# Water-Transport Properties in Polyetherimide Blends with a Liquid Crystal Polymer

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ABSTRACT: The effect of the addition of a liquid crystal polymer (Rodrun<sup>®</sup>) on the sorption and transport properties of water through films of a polyetherimide (PEI, Ultem 1000) was investigated. A Cahn electrobalance was employed for measuring the water uptake by the polymer samples. Sorption measurements were made with films of PEI, Rodrun, and heterogeneous PEI/Rodrun blends at different water activities at 30°C. In all cases, diffusion and sorption coefficients decreased when the amount of Rodrun increased. Values of the water-sorption isotherms were adjusted to different models. Permeabilities for the different samples were indirectly obtained using experimental values of the solubility and diffusion coefficients described above. Furthermore, permeabilities of the binary composite material were calculated on the basis of those of the pure components and some theoretical assumptions concerning blend morphology. Results were consistent with a Rodrun structure in the composite intermediate between a fibrillar and a laminar morphology. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 323–332, 1999

Key words: PEI; Rodrun<sup>®</sup>; blends; water sorption; sorption models

## **INTRODUCTION**

In a recent article,<sup>1</sup> we reported the transport properties of carbon dioxide through composite membranes based on polyetherimide (PEI, Ultem) and a liquid crystal polymer (LCP, Rodrun<sup>®</sup>). The addition of small amounts of the LCP was enough to induce relevant changes in the different steps involved in the global permeability process. According to the so-called solution-diffusion mechanism, gas permeation is a complex process controlled by both diffusion (a kinetic process) and solution (an equilibrium process) of the penetrant gas molecules in the membrane matrix. At the steady state and when the diffusion coefficient is independent of the penetrant concentration, the permeability coefficient of amorphous polymers can be written as the product of the effective diffusion, D, and the solubility, S, coefficients:

$$P = DS \tag{1}$$

The article cited above illustrates that both processes and, consequently, the global permeability are sensitive to changes in the membrane structure. In blends of a glassy polymer with a liquid crystal polymer (LCP), these changes can be particularly important given the excellent barrier properties usually exhibited by these materials<sup>2</sup> as a consequence of the particular microstructure that they adopt in the solid state. These characteristics seem to be well established in spite of one

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of the more relevant features of these composites: the immiscibility between the blend components. Transport properties of other liquid-crystalline copolyesters and polyamides were recently reported.<sup>3,4</sup>

Because of their excellent chemical, mechanical, and thermal properties, durability, and transport properties, polyimides have received much attention in the area of different separation processes.<sup>5</sup> Recently, water-vapor separation membranes have attracted great interest because of their application to the dehumidification of gases. air, and organic vapors.<sup>6,7</sup> Polyimides are also applicable as membranes for water-vapor separation and have applications in electronics, composite materials, and adhesives, in which water sorption can alter the performances. Consequently, studies of sorption and permeation in this material family have received recent attention in the literature, including the widely used commercial PEI (Ultem) film.<sup>8–11</sup>

In a comparative study of water-transport properties of different polyimides, Okamoto et al.<sup>11</sup> verified the low water permeability of the Ultem polyimide, in spite of its high diffusion coefficient. The low water sorption was the origin of this behavior.

As previously mentioned, the addition of small amounts of the LCP Rodrun to the Ultem polyimide modified its carbon dioxide transport properties. It would be interesting to study the influence of the Rodrun concentration on the Ultem watertransport properties. This was the aim of the present work for which the same composite membranes previously described<sup>1</sup> will be used. Their mechanical properties were previously studied by other members of our department.<sup>12</sup>

Water vapor is a special penetrant in studying polymer-transport properties. Water sorption deviates in some cases from the Henry's law with positive deviations attributed to swelling and clustering processes.<sup>13</sup> In the first case, this implies an increase in the available free volume which is reflected in an increase of the diffusion coefficient with the water-vapor activity. Clustering is a consequence of the water molecules association which restricts the water molecule motion and, consequently, decreases the diffusion coefficient at high water activities. However, this type of behavior is particularly evident in high- and medium-hydrophilic polymers and less important in hydrophobic materials.

The experimental data of the water-vapor transport properties in our mixtures were ana-

lyzed in light of different approaches. The main goal was to reproduce experimental data using the values of these properties in pure components and some assumptions concerning the influence of the heterogeneous structure of the films on their capacities to alter the transport of the penetrants through them.

# **EXPERIMENTAL**

## **Materials**

The PEI commercially sold under the trade name of ULTEM-1000 was supplied by General Electric. It is a thermoplastic with a glass transition temperature of 490 K and a nominal molecular weight of 20,000. The liquid LCP RODRUN LC-5000 is a random copolyester of ethylene terephthalate and *p*-hydroxybenzoic acid in an 18/82 molar composition, as determined<sup>14</sup> by <sup>1</sup>H-NMR. It was provided by UNITIKA (Tokyo, Japan).

