

# ***Sorption of Water in Polyethersulfone/ Poly (ethylene Oxide) Blends***

## **INTRODUCTION**

In a recent paper, we showed that polyethersulfone (PES) is miscible with poly(ethylene oxide) (PEO).<sup>1</sup> Blends were cast from a common solvent and were found to show a single composition-dependent glass transition temperature. The melting point depression was used to calculate an interaction parameter, which was negative. Blends were found to phase separate on heating.

In a more recent paper,<sup>2</sup> we investigated the thermodynamics of the PES/PEO blend system and simulated the spinodal curves of the phase diagram using a modified form of the equation-of-state theory of Flory and co-workers. Values of the melting point depression and of the heats of mixing of low molecular weight analogues were used to obtain the interaction energy parameter  $\chi_{12}$ . It has been suggested<sup>3</sup> that at certain compositions (80/20 and 90/10 PES/PEO) blends of PES and PEO absorb less water than pure PES. These measurements were done by soaking thin films of blends in water. In this work we report on the sorption of water vapor by PES and PEO blend compositions over a range of vapor activity and estimate values of the Flory-Huggins interaction parameter from sorption measurements. Approximate average diffusion coefficients for the PES/PEO blends have also been measured.

## **EXPERIMENTAL**

Polyethersulfone [ICI Victrex 200P,  $(C_6H_4-SO_2-C_6H_4O)_n$ ] has a quoted number average molecular mass of  $17651 \text{ g mol}^{-1}$ , a degree of polymerization of approximately 76, a reduced viscosity of  $0.41 \text{ cm}^3 \text{ g}^{-1}$  [as a 1% w/w solution in dimethylformamide (DMF) at 25°C], a density of  $1.37 \text{ g cm}^{-3}$  at 25°C, a refractive index of 1.65, and a glass transition temperature of 226°C. It was dried in an air oven at 150°C for 5 h before use.

The poly(ethylene oxide) used for this work was supplied by union Carbide (Polyox WSRN 80) having a quoted molecular mass of  $200,000 \text{ g mol}^{-1}$ , a density of  $1.089 \text{ g cm}^{-3}$  at 25°C, and a refractive index of 1.46. It was dried by keeping at 40°C under vacuum for one week before use.

Blends were prepared by solvent casting from a common solvent DMF, as reported earlier<sup>1</sup>.

## **Sorption Measurements**

The sorption isotherms were determined with a conventional vacuum system and a McBain-Bakr balance<sup>4</sup> with a calibrated silica spring having a sensitivity of  $36.2 \text{ cm g}^{-1}$ . The vapor pressure was measured with a pressure transducer (0–15 psi, Bell and Howell Ltd.). The pressure was measured with an error of  $\pm 0.02 \text{ cm Hg}$ . All samples were outgassed initially for 48 h at 30°C.

## **RESULTS AND DISCUSSION**

### **Sorption Isotherms**

The sorption isotherms at 30°C for PES, PEO, and 95/5, 90/10, 80/20, 70/30, and 60/40 PES/PEO blends are given in Figure 1. The errors involved in the measurement of the regain were negligible. The greatest errors were in the measurement of pressure (especially at lower activities) and are reflected in the errors of the  $\chi$  parameters in Table I. PEO is a crystalline polymer, and for comparison purposes the isotherm for the amorphous phase is also included in Figure 1 and was calculated on the assumption that the degree of crystallinity is unaffected

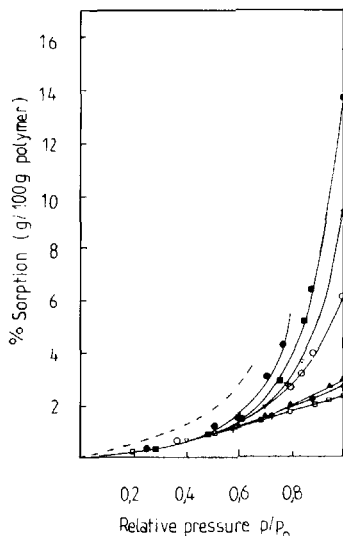


Fig. 1. Plots of % sorption against the activity of water at 30°C: (□) PES; (- -) PEO (amorphous); (●) 95/5, (▲) 90/10, (○) 80/20, (▽) 70/30, (■) 60/40 for PES/PEO blends; (●) PEO (semicrystalline).

