Porosity of membranes consisting of hydrophilic domains in a hydrophobic matrix

M. Pegoraro and A. Penati
Istituto di Chimica Industriale, Politecnico, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
and P. Clerici
Istituto di Ingegneria Meccanica, Politecnico, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
(Received 13 January 1977)

Vapour adsorption curves of water for poly(acrylic acid) (PAA) grafted onto polypropylene (PP) show a larger water uptake for membranes than for moulded samples. Both adsorptions are higher than that calculated for the water dissolved by adsorption in the PAA alone. This shows the existence of porosity, which was confirmed by permeance and ultrafiltration tests. Porosity can be related to microfractures in the PP matrix caused by the swelling of PAA domains. A simplified mechanical model of the system based on the stress analysis of a sphere which swells in a rigid matrix, shows the possibility of microfracture formation.

INTRODUCTION

Recently methods have been described[1–3] for the preparation of grafted films consisting of a water-insoluble hydrophobic backbone polymer with a hydrophilic polymer chemically bound to it.

Films formed from the grafted polymer solution directly after the chemical reaction show a structure consisting of regularly distributed spheroidal domains of the type shown in *Figure 1* (replica of the surface). Such films are fairly permeable to water both in the liquid and in the vapour state (*Table 1*) and may be conveniently used for ultrafiltration[4], but are not convenient for desalination[3]. These results are consistent with the existence of a microporous structure which can stop large molecules, but not all the small ones. We report in this paper some experimental water-adsorption measurements which indicate that these systems are porous. In general, microporosities are shown to arise from the internal stresses set up in a stiff matrix by the swelling of the hydrophilic domains regularly dispersed in it.

EXPERIMENTAL

The investigations described deal with poly(acrylic acid) (PAA) grafted onto polypropylene (PP). Grafting was carried out in the homogeneous phase[5] by dissolving isotactic PP in *ortho*-dichlorobenzene at 120°C and adding benzoylperoxide and acrylic acid. Membranes were obtained by evaporation of the reacted solution at 120°C; the membrane varied from 1 to 50 μm according to the operating conditions. Membranes were stored in water, in which the homopolymer formed in the reaction was soluble. By transmission electron microscopy the structure was shown to consist of spheroidical domains regularly disposed in a matrix.

In order to obtain the adsorption curves a pack of membranes was placed in a controlled environment with humidity regulated by the presence of sulphuric acid solutions at 25°C, according to ASTM E 104 51 (method B). Membranes were weighed in this environment. The zero humidity condition was obtained with P_2O_5. The order of carrying out the measurements was from saturation down to dryness. An illustrative equilibrium curve, referring to a sample containing 21% of grafted PAA, is plotted in *Figure 2*, (curve A). Samples having different amounts of grafted PAA show similar behaviour.

The same membranes were compression moulded (50 kg/cm^2) at 170°C for 5 min into discs 1 cm in diameter and 1 mm thick. Adsorption curves for the moulded polymer are shown in *Figure 2* (curve B). About one year was needed to obtain both equilibrium curves. The contact angle of water on the grafted membranes was measured in a conditioned room (23°C and 50% r.h.) by use of a telescope.

DISCUSSION

Comparison of the equilibrium adsorption curves and the adsorption (*Figure 2*, curve C) due to poly(acrylic acid) alone, obtained from the data of Thompson Hughes and Fordyce[6] by multiplying their values by 0.21 (% amount of polymeric acid in the sample examined), shows that the amount of water adsorbed in the three cases is quite different. Similar behaviour had already been observed by Lonsdale, Merten and Riley[7] for hydrophilic materials used as asymmetric membranes and moulded sheets of cellulose acetate. These authors attributed the difference to the water condensed in the capillary pores.