PEI and PEI/Rodrun films were extruded in a Brabender extruder. The materials were mixed at 330°C in a static mixer composed of five Kenics elements. The die temperature was 370°C. Drawing of the extruder ribbon was carried out in the melt state using an Axon three-roll drawing unit. The average thickness of the membrane samples used for the sorption measurements varied from 40 to 100  $\mu$ m, measured with a Duo-Check ST-10 apparatus with a thickness variation of  $\pm 1 \ \mu m$ . Given that, in the case of Rodrun, it was impossible to prepare films by extrusion. Rodrun films for sorption measurements were obtained by compression molding in a Schwabenthan press, Polystat 200T Model, with a maximum temperature of 300°C. A description of the films used in this study is given in Table I, where the sample composition is given in a weight fraction (as they will be denoted throughout this article). The phase behavior of the mixtures, characterized by differential scanning calorimetry (DSC) and electronic microscopy (EM) examination of the fracture surfaces of the samples, were previously reported.<sup>1</sup>

## **Apparatus and Procedure**

Water-sorption-desorption measurements in PEI, Rodrun, and PEI/Rodrun mixtures were determined using integral gravimetric sorption experiments performed on a Cahn D-200 electrobalance enclosed in a constant temperature chamber. A detailed description of the required setup

Sample	$\begin{array}{c} \text{Thickness} \\ (\mu) \end{array}$	Weight (mg)	Density (g cm <sup>-3</sup> )	Preparation Method
PEI	49	88.631	1.270	Extrusion
PEI/Rodrun 95/5	49	85.191	1.276	Extrusion
PEI/Rodrun 90/10	45	85.219	1.283	Extrusion
PEI/Rodrun 85/15	40	70.083	1.289	Extrusion
Rodrun	103	92.414	1.410	Compression

Table I	Film	Descri	ption
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for such a type of experiment was reported by Hernandez and Gavara.<sup>15</sup> It can be defined as a "dynamic method" in which a stream of nitrogen gas, flowing continuously through the balance and adjusted to specific values of water activity, provides the source of water vapor in equilibrium with the polymer films. The film sample was conditioned at 100°C in a vacuum oven for 48 h, maintained in the same oven at 60°C for 1 week, and finally suspended in the glass chamber of the electrobalance.

The weight gain of the polymer sample at each value of water activity was obtained from the difference between the weight at the initial and final steady states. However, this experimental setup does not provide the desired humidity (or water activity) instantaneously. As we will discuss later, this implies some difficulties in the correct determination of diffusion coefficients. Because of that and because of some water-condensation problems we found in our experiments, they were scheduled in a special manner that we describe below.

After having the right vacuum in the balance, the flow meters of the system were adequately adjusted in order to provoke a first relative humidity (RH) jump between 0% and the desired final value. Once the system reached equilibrium, the water activity of the gas surrounding the film sample was increased to a new value without removing the sample from the electrobalance and a new sorption process was carried out. The change in water activity for this second experiment was smaller than 0.1. In all cases, the humidity values were measured by using Type H-3 humidity hygrosensors from Newport Scientific, Inc. After these two different processes, the sample was removed from the chamber, which was then purged with a stream of dry nitrogen and a new process began with a new two-jump process. This procedure was repeated to cover the whole range of water activity for each temperature.

Blank runs were performed in order to properly account for and correct buoyancy effects as well as the possible adsorption on both metal and glass surfaces of the electrobalance. This was particularly important in the Rodrun case. In the RH interval considered here (0-70%), the adsorbed water on the electrobalance elements increased linearly with the RH percentage up to 0.012 mg at an RH of 65%. This adsorption supposed approximately a 25% of the total amount of water sorbed during the Rodrun experiments. In the rest of the investigated samples (PEI and composites), the influence of these adsorption effects were much less, being practically negligible.

#### Computations

Using sorption–desorption experiments and if the concentrations just within the surfaces of a plane sheet are maintained constant, the amount of the diffusant,  $M_t$ , taken up by the sheet in a time, t, is given by the equation<sup>16</sup>

$$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{D_w (2n+1)^2 \pi^2 t}{l^2}\right)$$
(2)

where  $M_t$  is the absorbed mass at time t;  $M_{\infty}$ , the total absorbed mass at equilibrium; l, the film thickness; and  $D_w$ , the diffusion coefficient (cm<sup>2</sup>/ s). For long times, eq. (2) may be approximated by

$$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \exp\left(-\frac{D_w \pi^2 t}{l^2}\right) \tag{3}$$

and  $D_w$  can be calculated from an adequate plot of the sorption data.

