The Transport and Sorption of Water in Polyethersulphone, Polysulphone, and Polyethersulphone/Phenoxy Blends

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Synopsis

Sorption isotherms and steady state permeabilities for water have been measured at 40°C for polyethersulphone, polysulphone, phenoxy polymer, and polyethersulphone–phenoxy blends. The pressure dependence of the permeability in all cases was weak and the permeability of phenoxy polymer is an order of magnitude smaller than that of polyethersulphone and polysulphone. The dependence of the permeability on blend composition is compared with an empirical expression often used to describe transport in miscible blends. The effect of phase separation on the permeability is studied briefly.

INTRODUCTION

The related thermoplastics, polyethersulphone (PES), and polysulphone (PSN) have the repeat units $(-C_6H_4-SO_2-C_6H_4-O-)$ and $(-C_6H_4-C(CH_3)_2-C_6H_4-O-C_6H_4-SO_2-C_6H_4-O-)$ respectively. They have been investigated as membrane materials for the separation of both gas and liquid mixtures but there have been few reported studies of water permeation in these materials or polymer blends containing these materials. PES is reported to be miscible with phenoxy polymer, $(-C_6H_4-C(CH_3)_2-C_6H_4-O-CH_2-CH(OH)-CH_2-O-)$ over the whole of the composition range at room temperature. The system exhibits lower critical solution type behavior with a cloud point minimum around 180°C and a PES content of $\sim$ 50 wt %.[1] PSN is found to be immiscible with phenoxy polymer.[2] In the present investigation the transport and sorption of water in PES/phenoxy blends has been studied at 40°C as a function of blend composition. In addition a brief comparison is made of water transport in PES and PSN.

EXPERIMENTAL

PES (Victrex 200P, ICI), PSN (Udel P1700, Union Carbide) and Phenoxy (PKCH, Union Carbide) were cast on glass plate as thin films from 15 wt % solutions in dimethylformamide after filtering (5 μm PTFE, Millipore). The films were outgassed in a vacuum oven at 95°C for $\sim$ 12 weeks. Films of the

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PES/phenoxy blends were prepared in a similar manner and were outgassed for several weeks under vacuum at room temperature. Prior to use each film was annealed for 24 h under vacuum at a temperature of about 25°C below its glass transition temperature. Film thicknesses were in the range 0.02–0.003 cm.

The densities of PES, PSN, and phenoxy are reported as 1.37, 1.20, and 1.18 g/cm^{-3}, respectively.[1,2] The densities of the blends were determined by the density gradient technique and are given in Table II.[3] The glass transition temperature T_g was measured by different scanning calorimetry (DuPont 9000) and for PES, PSN, and phenoxy was 218, 184, and 98°C, respectively. Transition temperatures for the blends are given in Table II.

Sorption isotherms and sorption–desorption kinetics were determined using an electronic vacuum microbalance (4433MP8, Sartorius Instruments).[4] Estimates of the water regain at unit activity were obtained by immersion in liquid water. A conventional vacuum system was used for the measurement of permeation rates.[9] The membrane was mounted in a glass diffusion cell and the downstream pressure monitored with a "Baratron" (390HA, MKS Instruments). A few measurements of the permeation rate were also made by sorbing the downstream vapor in dehydrated zeolite suspended from a calibrated silica spring. Steady-state fluxes measured by the two methods differed by less than 5%. Vapor pressures on the upstream face of the membrane were controlled by varying the temperature of a thermostatted liquid reservoir.

RESULTS AND DISCUSSION

Polyethersulphone, Polysulphone and Phenoxy

Sorption isotherms were determined at 40, 50, and 60°C for PES and at 40°C for PSN and phenoxy polymer in the order of increasing activity and are shown in Figure 1. The isotherms for PES are virtually coincident over the whole of the activity range indicating a heat of sorption close to the heat of condensation of water in agreement with an earlier study.[5] At unit activity the sorptive capacity at 40°C corresponds to ~ 2.5 wt % compared with earlier values of ~ 2.2 at 30°C[1] and ~ 1.7 for the range 20–40°C.[5] Also shown in Figure 1 is a second sorption isotherm for PES at 40°C completed after those at 50 and 60°C. The good agreement between the first and second sorptions suggest that hystersis effects were not significant.