Tankard[8] made a distinction between solvation and non-solvation water for the water adsorbed by organic polymers. Shporer and Frommer[9] found by n.m.r. investigations that

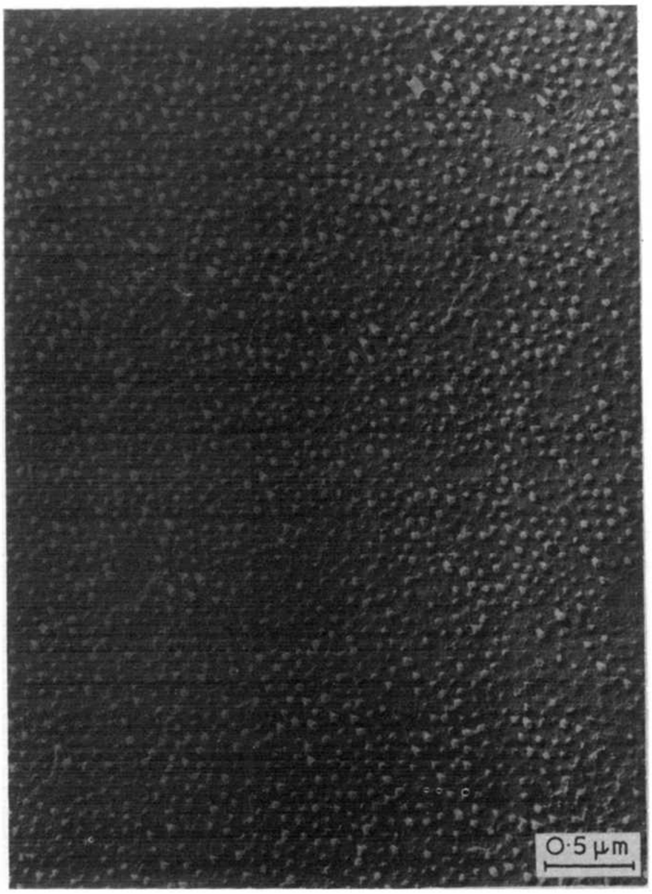

Figure 1 Surface replica of a PP membrane with 57% w/w grafted PAA

Table 1 Liquid and vapour permeance (mg H_2O h^{-1} cm^{-2} $mmHg^{-1}$) for membranes of grafted PP; T = 23°C

PAA grafted (%)	Thickness (μm)	Liquid permeance	Vapour permeance
26	15	5.7×10^{-2}	2.5×10^{-2}
40	8–10	6.3×10^{-2}	2.8×10^{-2}
41	25–40	7×10^{-2}	3.3×10^{-2}
43	3–6	8.3×10^{-2}	4.8×10^{-2}
52	8–15	11×10^{-2}	6.7×10^{-2}
57	2–6	14×10^{-2}	7.1×10^{-2}

two types of 'water' exist in the porous membranes of cellulose acetate, one 'bound' to the membrane and one free; they also found that bound water predominates in compact membranes.

Interpretation of the present results is more difficult because polypropylene is hydrophobic. The measured contact angle between water and a polypropylene film was 100° and that between water and the grafted polypropylene containing 21% of PAA was 30°. This result justifies the capillary condensation for water activities less than 1. The difference between the weight of water adsorbed in the samples and the weight of water calculated according to Thompson Hughes and Fordyce[6] should be considered as free water.

If we suppose the material to be homogeneous we can calculate the diameter and the distribution of pore diameters according to the equation[10,11]:

$$\ln \text{r.h.} = -\frac{V}{RT}\,\frac{2\gamma}{r}\cos\theta \qquad (1)$$

which relates the value of the radius r below which pores are filled by condensed water to relative humidity r.h.; V is the molar volume of water, γ its surface tension, and θ is the contact angle.

A distribution can be obtained if we know at each r.h. the volume of free water condensed in the pores. This is obtained by subtracting curve C from curve A of *Figure 2* and gives the volume of pores having radius less than or equal to the value of r filled by water according to equation (1). This is clearly an approximate calculation since it assumes circular pore sections and the same angle θ in the pores as that measured on large PAA and PP domains. These calculations give the integral distribution curve (*Figure 3*) and it should be noted that most pores show equivalent radii ranging from 3 to 20 Å.

