (Fig. 1). While the permeance of elastomeric membranes (amount of water passing through per unity of time, surface and driving pressure) is independent of the dry air flow, that of rigid-matrix membranes increases to a considerable extent by increasing the dry air flow. This proves that in rigid-matrix membranes resistance to flux depends essentially on the solid-gas interface, which indicates that the membrane is extensively porous. Elastomeric membranes already behave at atmospheric pressure as if they were compact or slightly porous.

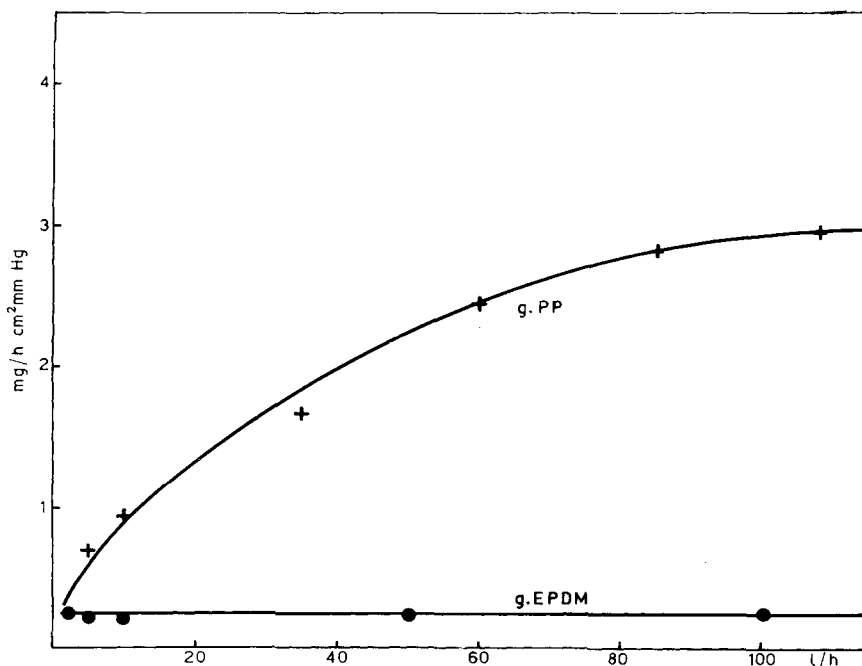


Fig. 1. Water permeance vs dry air flows measured at 23°C and at 1 atm, of a membrane of polypropylene grafted with 52% PAA and having thickness 11 μm (g PP) and of a membrane of EPDM grafted with 33% PAA and having thickness 35 μm (g EPDM).

MODEL OF THE SYSTEM

On the basis of the structure detected by electron microscopy¹ and from measurements of permeance, ultrafiltration,^{2,8} and pervaporation, we set up a model capable of explaining most of the properties of these two-phase membranes. The model consists of PAA elastic spheres regularly dispersed in a rigid or elastomeric matrix. In contact with water, hydration causes swelling, which may generate microfractures extended to the whole sample only in the case of a rigid matrix, due to its high elastic modulus which is responsible for very high stresses.

In a previous work,¹⁰ by adopting the classical theory of elasticity, we investigated the strains and stresses around one single spherical hydrophilic domain, which may be swollen by water and which is present in a hydrophobic matrix. A system of two equations was obtained,

$$\frac{\Delta L}{L_A} = \left[k - 1 - \frac{pk}{3K_1} - \frac{p}{4G_2} \left(1 - \frac{1}{(1 + a_0/R_A)^2} \right) \right] \left(1 + \frac{a_0}{R_A} \right)^{-1} \quad (1)$$

and

$$\Delta L/L_A = (\phi/3)(T - p/K_1) \quad (2)$$

where ΔL is elongation by swelling of the distance L_A between the center of the spherical domain of radius R_A and a generic point of the surrounding matrix ($L_A = R_A + a_0$) (Fig. 2); $T = \Delta V_A/V_A$ is the specific volume variation of the anhydrous sphere by hydration, k is an index related to T : $k = (1 + T^{1/3})$; K_1 is the bulk modulus of PAA; G_2 is the shear modulus of the matrix; p is the pressure at the sphere-matrix interface; and ϕ is the fraction by volume of anhydrous PAA in the initial system.