The equilibrium amount of water finally absorbed in the polymer will be expressed in the

% HR Jump	$\begin{array}{c} D_w ~(\mathrm{cm^{2}\!/\!s}) \\ \times ~10^{10} \end{array}$	% HR 2nd Jump	$\begin{array}{c} D_w~({\rm cm^2/s})\\ \times~10^{10} \end{array}$
0-4.1	14.57		
0-6.3	18.25	6.3 - 9.5	15.06
0 - 12.3	15.93	12.3 - 17.6	18.57
0 - 15.0	14.19		
0-20.0	17.62	20.0 - 25.4	15.64
0 - 24.0	19.42	24.0 - 29.8	16.73
0 - 31.3	18.69		
0-39.6	21.52	39.6 - 42.3	16.01
0 - 45.5	16.58		
0 - 50.5	17.06	50.5 - 53.5	16.31
0-64.5	14.35		

Table IIWater-Diffusion Coefficients at 30°Cfor the PEI/Rodrun 90/10 Film

following in two different forms: The so-called solubility coefficient of water in the polymer,  $S_w$ , was calculated from the  $M_\infty$  values at each temperature and the dry weight of the sample film,  $m_p$ , as indicated by equation

$$S_w = \frac{M_\infty}{m_p p_v^0 a} \tag{4}$$

where  $p_v^0$  is the saturation vapor pressure and a is the water activity. It is a solubility coefficient reduced to the penetrant activity in each experiment. On the other hand, the equilibrium volume fraction of water in the polymer,  $\phi_w$ , is calculated from the equation

$$\phi_w = \frac{M_{\infty}\rho_p}{M_{\infty}\rho_p + m_p\rho_w} \tag{5}$$

where  $\rho_w$  and  $\rho_p$  are the densities of pure water and the polymer. Finally, the permeability coefficient, *P*, can be calculated from the solubility coefficient, *S*, and the diffusion coefficient, *D*, obtained for each film, using eq. (1).

### **RESULTS AND DISCUSSION**

#### **Diffusion Coefficients**

As previously mentioned in the Experimental part, the sorption experiments were carried out in a series of two experiments. In the first one, humidity was changed from 0% to the desired value. After that, a smaller jump in RH was allowed. When the diffusion coefficient was calculated for each experiment, it was seen that  $D_w$  was almost constant in each blend composition, independently of the final activity in the balance and of the magnitude of the RH jump. As an example, Table II illustrates the results obtained with the films of the composite membrane containing 90% PEI and 10% Rodrun (weight percentage). Similar behavior was observed both with the other two blends and with the pure components.

Therefore, we decided to calculate an average diffusion coefficient for each sample. The values are shown in Table III. As can be seen, when the percentage of Rodrun in the sample increases, the diffusion coefficient decreases. However, the value for pure Rodrun is similar to that of the pure PEI. A possible explanation for this last result could be the fibrous nature of pure Rodrun which did not allow the preparation of films by extrusion in similar conditions to those used in the rest of the films. The preparation of Rodrun films by compression, leading to a microstructure substantially different from those encountered in the PEI/Rodrun blends, and perhaps its different thickness, could be the origin of the relatively high diffusion coefficient of the pure Rodrun.

In spite of their potential use as membranes for water-vapor separation, few articles have been published<sup>8-11,17</sup> concerning water transport in polyimides. Okamoto et al.<sup>11</sup> studied the sorption and diffusion of water vapor in different polyimide films, including Ultem polyimide. They studied a 50-µm film at 50°C. Using activation energies given in the same article for other members of the polyimide family, the calculated PEI value of  $D_w$  at 30°C is five to six times higher than that reported in this article. Such a difference could arise from the different experimental setup. In our dynamic method in which the % RH is not instantaneously attained, the calculation of  $D_w$  at a constant RH could be erroneous, although the nearly constant value obtained at different RH

Table IIIAverage Water-Diffusion Coefficientsat 30°C

Sample	$D_w~(\rm cm^2\!/\!s)\times 10^{10}$
PEI	$20.5\pm1.8$
PEI/Rodrun 95/5	$18.6 \pm 2.1$
PEI/Rodrun 90/10	$16.9\pm1.9$
PEI/Rodrun 85/15	$12.3\pm2.2$
Rodrun	$22.6\pm2.6$



**Figure 1** Water-sorption coefficient  $S_w$  at 30°C as a function of the RH: ( $\bullet$ ) PEI; ( $\bigcirc$ ) Rodrun.

jumps seems to validate our procedure. However, both series of data agree in a nearly independent value of the diffusion coefficient on the water activity.