We found[4] experimentally that sodium alkylbenzene sulphonate can be completely rejected by these membranes when present in a concentration higher than the critical one at which micelles are formed. Mankovich[12] estimated the micelles' average diameter to be 48 Å.

Curve B of *Figure 2* for the moulded material shows a porosity which is obviously lower than that of the membranes. This was not observed in more homogeneous materials such as cellulose acetate[7], which do not contain domains of different chemical nature from that of the matrix which, by swelling, may cause microfractures.

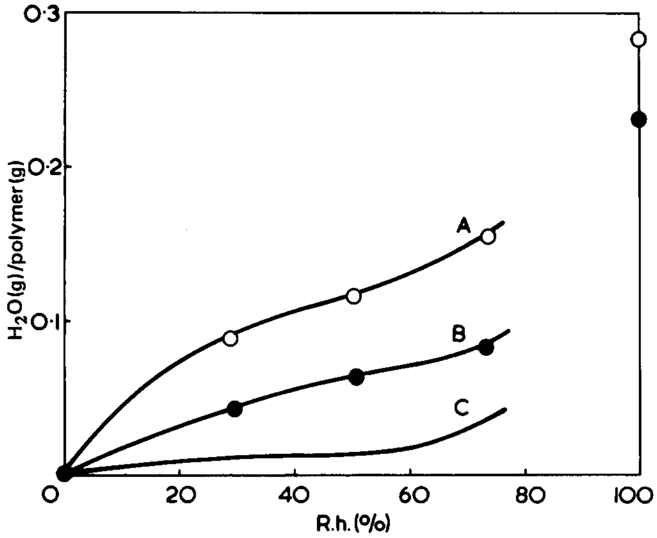

Figure 2 Water equilibrium adsorption curves. A, Membrane of PP grafted with 21% w/w PAA; B, moulded disc of the same material; C, PAA alone (adsorption curve according to ref 6)

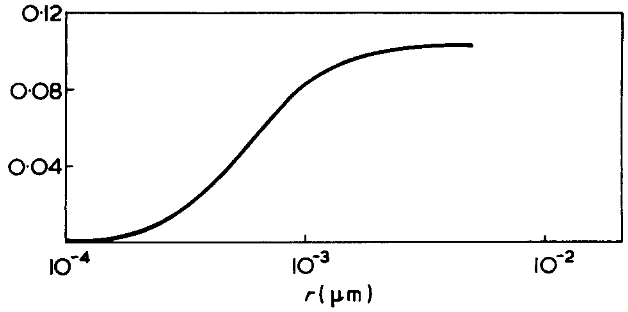

Figure 3 Water volume sorbed in pores of membrane in *Figure 2* curve A (w = water volume (cm^3) per gram of grafted polymer in pores of radius less than r)

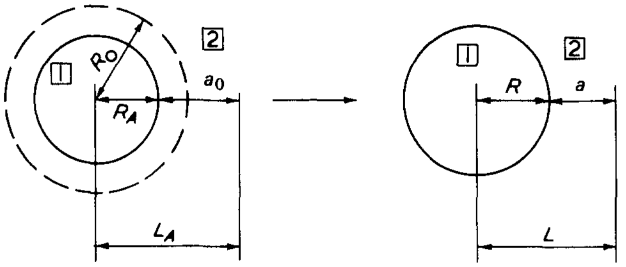

Figure 4 Domain of a hydrophylic material (1) inserted in a hydrophobic matrix (2). Deformation geometry

Table 2 Stress/strain relationships in a sphere hydrostatically compressed from outside

$\sigma_{rr} = \sigma_{\phi\phi} = \sigma_{\theta\theta} = -p$	$e_{rr} = e_{\theta\theta} = e_{\phi\phi} = -p/(3\lambda + 2\mu)$
$\sigma_{r\theta} = \sigma_{r\phi} = \sigma_{\theta\phi} = 0$	$e_{r\theta} = e_{r\phi} = e_{\theta\phi} = 0$
$3e_{rr} = \Delta = -p/k$	

Table 3 Stress/strain relationships in a hollow sphere internally loaded at $R = R_0$ with pressure p, unloaded at $R = \infty$