By solving the above equations, one obtains in the elastic field the strain and pressure at the interface as a function of swelling T . The results we obtained from the calculations carried out with PAA, respectively, in PP and EPDM matrix are shown in Figure 3. The parameters used were $a_0/R_A = 0.37$, $\phi = 0.4$, $K_1 = 100,000 \text{ kg/cm}^2$, $G_2 = 10,500$ and 1 kg/cm^2 for PP and EPDM, respectively.

As may be seen, yield pressure in the case of PP is reached with very slight swelling; on the contrary, the pressures that arise in the elastomeric matrix are very low even with much greater swelling and hydration being the same, elongations are higher.

Actual elongations of membranes from grafted PP (Fig. 4) are much higher than those calculated at the yield limit: this indicates that the formation of nucleated microfractures from spherical domains may occur. In elastomeric membranes, however, the pressure generated at the interface is not high and the formation of microfractures is unlikely.

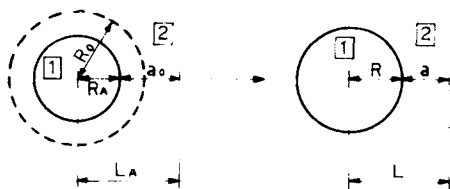


Fig. 2. Geometry of deformation of a hydrophilic domain 1 immersed in a hydrophobic matrix 2.

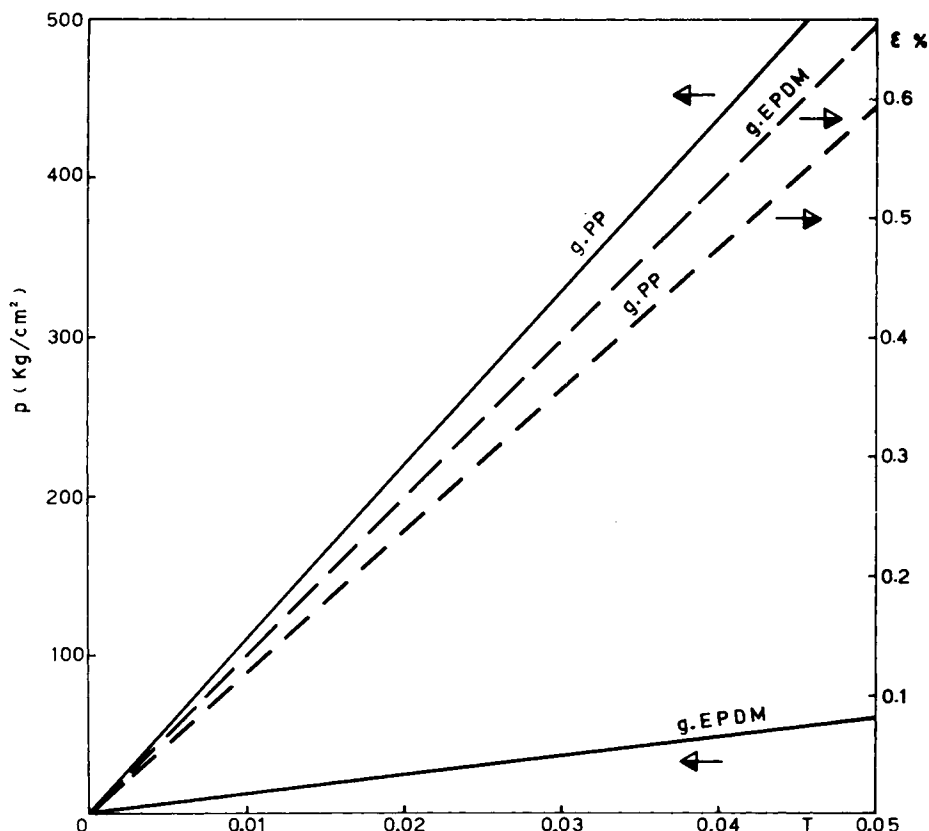


Fig. 3. Sphere-matrix interface pressure p (full line) and percent elongation $\epsilon\%$ (dashed lines) vs the swelling ratio T for models of grafted membranes with rigid matrix (g PP) and with elastomeric matrix (g EPDM) obtained through eqs. (1) and (2) by the parameters given in the text.

DILATOMETRIC BEHAVIOR

The percent elongation of membranes, previously conditioned at 23°C and at a relative humidity of 50%, depends on the contact time with water or salt water (3.5% NaCl).