#### Water Solubility

The values of the solubility coefficient of water in PEI and Rodrun,  $S_w$ , were calculated as indicated in eq. (4) and are presented in Figure 1. These data show the usual behavior in this kind of experiment, that is, the solubility coefficient decreases as water activity increases. This decrease is observed until 25% RH; above this value,  $S_w$  becomes almost constant. The sharp fall at low activities followed by an almost constant value can be considered as supporting evidence of the hypothesis of a bimodal sorption mechanism. This behavior has been observed in other polymer/penetrant systems, as is the case of Nylon 6 membranes and water vapor.<sup>15</sup>

Using average  $S_w$  data after the "steady-state" plateau, a decrease of the solubility coefficient with an increase of the Rodrun quantity in the samples was observed. The average values calculated at the steady state are shown in Table IV.

The value for PEI is reasonably consistent with that of Okamoto et al.<sup>11</sup> if we take into account the differences in temperature and the sorption enthalpies for other polyimides of the family reported in the same article. In this case, the differences in the experimental setups should not be so decisive as in the case of the diffusion coefficient.

In the literature, there are different theoretical expressions that could explain the solubility experimental data. For polymers below their glass transition temperatures, the dual-mode approximation is useful. Two contributions to the sorption can be distinguished: One of them is attributed to the Henry's mechanism and the other one is similar to a Langmuir-type process<sup>18</sup> which corresponds to the molecules which are trapped in the free-volume holes of the glassy polymer. Both populations are in dynamic equilibrium. The dual-sorption mechanism explains the curvature usually found at low activities, reflecting that the gas is adsorbed in an amount slightly higher than expected in the Henry's mechanism. The experimental sorption data can be fitted, according to the dual-mode sorption, as

$$C = C_{H} + C_{L} = k_{D}p + \frac{C'_{H} bp}{1 + bp}$$
(6)

where the total solute concentration in the polymer, C, is the sum of two contributions,  $C_H$  and  $C_L$ , due to the Henry and Langmuir mechanisms, respectively.  $k_D$  is the Henry's law constant; b, the Langmuir affinity constant;  $C'_{H}$ , the Langmuir capacity constant; and p, the equilibrium pressure. When the penetrant is water vapor, it is usual to express concentration as a volume fraction,  $\phi_w$ . Equation (6) can be then rewritten as

$$\phi_w = K_D a + \frac{Ka}{1 + Ba} \tag{7}$$

where *a* is the penetrant activity,  $K_D = k_D p_s$ ,  $K = C'_H f b p_s$ , and  $B = b p_s$ , with  $p_s$  the penetrant saturated vapor pressure and *f* a conversion factor.<sup>19</sup> The model that we summarized above has been particularly useful in describing the sorption data of permanent gases in glassy polymers. However, eq. (7) did not reproduce, with a similar accuracy, the sorption data of organic or water vapors on polymer films,<sup>20,21</sup> showing positive deviations to the Henry's mechanism, especially at

Table IVWater-Sorption Coefficients at 30°C atthe Steady State

Sample	$S_w (g_{\text{water}}/g_{\text{pol}} \text{ atm})$
PEI PEI/Rodrun 95/5 PEI/Rodrun 90/10 PEI/Rodrun 85/15 Rodrun	$egin{array}{c} 32.03 imes10^{-2}\ 30.68 imes10^{-2}\ 29.64 imes10^{-2}\ 28.67 imes10^{-2}\ 3.145 imes10^{-2}\ \end{array}$

high activities. As pointed out in the Introduction, this kind of behavior has been related to the swelling of the polymer by the solute. This swelling generates new free-volume sites where additional solute molecules can be sorbed. In other cases, solute molecules seem to cluster in aggregates.<sup>22</sup> This clustering effect can immobilize solute molecules, with an experimental decrease in the diffusion coefficient.

These deviations from the classical dual model have been explained with the introduction of new formulations. A concentration dependence of the Henry's coefficient has been proposed in some cases,<sup>23–25</sup> whereas Berens<sup>26</sup> introduced the Flory– Huggins theory, as a generalized version of the Henry's term, in order to fit sorption data in the vinyl choride/PVC system. Similar, satisfactory, results using a Flory–Huggins contribution were reported by Hernandez et al.<sup>19</sup> in fitting the experimental data of water sorption to an amorphous polyamide.