$\sigma_{rr} = -p(R_0/R)^3$	$e_{rr} = -(p/2\mu)(R_0/R)^3$
$\sigma_{\theta\theta} = \sigma_{\phi\phi} = \frac{1}{2}p(R_0/R)^3$	$e_{\theta\theta} = e_{\phi\phi} = (p/4\mu)(R_0/R)^3$
$\sigma_{r\phi} = \sigma_{r\phi} = \sigma_{\phi\theta} = 0$	$e_{\theta\phi} = e_{r\phi} = e_{r\theta} = 0$
	$\Delta = 0$

MECHANICAL MODEL OF MICROFRACTURE GENERATION

In order to understand the behaviour described above. we propose as a first approximation a mechanical model based on electron microscope observations which show PAA domains of about 500 Å diameter in a PP matrix.

Consider an initially anhydrous sphere of hydrophilic material, of radius R_A (A = anhydrous), immersed in an indefinite hydrophobic matrix that is unloaded and free from internal stresses, and determine the mechanical effect of swelling both inside the sphere and in the matrix will be determined at any distance L_A from the sphere centre (*Figure 4*).

If we remove the sphere and swell it without constraint to a radius R_o, and insert it in the cavity again, then in order to fulfil congruency, the sphere will become uniformly and hydrostatically compressed; its radius becomes R, and an interface pressure p arises. The surrounding matrix enters into a triple stress state, which is characteristic of a hollow sphere internally loaded by pressure p and unloaded at the extremity ($L_A = \infty$). Strain and deformation states are summarized in *Tables 2* and *3* with regard to sphere and matrix respectively, according to Love's notation[13].

For a swelling ratio t given by:

$$t = \frac{\Delta V_A}{V_A} = \frac{R_0{}^3 - R_A{}^3}{R_A{}^3} \tag{2}$$

the radius R_0 of a sphere of anhydrous volume V_a is:

$$R_0 = R_A(1+t)^{1/3} = kR_A \tag{3}$$

As shown in *Table 2*, the specific elastic variation of the radius, conforming to the congruency conditions, is:

$$\frac{R - R_0}{R_0} = -\frac{p}{3K_1} \tag{4}$$

where K_1 is the compressibility modulus of the sphere material. From equations (3) and (4):

$$R = kR_A\left(1 - \frac{p}{3K_1}\right) \tag{5}$$

and the length variations of the a_0 ($= L_A - R_A$) segment in the matrix (*Figure 4*) is (*Table 3*):

$$a - a_0 = \int_{R_A}^{R_A + a_0} e_{rr}\,\mathrm{d}R = -\frac{p}{2\mu_2}\int_{R_A}^{R_A + a_0}\left(\frac{R_A}{R}\right)^3 \mathrm{d}R$$

$$= -\frac{p}{2\mu_2}R_A{}^3 \int_{R_A}^{R_A + a_0} R^{-3}\mathrm{d}R \tag{6}$$

where e_{rr} is the radial strain according to Love's notation[13]. Therefore:

$$a - a_0 = -\frac{p}{4\mu_2}R_A\left[1 - \frac{1}{\left(1 + \frac{a_0}{R_A}\right)^2}\right] \tag{7}$$

Consequently the radial total elongation caused by hydration and by related elastic phenomena is:

$$\Delta L = L - L_A = R + a - (R_A + a_0) \tag{8}$$

and the total strain is:

$$\frac{\Delta L}{L_A} = \left\{k - 1 - \frac{pk}{3K_1} - \frac{p}{4\mu_2}\left[1 - \frac{1}{\left(1 + \frac{a_0}{R_A}\right)^2}\right]\right\}\left(1 + \frac{a_0}{R_A}\right)^{-1} \tag{9}$$

This strain is a function of k and hence of the hydration ratio t, as well as the interfacial pressure.