by the sorption of water. This assumption is clearly not valid at the higher activities where eventually complete dissolution of the crystallites occurs. For this reason the isotherm for the amorphous content is only given for the lower activities where dissolution of the crystallites is less likely. The degree of crystallinity was estimated from density measurements to be 50% ( $\pm 5\%$ ) which is in agreement with the literature.<sup>5</sup> The level of sorption for the PES and for the PES/PEO blends are similar up to activities of approximately 0.6. For water vapor activities of less than  $\sim 0.6$  the affinity for water of PEO is not abnormally high even allowing for crystallinity. As the activity of the vapor is increased, the sorption rises steeply around activities of 0.7–0.8. Clearly some highly favorable interaction occurs at these higher activities probably through the formation of PEO/water complexes sufficient to overcome constraints imposed by crystallites and cause eventual dissolution of the polymer. This behavior is reflected in the isotherms for blends containing more than 10% PEO and may indicate the presence of incipient or induced PEO nuclei with properties approaching that of bulk PEO; the inter-

TABLE I  
 $\chi'_{23}$  Interaction Parameter Values at Different Activities

Blend composition PES:PEO	Water vapor activity	$\chi'_{23} \pm \text{error}$
90:10	0.27	$-0.33 \pm 2.5$
	0.49	$-0.99 \pm 1.5$
	0.60	$-0.47 \pm 1.2$
80:20	0.36	$-0.47 \pm 1.26$
	0.60	$-0.61 \pm 0.76$
70:30	0.38	$-0.8 \pm 0.66$
	0.51	$-0.42 \pm 0.65$
	0.60	$-0.79 \pm 0.62$
60:40	0.37	$-0.86 \pm 0.74$
	0.50	$-0.55 \pm 0.58$
Calculated mean (see text)		$-0.64 \pm 0.26$

action of water with these small domains if present would eventually be restricted by the surrounding PES continuum. Water regains less than for PES were not observed for any of the blends either at unit or lower activities as had been reported<sup>3</sup> for 80/20 and 90/10 PES/PEO blends at unit activities.

Sorption isotherms were not obtained for blends containing more than 40% PEO; previous studies,<sup>1</sup> by differential scanning calorimetry and light scattering, on crystallization and melting point behavior showed no indication of PEO crystallization up to this value. At higher fractions of PEO there is evidence of some degree of crystallization of the PEO component.

The effect of temperature on the sorption of water vapor was studied for the 80/20 PES/PEO blend. Isotherms obtained at 30, 40, and 50°C were virtually coincident over the entire range of activity as shown in Figure 2, indicating that the heat of sorption is close to the heat of condensation of water.

The shape of the isotherm at lower activities was not measured with a sufficient accuracy to detect any initial Langmuir type curvature associated with specific localised interactions.

For the homogenous blends the experimental isotherms lie below that predicted by the additivity rule, calculated using a PEO isotherm for the amorphous phase, and typical examples are shown in Figure 3. The uncertainty in the isotherm for the PEO amorphous phase at higher activities will be reflected in the isotherm for the blend predicted by the additivity rule and for this reason the latter is given for the lower activities only.

The effect of phase separation on the isotherm is shown in Figure 2 for an 80/20 PES/PEO miscible blend at 30°C. Phase separation produced by heating at 150°C resulted in an increased regain at the higher activities consistent with the formation of PEO rich domains with a water regain more characteristic of bulk PEO. There was no significant extraction of PEO from the phase-separated blend after prolonged soaking in water consistent with discrete PEO-rich domains dispersed in a PES continuum.

Estimates of the average diffusion coefficient were obtained in some instances from the half-time expression<sup>6</sup> and were in the range  $1 \times 10^{-6}$  (PEO) to  $5 \times 10^{-8}$  (PES)  $\text{cm}^2 \text{s}^{-1}$ .

### The Interaction Parameter $\chi$

Analysis of equilibrium sorption of a vapor by the blend can provide information regarding polymer-polymer interaction.<sup>7</sup> Polymer solution theory applied to a ternary system consisting of one solvent and two polymers has been utilized to calculate the polymer-polymer interaction parameter.<sup>8</sup> The activity of the solvent in a ternary mixture is given by

$$\ln a_1 = \ln \phi_1 + (1 - \phi_1) + (\chi_{12} \phi_2 + \chi_{13} \phi_3)(1 - \phi_1) - \chi'_{23} \phi_2 \phi_3 \quad (1)$$

where  $a$  is the activity of the solvent. Subscript 1 refers to the solvent, and subscripts 2 and 3 refer to the two polymers.  $\phi$  is the volume fraction, and  $\chi_{12}$  and  $\chi_{13}$  are the solvent polymer interaction parameters and  $\chi'_{23}$  is the polymer-polymer interaction parameter expressed per

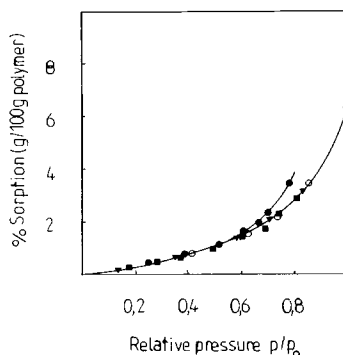


Fig. 2. Plots of % sorption against the activity of water for 80/20 PES/PEO miscible blends at 30 (▼), 40 (■), and 50°C (○) and for phase-separated sample at 30°C (●).