At a high molecular weight of the polymer, the Flory–Huggins expression predicts a relationship between activity and equilibrium concentration:

$$\ln a = \ln \phi_w + \phi_p + \chi \phi_p^2 \tag{8}$$

where  $\phi_w$  is the water volume fraction,  $\phi_p$ , the polymer volume fraction; and  $\chi$ , the well-known Flory–Huggins interaction parameter. Equation (8) does not give, in most cases, a quantitative description of the polymeric solutions, although reasonable qualitative trends can be inferred from it. As previously mentioned, the Flory–Huggins equation is a generalization of the Henry's law for low penetrant activities. Therefore, it is possible to express the equilibrium concentration as a penetrant volume fraction separated into two contributions:

$$\phi_w = \phi_w^{FH} + \phi_w^L \tag{9}$$

where  $\phi_w^{FH}$  is the Flory–Huggins contribution to the total amount of the sorbed penetrant and  $\phi_w^L$ is the corresponding Langmuir contribution. This Langmuir contribution has the same mathematical form as that in eq. (7), whereas the Flory– Huggins one is not linear and should be resolved by iterative or numerical methods, for instance, Newton–Raphson. In doing so, eq. (7) can be rewritten as

$$\phi_w = \phi(a,\chi) + \frac{Ka}{1+Ba} \tag{10}$$



**Figure 2** Water-sorption isotherm for the PEI film: (squ;) experimental points; (•) dual-mode theoretical data; (—) modified dual-mode theoretical data.

where  $\phi(a,\chi)$  is the penetrant volume fraction obtained from the Flory–Huggins equation for each activity and interaction parameter value. When the Flory–Huggins and Langmuir contributions are used together to explain sorption data, we will denote the model as the modified dual model (MDM).

Sorption data, similar to those exhibited in Figure 1 but in the form of the volume fraction  $\phi_w$  (i.e., without reducing to the water-vapor activity) were used in order to check different fitting expressions. In all cases, the efficiency of the fitting method was quantified as the average error:

$$\operatorname{Error} = \frac{1}{n} \sum_{i=1}^{n} \frac{\operatorname{abs}[\phi_w(\operatorname{experimental}) - \phi_w(\operatorname{theoretical})]}{\phi_w(\operatorname{experimental})} \quad (11)$$

As shown in Figure 2, our data have small contributions of the Langmuir term. This is reflected in the nearly linear appearance of the figure. On the other hand, similar fits were obtained using both the dual mode or the modified dual mode. For the other membranes, we obtained similar behavior. Tables V and VI give the results corresponding to the fitting parameters appearing in eqs. (7) and (10), respectively. Subtle differences favoring the modified dual model are revealed by these tables, but the low water solubility in the different investigated films does not allow any deeper comparison.

Other fitting attempts can be undertaken if we consider the heterogeneous character of our samples. In the preceding fittings, the blend films

Table VII Average Freeze Between

Sample	$K_D$	В	K	Error
PEI	0.0160	163.4	0.074	0.0277
PEI/Rodrun 95/5	0.0150	347.4	0.200	0.0273
PEI/Rodrun 90/10	0.0143	181.0	0.112	0.0198
PEI/Rodrun 95/15	0.0128	258.0	0.199	0.0217
Rodrun	0.0138	358.0	0.199	0.0217
	0.0017	380.0	0.0131	0.0281

Table VDual-Model Parameters [eq. (7)] forthe PEI/Rodrun at 30°C

Tuble VII Inverage Errors Derween
Experimental Water Solubilities and Those
Calculated Using Dual and Modified Dual
Model Assuming Additivity [eq. (12)]

Model	PEI/Rodrun	PEI/Rodrun	PEI/Rodrun
	95/5	90/10	85/15
Dual Modified	$0.0338 \\ 0.0291$	$0.0353 \\ 0.0294$	$0.0396 \\ 0.0297$

were considered as isotropic and the fitting parameters characterized the whole solubility process in the blend. However, EM evidenced<sup>1</sup> the heterogeneous character of our samples. In trying to fit data to heterogeneous samples, the first and easier idea is to assume an additive character, using the data of the pure components and the blend composition. Furthermore, we must consider that both polymers are totally separated; thus, each component constitutes its own phase where the other component is not present.

If this assumption is correct, the water-volume fraction in the blend film could be calculated as

$$\phi_w = \phi_A \, V_A + \phi_B \, V_B \tag{12}$$

where  $\phi_w$  is the total volume fraction of water in the film,  $\phi_i$  the volume fractions of the *i* component in the polymer blend, and  $V_i$ , the water volume fraction absorbed at a given activity in the *i* pure polymer. For instance, when it is assumed that the dual model is obeyed in both separated phases, the latter equation takes the following form:

$$\phi_w = \phi_A \left( K_{D_A} a + \frac{K_A a}{1 + B_A a} \right) + \phi_B \left( K_{D_B} a + \frac{K_B a}{1 + B_B a} \right) \quad (13)$$