A second independent relationship relating the total strain to the same variables is given by the isotropy hypothesis:

$$3\frac{L - L_A}{L_A} = \frac{\Delta V_s}{V_s} = \frac{\Delta V_{1,A} + \Delta V_2}{V_{1,A} + V_2} \tag{10}$$

where V_s is the initial volume of the system and V_1 and V_2 are the volumes of materials 1 and 2 of the spherical composite system of radius L_A. Index A as to the first material indicates that this is considered anhydrous, i.e. in the initial reference state. ΔV_1 is due both to hydration and to elastic phenomena (*Table 2*) and ΔV_2 is zero since the material is hydrophobic and in the stressed state (*Table 3*) the volume is unaltered. Thus

$$\Delta V_s = \Delta V_{1,A} = tV_{1,A} - \frac{p}{K_1}V_{1,A} \tag{11}$$

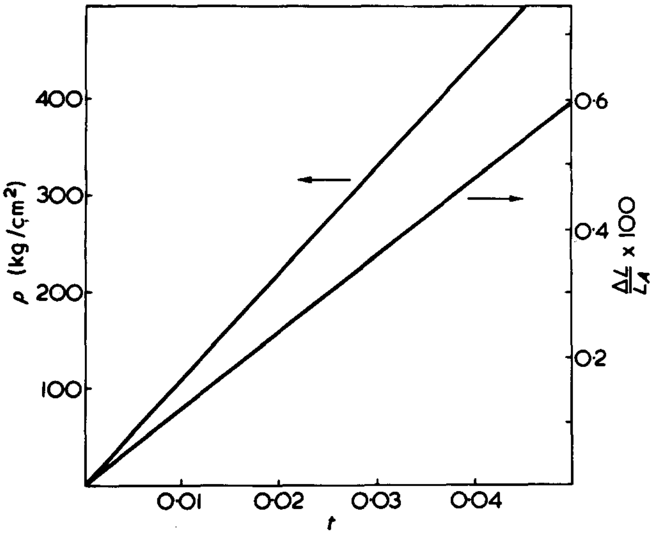

Figure 5 Pressure p and elongation against swelling ratio t for the model of the film of PP containing 40% v/v of PAA

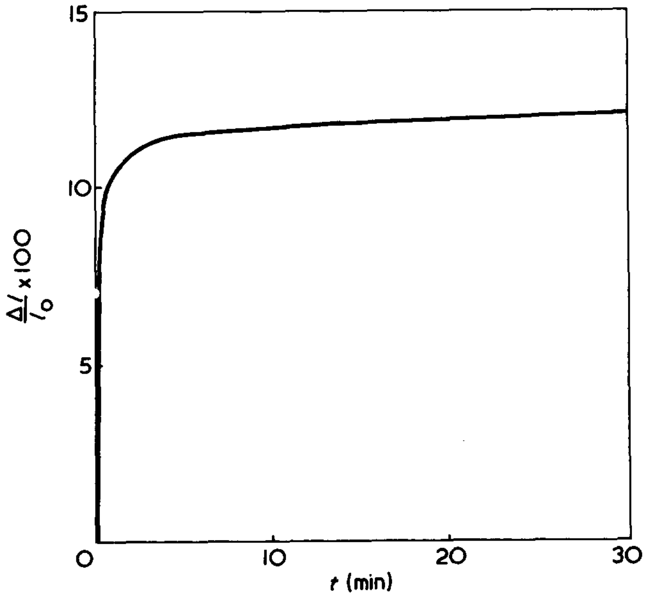

Figure 6 Percentage elongation vs. time of a membrane of PP grafted with 32% w/w PAA in contact with water

and by substitution

$$\frac{L - L_A}{L_A} = \frac{\varphi}{3}\left(t - \frac{p}{K_1}\right) \qquad (12)$$

where $\varphi = V_{1,A}/V_s$ is the volume ratio of the anhydrous material.

Using equations (9) and (12) the plots of p vs. t and $\Delta L/L_A$ vs. t are shown in *Figure 5* for a system with the following characteristics: K_1 = 100 000 kg/cm², μ_2 = 10 500 kg/cm², φ = 40% corresponding to 52% by weight of PAA, a_0/R_A = 0.37. This represents fairly well one of the grafted samples prepared by us.