For all 3 polymers the sorption isotherm is essentially linear over much of the activity range although there is an indication of some weak Langmuir-type curvature to the PES isotherm at low activities. The lower sorptive capacity of PSN relative to PES is partly a reflection of the lower concentration of polar SO_2 groups, approximately half that for PES. In an earlier study[1] PES and phenoxy isotherms at 30°C are reported as coincident up to a vapor activity of ~ 0.7; at higher activities the phenoxy sorption exceeds that of PES and reaches a value of ~ 3.3 wt % compared with a value of ~ 1.1 wt % at 40°C in the present study. It is difficult to account for this discrepancy although differences in sample preparation or incomplete removal of casting solvent may be partly responsible.
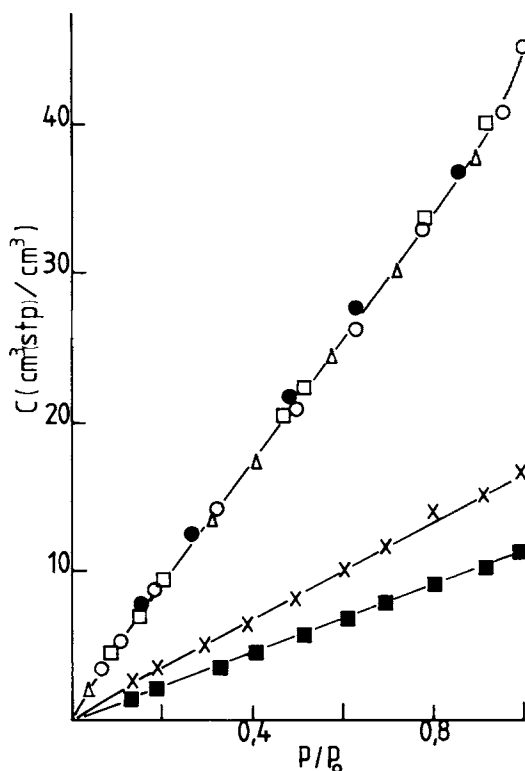
Fig. 1. Sorption isotherms for water. PES at ($\bigcirc$) 40, ($\square$) 50, ($\triangle$) 60, and ($\bullet$) 40°C (repeat); phenoxy at ($\times$) 40°C; PSN at ($\blacksquare$) 40°C.

Steady-state permeabilities were measured at 40, 50, and 60°C for PES and at 40°C for PSN and phenoxy as a function of vapor activity as shown in Figure 2. The dependence of the permeability on relative pressure is weak with slight curvature at lower activities for PES and PSN. The permeability of PES decreases slightly with increasing temperature corresponding to an activation energy for permeation of $\sim$ -3 kJ mol^{-1} at $p/p_0 = 0.5$.

The permeability of PSN is slightly less than that for PES but that for the phenoxy polymer is an order of magnitude less. Also shown in Figure 2 are PES permeabilities at 40°C determined on completion of the original set at 40, 50, and 60°C; as with the sorption isotherms the agreement between the two sets of results is satisfactory.

Steady-state diffusion coefficients D_{ss} were obtained from plots of steady state flux J_{ss} against concentration using the relation, $D_{ss} = d(J_{ss}l)/dc$, where l is the membrane thickness. The diffusion coefficient was practically independent of concentration and values are given in Table I. Sorption, desorption, and conjugate rate curves at 40°C were practically coincident confirming that the diffusion coefficient was constant or weakly dependent on concentration. Average values of the coefficients, $\bar{D}$, obtained from the initial slopes of the conjugate rate curves are also included in Table I. The agreement between the steady-state and transient state coefficients is acceptable. The larger discrepancies for PSN are attributed to errors in the membrane thickness as in this
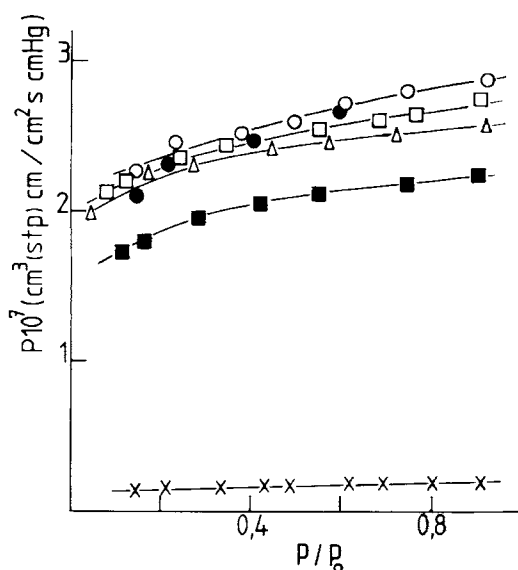
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Fig. 2. Pressure dependence of permeability of water. PES at (○) 40, (□) 50, (△) 60, and (●) 40°C (repeat); PSN at (■) 40°C; phenoxy at (×) 40°C.

instance the permeation and sorption kinetic measurements were made on samples from different films; also the film thickness for the kinetic measurements were at the lower end of the range studied, ~ 0.003 cm.