Table VIModified Dual-Model Parameters[eq. (10)] for the PEI/Rodrun at 30°C

Sample	χ	В	K	Error
PEI	3.24	33.8	0.028	0.0261
PEI/Rodrun 95/5	3.27	149.2	0.100	0.0232
PEI/Rodrun 90/10	3.30	224.6	0.146	0.0188
PEI/Rodrun 85/15	3.33	645.0	0.380	0.0179
Rodrun	5.37	1063.0	0.050	0.0269

A similar expression can be written for the modified dual model. As expected, solubilities calculated according to eq. (12) reproduced the experimental results reasonably well and with similar average errors to those previously described. The observed variations when pure parameters were taken from dual-model or modified dual-model fittings were also unimportant, at least in a first approximation. However, in studying the variation of the average errors with the blend composition, it appears that they deviate from additivity when the Rodrun concentration in the blend increased (see Table VII).

To explain this slight tendency to nonadditivity, we used a recent proposal of Morisato et al.<sup>27</sup> According to the authors, even in phase-separated samples, a free-volume excess can appear as a consequence of the presence of the second component. They applied this idea to a mixture of poly(1-trimethylsylyl-1-propine) (PTMSP) and poly(1-phenyl-1-propine) (PTP), exposed to vapors of *n*-propane and *n*-butane. Although this is a mixture in which the free volume should play a more important role than in the mixture that we are studying in this article, we would like to test the implications of such a type of analysis for our membranes.

In the above-mentioned article, although PTMSP and PPP are stated to be clearly immiscible, experimental gas solubilities and those calculated using additivity were different.<sup>27</sup> Based on the large excess of the free volume exhibited by PTMSP, the authors hypothesized that these differences could arise from a deviation of the real free volume with respect to the additive one. This deviation should affect mainly the Langmuir parameters K and B. In other words, the free volume in the phase-separated mixtures is influenced by the presence of the second component and this influence is interpreted as a consequence of the presence of an interphase which contributes to the total free volume of the mixture.

	- 1		
	PEI/Rodrun	PEI/Rodrun	PEI/Rodrun
	95/5	90/10	85/15
$K_M$	$0.5171 \\ 1043.3 \\ 0.0302$	0.5074	0.5619
$B_M$		967.3	1063.3
Error		0.0208	0.0218
101	0.0302	0.0208	0.0210

Table VIII Langmuir Contribution Parameters to the Water Solubility in Three Different PEI/ Rodrun Films Assuming No Additivity of the Dual Mode [eq. (15)]

With this idea in mind, the total solubility can be calculated by assuming an additive behavior of the Henry's law term whereas the Langmuir contribution is not supposed to be additive and can be represented by characteristic parameters of the blend under consideration. A similar treatment could also be proposed for the modified dual mode, but since the fittings of both models are quite similar and given the mathematical simplicity of the dual model, in this work, we focused only on this latter one. In mathematical terms, the Henry's constant of the mixture can be written as

$$K_{D_M} = \phi_A K_{D_A} + \phi_B K_{D_B} \tag{14}$$

but the Langmuir term will contain parameters  $K_M$  and  $B_M$ , which can be seen as characteristic of each mixture. Consequently,

$$\phi_w = K_{D_M} a + \frac{K_M a}{1 + B_M a} \tag{15}$$

Table VIII summarizes the values of  $K_M$  and  $B_M$  for the investigated films calculated according to eq. (15), as well as the average deviations from eq. (11). There are not significant differences in the values of  $K_M$  and  $B_M$  corresponding to the different films, although they are very different from those calculated for the pure components using the dual mode (see Table V). However, this is not very important, because, even with these differences, the Langmuir contribution is small and of the same order.

The average deviations shown in Table VIII are smaller than those summarized in Table VII, where additivity is assumed. Furthermore, the improvement has been obtained only by modifying the parameters related to the Langmuir fraction, which is the term having a minor contribution to the total sorbed water. Besides, the error values in the last table actually are very close to those summarized in Table V, in spite of the three adjustable parameters used there instead of the two used in Table VIII. Both comparisons seem to support the idea of a nonadditive character of the Langmuir contribution and the necessity of fitting the most adequate parameters for each blend. Figure 3 illustrates that the Langmuir contribution, calculated according to eq. (15), is higher than the additive one. It should be remembered that, implicit in eq. (15), is the idea of an excess free volume as a consequence of the interphase in the biphasic mixture.

This is just the opposite behavior to that found by Morisato et al.<sup>27</sup> in PTMSP/PPP blends. But PTMSP is a high free-volume polymer, for which it seems reasonable to think that any blend with a second component could reduce the free volume available. The situation for both PEI and Rodrun is completely different with a substantially lower free volume which could be increased by the effect of an interphase, which, on the other hand, should be different for every film.