Generally, for a stiff matrix, the possible pressures are high and the yield or break stress of the matrix may be reached even with a low hydration percentage.

A stability criterion[14] indicates that a critical situation is reached when the elastic energy induced in the volume unit by applied stresses equals the energy density obtainable at yield in a simple tensile test. We can therefore write:

$$\frac{\sigma_0^2}{2E} = \frac{\sigma_x^2 + \sigma_y^2 + \sigma_z^2}{2E} - \frac{\upsilon}{E}(\sigma_x\sigma_y + \sigma_x\sigma_y + \sigma_x\sigma_z + \sigma_y\sigma_z) \qquad (13)$$

where σ_0 is the yield stress, σ_i is the stress in the i-direction, E is Young's modulus[1], and υ is Poisson's ratio. Substituting the σ_i expression of *Table 2* in equation (13) we obtain

$$\sigma_0 = \bar{p}\,[3(1 - 2\upsilon)]^{1/2} \qquad (14)$$

where $\bar{p}$ is the critical interface pressure.

In the case of a stiff polymer such as PP (σ_0 = 300 kg/cm², υ = 0.33) we calculate $\bar{p}$ = 297 kg/cm². By introducing this value in *Figure 5* we obtain t = 0.027 and $\Delta L/L_A$ = 0.0031. Elongations of real membranes immersed in water are far higher. For the sample of *Figure 6* the elongation is 12%. This demonstrates that the yield strength of PP can be exceeded.

CONCLUSION

The mechanical model we have described is a first approximation one because the actual system consists of several spherical or spheroidal domains with interfering stress fields. Notwithstanding this, the model is useful for interpreting the formation of porosity due to the pressure induced by swelling. The occurrence porosity was experimentally demonstrated for this morphological type of membrane from the adsorption curves, from the measurement of water permeance both in the liquid and in the vapour phase (the results in *Table 1* are practically independent of thickness, at least within certain limits [1–50μm]) and finally from the ultrafiltration test[3,4] which showed that small molecules (such as NaCl) are only partially rejected while bigger micelles are completely rejected.

ACKNOWLEDGEMENTS

The authors thank the Istituto delle Ricerche sulle Acque (IRSA) of the CNR for financial support, and Dr M. Nascimbene for the contact angle measurements.

REFERENCES

1 Pegoraro, M. *Pure Appl. Chem.* 1972, **30**, 199
2 Pegoraro, M., Penati, A. and Alessandrini, G. *Chim. Ind. Milan* 1972, **54**, 505
3 Pegoraro, M. and Penati, A. *Proc. 4th Int. Symp. Fresh Water from the Sea Heidelberg* 1973, 3, 129
4 Pegoraro, M., Penati, A. and Pizzamiglio, A. *J. Appl. Polym. Sci.* 1974, **18**, 379
5 Pegoraro, M., Penati, A. and Natta, G. *Chim. Ind. Milan* 1971, **53**, 235
6 Thompson Hughes, L. J. and Fordyce, D. B. *J. Polym. Sci.* 1956, **22**, 509
7 Lonsdale, H. K., Merten, U. and Riley, R. L. *J. Appl. Polym. Sci.* 1965, **9**, 1341
8 Tankard, J. *J. Text. Inst. Trans.* 1937, **28**, 263
9 Shporer, M. and Frommer, M. A. *J. Macromol. Sci. (B)* 1974, **10**, 529
10 Glasstone, S. 'Textbook of Physical Chemistry, 2nd Edn, Van Nostrand, New York, 1946, pp 446–486
11 Paul, M. A. 'Principles of Chemical Thermodynamics', McGraw-Hill, New York, 1951, p 275
12 Mankovich, A. M. *J. Phys. Chem.* 1954, **58**, 1027
13 Love, A. H. E. 'A treatise on the Mathematical Theory of Elasticity', Dover Publications, New York, 1944, p 103
14 Nadai, A. 'Theory of Flow and Fracture of Solids', McGraw Hill, New York, 1950, p 209