The value of D for PES at 40°C is in good agreement with an earlier value of ~ 4.6×10^{-8} cm^2 s^{-1} obtained from immersion experiments. From the temperature dependence of D for PES an activation energy of 26 kJ mol^{-1} is obtained compared with an earlier value of 33 kJ mol^{-1}.[6] The value of D for PSN at 40°C may be compared with a value of 4.72×10^{-8} cm^2 s^{-1} obtained from immersion experiments at 23°C.[7]

The order of increasing diffusion coefficient at 40°C is PSN > PES > phenoxy and of increasing sorptive capacity is PES > phenoxy > PSN leading to permeabilities which increase in the order PES > PSN > phenoxy.

TABLE I
Permeability P and Diffusion Coefficient D for Water in PES, PSN, and Phenoxy Polymer

Polymer	T (°C)	$P \times 10^{8}$ [a] (cm^3 stp cm/cm^2 cm Hg s)	$D_{os} \times 10^{8}$ (cm^2/s)	$\bar{D} \times 10^{8}$ (cm^2/s)
PES	40	26.2	4.1	3.5
	50	25.2	5.1	—
	60	24.2	7.6	—
	40 (repeat)	25.8	3.4	—
PSN	40	21.1	11.4	7.2
Phenoxy	40	1.7	0.65	—

[a] P at a vapor activity of 0.5.

Polyethersulphone–Phenoxy Blends

For these studies the PES samples for both sorption and permeation experiments were annealed at 200°C. Sorption isotherms were determined at 40°C in order of increasing vapor activity and are shown in Figure 3. The isotherms are again essentially linear over much of the activity range with some indication of a weak Langmuir-type contribution at low activities. In an earlier study of this system, the isotherms for the pure components and blends were reported to be practically coincident except for activities $\gtrsim 0.7$ where the sorption at a given activity increased significantly with the phenoxy content of the blend.[1] As already indicated, differences in sample preparation or incomplete removal of solvent may be responsible for these discrepancies.

Permeabilities were determined at 40°C as a function of ingoing pressure and are shown in Figure 4. The dependence of P on vapor activity is weak and values of P at $p/p_0 = 0.5$ are given in Table II for comparison purposes. As for the pure components, diffusion coefficients for the blends were virtually independent of concentration and values for the steady-state and sorption–desorption coefficients, D_{ss} and $\bar{D}$ respectively are also given in Table II. The agreement between the two sets of coefficients is satisfactory.

In Figure 5 $\ln P$ is given as a function of blend composition and is compared with the expression
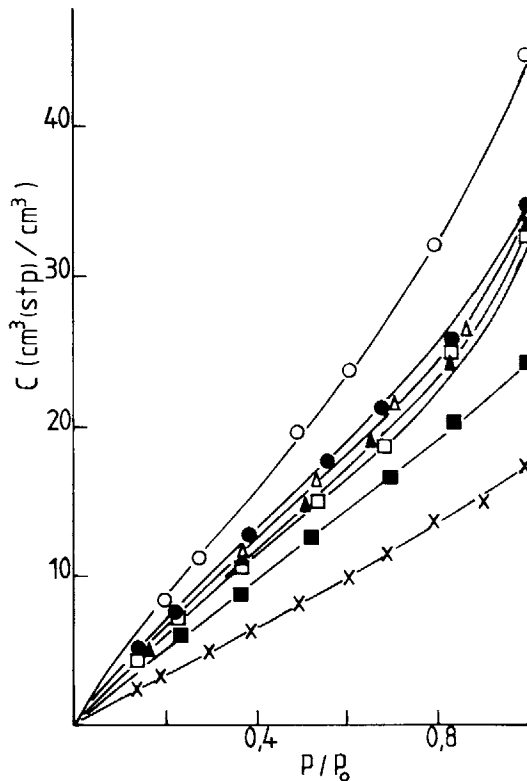