In this respect, membranes show a quite different behavior depending on whether the matrix is rigid or elastomeric. The behavior of a rigid-matrix membrane (PP) in the first hour of contact with the diffusing liquid is shown in Figure 4. A very rapid elongation is observed both in the case of water hydration and in contact with a saline solution. While with the saline solution the percent elongation is higher and continues with time (26% after 72 hr for the sample in Fig. 4), in the case of water, elongation maintains the value initially attained.

Figure 5 shows the behavior of membranes with an elastomeric matrix of similar composition and domain structure under the same conditions: elongation is much slower than in the previous case and in this case too, it is higher in the presence of the saline solution.

Figure 6 shows the percent elongation $\epsilon\%$ and the initial rate of deformation of membranes with an elastomeric matrix with different values of thickness. The latter reacts inversely to thickness. Membranes with a rigid matrix behave in a quite different manner: the percent elongation in the range of thicknesses

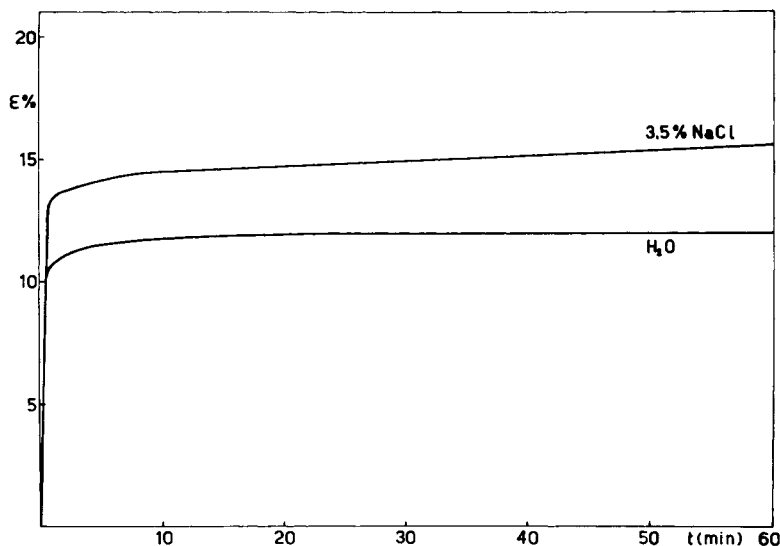


Fig. 4. Percent elongation $\epsilon\%$ vs contact time with H_2O and a 3.5% NaCl solution for membranes of PP grafted with 33% PAA and having thickness $16\ \mu m$.

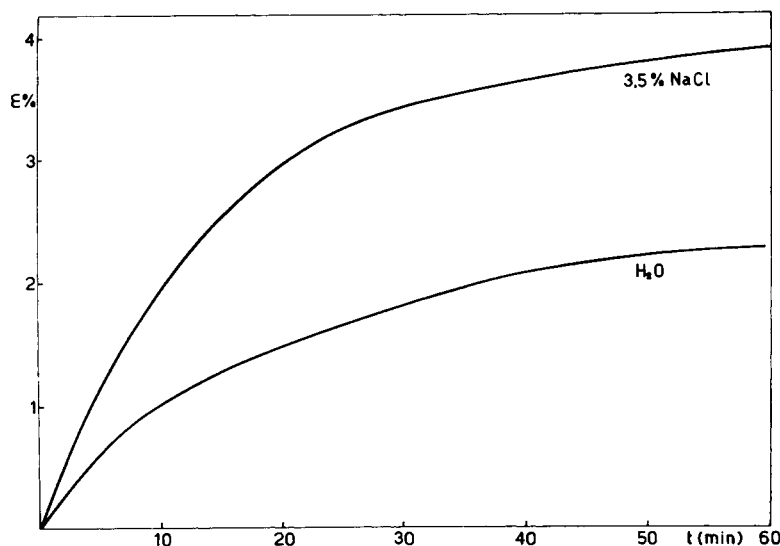


Fig. 5. Percent elongation $\epsilon\%$ vs contact time with H_2O and 3.5% NaCl solution for membranes of EPDM grafted with 24% PAA and having thickness $45\ \mu m$.

considered (between 8 and $20\ \mu m$) at constant PAA percentage reaches values that are very close to one another and the initial rates of deformation are very similar ($d\epsilon/dt \approx 20\ min^{-1}$).

Since swelling depends on the hydration of the hydrophilic domains, this agrees with the existence of a porous structure in the membranes with a rigid matrix and of a more compact structure in the elastomeric ones.