#### Permeability and Morphology: Two-phase Model

Table IX shows the water permeabilities (in Barrer) of the different investigated films. These permeabilities were calculated from the experimental data of  $D_W$  and  $S_W$  (in adequate units) using eq. (1). It is clear that the presence of small contents of Rodrun induces a marked decrease in the water permeability, as expected.

In the following, we resume our attempt to explain this behavior, taking into account the



**Figure 3** The Langmuir contribution to the water sorption for both the PEI/Rodrun 95/5 and 85/15 where additive values are compared with those calculated using eq. (15).

Sample	P (Barrer)
PEI PEI/Rodrun 95/5 PEI/Rodrun 90/10 PEI/Rodrun 85/15 Rodrun	$136.6 \\ 119.3 \\ 105.1 \\ 74.5 \\ 16.4$

Table IX Water Permeability Coefficients at  $30^{\circ}$ C Obtained from  $S_W$  and  $D_W$ 

blend morphology, previously evidenced by  $\text{EM.}^1$ In a similar manner to that used in the previous article,<sup>1</sup> and using the so-called two-phase model, the permeability coefficient of the mixture can be calculated on the basis of the permeabilities of the pure components and the morphology of the membrane.<sup>28,29</sup>

In this approach, membranes are considered to be composed of distinct microscopic domains of noninteracting components A and B, characterized by the permeability coefficients  $P_A$  and  $P_B$ , similar to those of the corresponding bulk phases. The composite is conceived as a microparticulate dispersion of the minority component (A) in a continuous matrix of the other (B). The dispersed phase can be defined in terms of particle shape, size, orientation, and mode of packing.<sup>28,30,31</sup> After defining the relation between the permeabilities of the same penetrant in both components,  $\alpha$ , as

$$\alpha = \frac{P_A}{P_B} \tag{16}$$

it is possible to obtain simple expressions for dispersions of spheres or long cylindrical rods. The different equations can be included in a general equation<sup>28,29</sup> which relates the composite permeability with the pure components permeabilities ( $P_A$  and  $P_B$ , which are supposed to be independent of the concentration of the permeant), the relation between the permeabilities,  $\alpha$ , the composition (in terms of the volume fractions of the components,  $\phi_A$  and  $\phi_B = 1 - \phi_A$ ), and the morphology of the composite medium:

$$P = P_B \left[ 1 + (1+A)\phi_A \left( \frac{\alpha+A}{\alpha-1} - \phi_A \right)^{-1} \right]$$
 (17)

Different morphologies are considered through the A parameter. When  $A \rightarrow \infty$  or A = 0, eq. (17) leads, respectively, to the arithmetic or the harmonic mean permeability of laminate of A and Boriented so that the laminations are parallel or normal to the direction of flow. A = 2 yields the Maxwell equation for a dilute dispersion of spheres, in which interparticle distances are sufficiently large to ensure that the flow around any sphere is practically undisturbed by the presence of the others. Finally, when A = 1, eq. (17) describes the case of long transverse cylinders oriented at right angles to the direction of the flow, with the morphology related to the fibers.

Using eq. (17) with different values of the A parameter of the simplified models (A = 0, A = 1, A = 2 and  $A \rightarrow \infty$ ), we found that none is adequate to describe the observed experimental behavior. Also, a deviation is particularly relevant for the film with 15% of Rodrun. As EM photomicrographs have demonstrated,<sup>1</sup> whereas the films with 5 and 10% of Rodrun showed a fibrillar structure, the film with 15% of Rodrun is basically laminate. Then, our film structure is a mixture between fibers and lamellae, these last increasing with the Rodrun amount in the mixture. That could be the reason why our experimental data do not fit the equations properly.

Values of *A* may be calculated using eq. (17) for each composite composition. Table X summarizes the results of this calculation using water-vapor data as well as carbon dioxide data taken from our previous article.<sup>1</sup>

The table clearly evidences that, both with water vapor and carbon dioxide, the 85/15 composite behaves in a different manner from that of the other two compositions. This is consistent with our previous conclusion,<sup>1</sup> according to which experimental data of the transport properties could be of interest in extracting qualitative conclusions about membrane morphology.