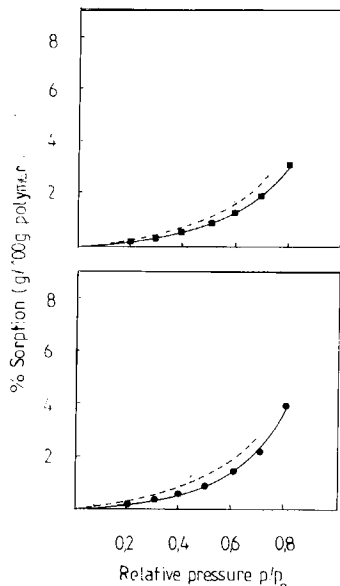


Fig. 3. Plots of % sorption against activity for 60/40 (●) and 70/30 (■) PES/PEO blends: (- - -) calculated assuming additivity of PES and PEO (amorphous) sorptions.

segment of polymer 2. The solvent polymer interaction parameters  $\chi_{13}$  and  $\chi_{12}$  can be calculated using the binary solution equation:

$$\ln a_1 = \ln \phi_1 + \phi_2 + \chi_{12}\phi_2^2 \quad (2)$$

thus one can determine  $\chi_{12}$  for H<sub>2</sub>O/PES and  $\chi_{13}$  for H<sub>2</sub>O/PEO in separate experiments and utilize these values to calculate  $\chi'_{23}$  from the vapor sorption data of the polymer blend using eq. (1).

From the sorption data of pure PES and PEO and eq. (2), the interaction parameters  $\chi_{12}$  and  $\chi_{13}$  for H<sub>2</sub>O/PES and H<sub>2</sub>O/PEO were found to be 2.66 and 2.22, respectively. Knowing  $\chi_{12}$  and  $\chi_{13}$  and sorption for different blend compositions  $\chi'_{23}$  were calculated using eq. (1). These values of  $\chi'_{23}$  for different blend compositions at various activities are given in Table I. The relatively large errors in  $\chi'_{23}$  especially at lower activities were a result of errors in the pressure. A mean value of  $\chi'_{23}$  was found by weighting each result according to  $w_i = (\text{error})^{-2}$  so that

$$\chi'_{23} = \frac{\sum \chi'_{23} \cdot w_i}{\sum w_i}$$

and a weighting for this average given by

$$w = \sum w_i$$

This gave a result  $\chi'_{23} = -0.64 \pm 0.26$ . The negative values are consistent with the observed miscibility of the components. Negative values have also been reported from melting point depression measurements.

## CONCLUSIONS

The equilibrium sorption isotherms of water vapor in PES/PEO blends over the whole of the activity and composition range was always greater than for pure PES. The isotherms for blends gave sorptions in general less than predicted from the additivity of component sorptions

consistent with some degree of interaction of the components on forming the blend. The polymer-polymer interaction parameter calculated from sorption data has been found to be negative and this confirmed previous findings from melting point depression.<sup>1</sup> The approximate values of average diffusion coefficients were obtained from sorption measurements. These were found to increase with the increasing concentration of PEO in the blend.

### References

1. D. J. Walsh, and V. B. Singh, *Makromol. Chem.*, **185** (9), 1979 (1984).
2. D. J. Walsh, S. Rostami, and V. B. Singh, *Makromol. Chem.*, to appear.
3. A. B. Newton (I.C.I.), Eur. Pat. Appl., E.P. 37, 181 (1981).
4. J. W. McBain and A. M. Bakr, *J. Am. Chem. Soc.*, **48**, 690 (1926).
5. N. K. Kalfoglou, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 1259 (1982).
6. J. Crank and G. S. Park, in *Diffusion in Polymers*, Academic, London and New York, 1968.
7. D. R. Paul and Seymour Newman, in *Polymer Blends*, Academic, New York, 1978.
8. T. K. Kwei, T. Nishi, and R. F. Roberts, *Macromolecules*, **7**, 667-674 (1974).

V. B. SINGH  
J. A. BARRIE  
D. J. WALSH

Department of Chemistry and Chemical Engineering and Chemical Technology  
Imperial College of Science and Technology  
London, SW7, United Kingdom

Received January 25, 1985

Accepted April 1, 1985