Membranes with a different matrix also show a different behavior on drying. Drying was carried out by leaving membranes on the dynamometer in air at $23^\circ C$ and at a relative humidity of 50%. As a matter of fact, shortening of elastomeric matrix membranes is slow and continuous, while the rigid ones show a rapid

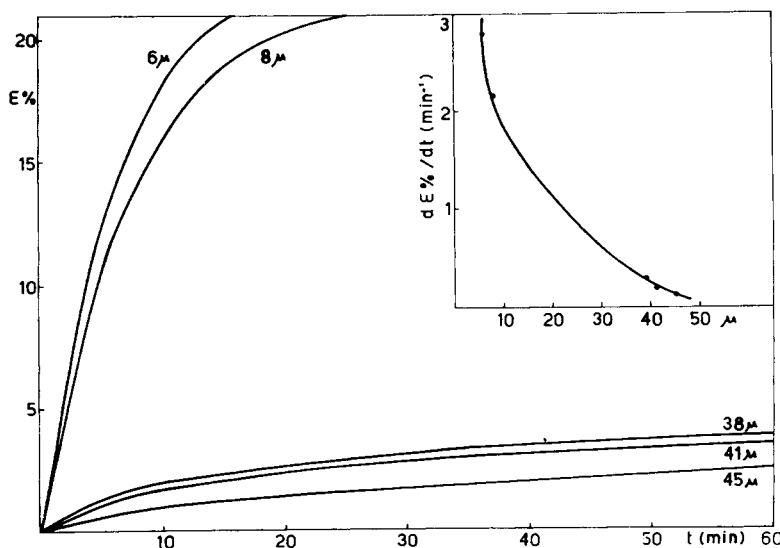


Fig. 6. Percent elongation $\epsilon\%$ vs contact time with H_2O for membranes of EPDM grafted with 24% PAA (8, 41, and 45 μm) and with 33% PAA (6 and 38 μm). Initial elongation rates vs membrane thicknesses are shown in detail.

initial contraction followed by a slow one. Rapid contraction corresponds to an easy water outlet through the microfractures, while the slow shortening may correspond to the higher resistance to diffusion offered by the tightening microfracture.

EFFECTS OF SODIUM CHLORIDE

Sodium chloride¹¹⁻¹³ causes the extension of polyacrylic acid chains; hence, membrane swelling is higher in salt water than in water (Figs. 4 and 5). Another interaction is due to ion exchange:



though this is of little importance from the quantitative point of view.¹⁴

Swelling membranes with pure water first and later with salt water offered the following results: if the saline solution contacts the membranes after their swelling by water and approach equilibrium, swelling and further specific elongation are observed (Fig. 7), which is slow even in the case of PP rigid membranes. This is obvious since the process is now governed by the diffusion rate of sodium chloride in the hydrophilic domains only. If salt water is directly put in contact with rigid-matrix membranes, we initially observe a rapid swelling due to the adsorption of the solution through the microfractures followed by a slow and continuous swelling caused by the diffusion of sodium chloride and by its interacting with the polyacid (Fig. 4).

In the case of elastomeric matrix membranes, swelling is more extensive and more rapid with the saline solution than with water (Fig. 5); in any case, it is always much slower than in the case of a porous matrix. The structure of the material controls swelling processes whether the penetrating liquid is water or salt water: the higher swelling rate of PP membranes must be attributed to the existence of permanent porosity.