## **CONCLUSIONS**

The addition of an LCP (Rodrun) to a glassy polymer (PEI) has an important effect on the water-

Table X Values of the Morphological
Parameter A [See eq. (17)] from Experimental
Data of Permeability Coefficients of Water
Vapor and Carbon Dioxide <sup>1</sup>

	PEI/Rodrun	PEI/Rodrun	PEI/Rodrun
	95/5	90/10	85/15
$\begin{array}{c} \mathrm{H_{2}O}\\ \mathrm{CO_{2}} \end{array}$	$\begin{array}{c} 0.16\\ 0.28\end{array}$	$\begin{array}{c} 0.23\\ 0.26\end{array}$	$\begin{array}{c} 0.03\\ 0.14\end{array}$

vapor transport properties of the thermoplastic. Diffusion, solubility, and the global process, permeability, were quantified. In all cases, the effect of a high barrier material, such as Rodrun, is clearly evident. The experimental results of solubilities and permeabilities were analyzed on the basis of some approaches which take into account the deviations from the simple additive rules. These deviations are caused mainly by the morphology of the heterogeneous blends. In the case of the solubility results, the possible excess free volume arising from the interphase region seems to cause the Langmuir contribution to deviate from additivity. In the permeability case, the different morphologies induced during the blend preparation are the origin of the deviations from the additive rule.

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#### REFERENCES

- Uriarte, C.; Alfageme, J.; Iruin, J. J. Eur Polym J 1998, 34, 1495.
- Chiou, J. S.; Paul, D. R. J Polym Sci Polym Phys Ed 1987, 25, 1699.
- 3. Weinkauf, D. H. Paul, D. R. J Polym Sci Polym Phys Ed 1992, 30, 817.
- Weinkauf, D. H.; Kim, H. D. Paul, D. R. Macromolecules 1992, 25, 788.
- Koros, W. J.; Fleming, G. K. Jordan, S. M. Kim, T. H.; Hoehn, H. H. Prog Polym Sci 1988, 13, 339.
- Schult K. A.; Paul, D. R. J Appl Polym Sci 1996, 61, 1865.
- Schult, K. A.; Paul, D. R. J Polym Sci B Polym Phys Ed 1997, 31, 993.
- Sykes, G. F.; St. Clair, A. K. J Appl Polym Sci 1986, 32, 3725.

- Sacher, E.; Susko, J. R. J Appl Polym Sci 1981, 26, 679.
- Yang, D. K.; Koros, W.J.; Hopffenberg, H. B.; Stannet, W. T. J Appl Polym Sci 1986, 31, 1619.
- Okamoto, K.; Tanihara, N.; Watanabe, H.; Tanaka, K.; Kita, H.; Nakamura, A.; Kusuki, Y.; Nakagawa, K. J Polym Sci Polym Phys Ed 1992, 30, 1223.
- 12. Bastida, S.; Eguiazabal, J. I.; Nazabal, J. Eur Polym J, in press.
- Vieth, W. R.; Aminy, M. A. In Permeability of Plastic Films and Coatings to Gases, Vapors and Liquids; Hopfenberg, H. B., Ed.; Plenum: New York, 1974; p 49.
- Bastida, S.; Eguiazabal, J. I.; Nazabal, J. J Appl Polym Sci 1995, 56, 1487.
- Hernandez, R. J.; Gavara, R. J Polym Sci Polym Phys Ed 1994, 32, 2367.
- Crank, J. The Mathematics of Diffusion, 2nd ed.; Clarendon: Oxford, 1975.
- Lokhandwala, K. A.; Nadakatti, S. M.; Stern, S. A. J Polym Sci Polym Phys Ed 1995, 33, 965.
- Barrer, R. M.; Barrier, J. A.; Slater, J. J Polym Sci 1958, 27, 177.
- Hernandez, R. J.; Giacin, J. R.; Grulke, E. A. J Membr Sci 1992, 65, 187.
- 20. Mauze, G. R.; Stern, S. A. J Membr Sci 1982, 12, 51.
- 21. Mauze, G. R.; Stern, S. A. J Membr Sci 1984, 18, 99.
- 22. Lundberg, J. L. J Pure Appl Chem 1972, 31, 261.
- Yang, D. K.; Koros, W. J.; Hopfenberg, H. B.; Stannett, V. T. J Appl Polym Sci 1985, 30, 1035.
- Barrer, J. A.; Sagoo, P. S.; Johncock, P. J Membr Sci 1984, 18, 197.
- Apicella, A.; Tessieri, R.; De Cataldis, C. J Membr Sci 1984, 18, 211.
- 26. Berens, A. R. Angew Makromol Chem 1975, 47, 97.
- Morisato, A.; Freeman, B. D.; Pinnau, I.; Casillas, C. G. J Polym Sci Polym Phys Ed 1996, 34, 1925.
- Barrer, R. M. In Diffusion in Polymers; Cranck, J.; Park, G. S., Eds.; Academic: London, 1968; Chapter 6.
- Petropoulos, J. H. J Polym Sci Polym Phys Ed 1985, 23, 1309.
- 30. de Vries, D. A. Bull Inst Int Froid Ann 1952-1, 115.
- 31. Nielsen, L. E. Ind Eng Chem Fund 1974, 13, 17.