Fig. 3.   Sorption isotherms for PES–phenoxy blends (vol % PES) at 40°C: (○) 100; (●) 89; (△) 78; (▲) 67; (□) 49; (■) 28; (×) 0.
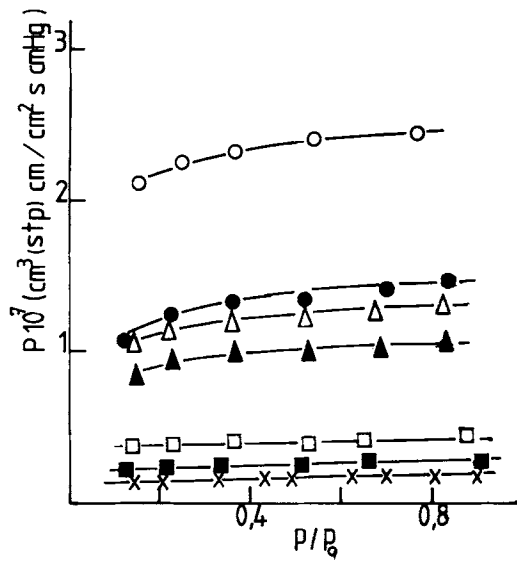
Fig. 4. Pressure dependence of permeability for PES–phenoxy blends (vol % PES) at 40°C: (○) 100; (●) 89; (△) 78; (▲) 67; (□) 49; (■) 28; (×) 0.

$$\ln P = \phi_1 \ln P_1 + \phi_2 \ln P_2 \qquad (1)$$

where ϕ denotes volume fraction and subscripts 1 and 2 denote the components of the blend. Equation (1) is often used as an empirical description of transport in miscible blends. Generally the permeability of a miscible blend falls either on or below the line of eq. (1) as is the case here.[8] The experimental points, fall on a smooth curve except for ϕ_{PES} = 0.67, 0.78. This may be a result of errors in film thickness as thin films (.003 to .009 cm) were used, alternatively some degree of phase separation may have occurred in this region although not sufficient to be detected from a glass transition temperature analysis. In this

TABLE II
Density ρ, Glass Transition Temperature T_g, Permeability P, and Diffusion Coefficient D for Blends of PES and Phenoxy Polymer

φ_{PES}[a]	ρ (g/cm^3)	T_g (°C)	$P \times 10^8$ [b]	$D_{ss} \times 10^8$ (cm^2/s)	$\bar{D} \times 10^8$ (cm^2/s)
1.00	1.37	218	23.8	3.2	3.8
0.89	1.36	202	13.5	2.9	3.3
0.78	1.33	200	12.3	2.5	2.6
0.67	1.32	174	10.1	2.2	2.3
0.49	1.28	153	4.2	0.89	—
0.28	1.24	129	2.7	0.71	—
0.00	1.18	98	1.7	0.65	—

[a] Volume fraction of PES.

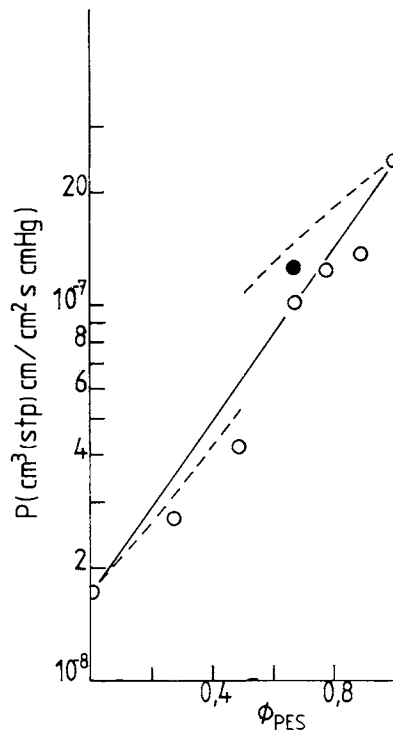[b] $P \times 10^8$ (cm^3(stp) cm/cm^2 s cm Hg) at vapor activity of 0.5.

Fig. 5. Dependence of the permeability on blend composition at 40°C: (O) exptl; (●) phase separated sample; (———) eq. (1); (– – –) Maxwell equation.

region of composition the difference between glass transition temperatures and cloud points is roughly 10°C and the possibility of phase separation is increased.

The effect of phase separation on the permeability was investigated for the blend, $\phi_{PES} = 0.67$. On heating to $\sim 225°C$, phase separation was induced and the resultant film gave 2 glass transition temperatures of 118 and 203°C. As shown in Figure 5 the permeability of the phase separated membrane has increased and lies close to that predicted by the Maxwell equation for a heterogeneous dispersion of spheres.[9]

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