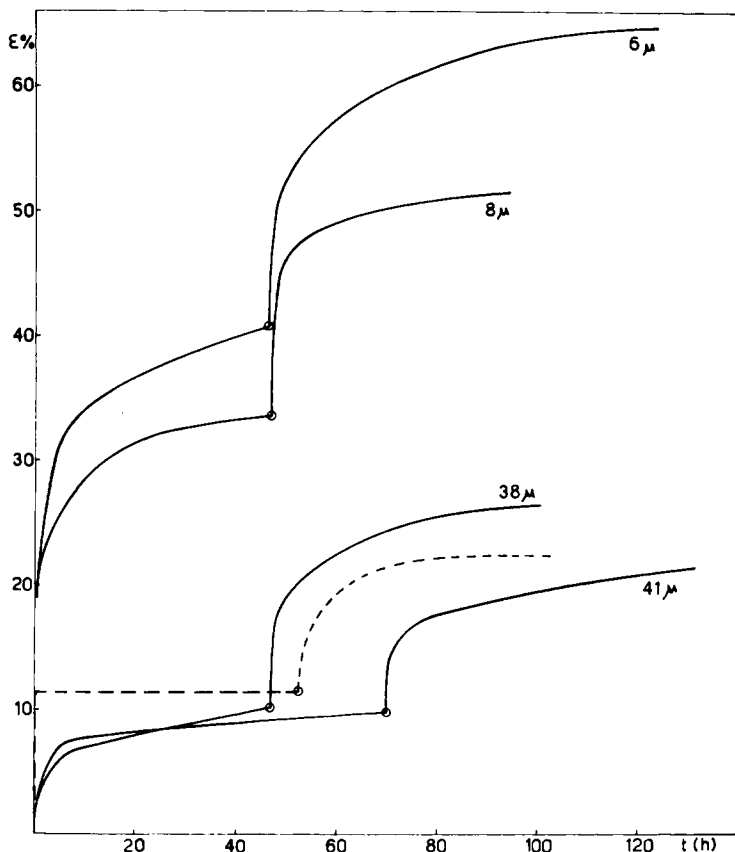


Fig. 7. Percent elongation $\epsilon\%$ vs contact time with H_2O and (O) with 3.5% NaCl solution, for membranes of EPDM grafted with 24% PAA (8 and 41 μm) and with 33% PAA (6 and 38 μm). The dashed curve refers to a membrane of PP grafted with 33% PAA and having thickness 11 μm .

DIFFUSION RELATED TO ELONGATION

Our membranes must be considered as isotropic with their structure consisting of homogeneously distributed domains.

Hence elongations may be correlated to the volume increase according to the equation

$$3\epsilon = 3\Delta l/l_0 = \Delta v/v_0 \quad (4)$$

where l_0 and v_0 , respectively, are the initial length and volume of the membrane at a prefixed temperature, pressure, and humidity. It allows one to determine the volumetric swelling connected with hydration by simple linear dilatometric measurements. The volume variation of the membrane is caused by the swelling of the hydrophilic domains as well as by the elastic deformations, consequent to hydration, acting on both hydrophilic domains and matrix. It may be generally written

$$\Delta v = \Delta v_H^{(1)} + \Delta v_{el}^{(1)} + \Delta v_H^{(2)} + \Delta v_{el}^{(2)} \quad (5)$$

where 1 and 2, respectively, are the hydrophilic and hydrophobic phases, H is hydration and el denotes elastic.

Given the hydrophobicity $\Delta v_H^{(2)} = 0$, in a proportional elastic range¹⁵ one ob-

tains $\Delta v_{el}^{(2)} = 0$ and hence the volume variation is exclusively that of the hydrophilic phase

$$\Delta v = \Delta v_H^{(1)} + \Delta v_{el}^{(1)} = \Delta v^{(1)} \quad (6)$$

Out of the proportionality field, when microfractures are present in the hydrophobic material 2 (PP membranes) or when the system 2 is elastomeric, it may be assumed that $\Delta v_{el}^{(1)}$ is small in respect to $\Delta v_H^{(1)}$. On the basis of this approximate hypothesis it will be

$$\Delta v \simeq \Delta V_H^{(1)} \quad (7)$$

both for a crystalline and for an elastomeric matrix. This equality, joined with the hypothesis put forth concerning the volume additivity in the PAA and water mixture and with equality (4), allows one to draw a correlation between elongation and liquid entered in the membrane. In the case of water (density one), by calling M_0 the water volume initially present in the sample, within the limits of the previous hypotheses one obtains

$$v_0 = M_0 + v_0^{(1)} + v_0^{(2)} = M_0 + \text{const} \quad (8)$$

and even

$$3\epsilon = 3\Delta l/l_0 = \Delta v_H/v_0 = \Delta M/v_0 \quad (9)$$

By integrating the differential equation

$$3d \ln l = d \ln(M + \text{const}) \quad (10)$$

where M is the water volume present in the film with length l between the limits l_∞ and l , where l_∞ corresponds to the equilibrium length of the membrane (at infinite time), one obtains

$$l/l_\infty = [(M + \text{const})/(M_\infty + \text{const})]^{1/3} \quad (11)$$

This equation also holds in the case of one-phase membranes, provided that the volume variation of elastic type is negligible. It could, thus, be possible to calculate the true diffusion coefficient of a liquid into one-phase membrane starting from dilatometric measurements, knowing the correlations among the amount of liquid adsorbed from a sheet at time t , the time, the diffusion coefficient and the thickness. The boundary conditions are: at time zero, the concentration of water at any point of the membrane is uniform (equilibrium humidity); during the whole hydration time, the concentration of water on the side surfaces of the film is constant. If M_t is the volume (or mass) of water entered into the membrane at time t from the very moment of its contact with water, and M_∞^* is the water volume entered after an infinite time, according to the Fick equation, one obtains¹⁶

$$\frac{M_t}{M_\infty^*} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-D(2n+1)^2\pi^2 t}{4s^2}\right) \quad (12)$$

if the film diffusion coefficient D and the thickness s are constant. According to Matano,¹⁷ thickness variation could be accounted for; its importance is negligible at least in the early hydration times, when eq. (12) becomes

$$M_t/M_\infty^* = 4(t/s^2)^{1/2}(D/\pi)^{1/2} \quad (13)$$

If R_0 is the initial gradient of the absorption curve $R_0 = d(M_t/M_\infty^*)/d(t/s^2)^{1/2}$, one obtains¹⁸

$$D = (\pi/16)R_0^2 \quad (14)$$

By plotting the experimental curves l/l_∞ as a function of $(t/s^2)^{1/2}$ the slope may be easily measured. By a few simple calculations, one obtains

$$R' = \frac{dl/l_\infty}{d(t/s^2)^{1/2}} = \frac{1}{3} \frac{l}{M + \text{const}} \frac{M_\infty^*}{l_\infty} \frac{d(M_t/M_\infty^*)}{d(t/s^2)^{1/2}} \quad (15)$$

At the absorption start (index 0) we have, according to (8),

$$R'_0 = (1/3)(l_0/l_\infty)(M_\infty^*/v_0)R_0 \quad (16)$$

Since $M_\infty^*/v_0 = 3(l_\infty - l_0)/l_0$ finally results in

$$D = \frac{\pi}{16} R_0'^2 \frac{1}{(1 - l_0/l_\infty)^2} \quad (17)$$

From the above calculation scheme it is possible to obtain only apparent diffusion coefficients, in the case of two-phase membranes, its validity being limited to homogeneous systems characterized by diffusion coefficients independent of thickness. Furthermore, the presence of microfractures in PP membranes is another reason that the obtained D coefficients are only apparent ones. We calculated the apparent diffusion coefficient by elaborating the data shown in Figures 4–6 as well as other data obtained from runs not reported here. The water diffusion coefficient was thus found to be of the order of $10^{-8} \text{ cm}^2\text{sec}^{-1}$ for grafted polypropylene membranes and lower by about 100 times for membranes with an elastomeric matrix. What has been found for PP membranes agrees with literature data¹⁹ for diffusion coefficients of liquids in polymers, and the findings related to the elastomeric matrix evidences a much lower permeability. This is in agreement with the hypothesis put forth concerning the presence of extended microfractures in the whole rigid matrix: in compact hydrophobic matrices, the diffusion coefficient should be quite small. The deduction is also possible that a limited porosity should exist in elastomeric membranes. Under pressure, such a porosity disappears due to the rubber compressibility and water fluxes becoming negligible.

We calculated the apparent diffusion coefficient of NaCl by the method described above using the data obtained on water swollen membranes under conditions close to equilibrium in water (Fig. 7).

It is interesting that D of NaCl results in an order of magnitude of $10^{-12} \text{ cm}^2 \text{ sec}^{-1}$ in both polypropylene and elastomeric membranes; the diffusion rate governing process is salt diffusion inside the PAA domains. NaCl diffusion is much slower than the water diffusion from the membrane outer surface to the domains, in both microfractured and nonmicrofractured structures. This justifies the use of polyacrylic acid in the salt-water hyperfiltration process.

CONCLUSIONS

Experimental results concerning the permeance and diffusion rates of water within two-phase films consisting of hydrophilic domains chemically bound to hydrophobic matrices either rigid crystalline or elastomeric amorphous were presented. Permeance is higher in the case of rigid matrix due to the wide net of microfractures originating from swelling the hydrophilic domains, possible only in the case of a rigid matrix.

A calculation method has been described which allows the evaluation of the apparent diffusion coefficient of both water and salt, starting from dilatometric measurements.

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