# Oxygen Permeation Through Films of Compatibilized Polypropylene/Polyamide 6 Blends

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**ABSTRACT:** Polypropylene/polyamide 6 blends were prepared by melt mixing, without or with the addition of a suitable commercial product, a polypropylene grafted with 1% maleic anhydride, used as an interfacial modifier. The oxygen permeation through their films was studied as a function of temperature and the effect of the presence of the compatibilizer on the barrier properties of the material was examined. In addition, the diffusion coefficients were measured. The relationships between transport parameters and blend morphology were investigated by microscopic observations, together with chemical etchings, and a simple model was applied for interpreting the experimental permeation data. Differential scanning calorimetry was used in the determination of the degree of crystallinity of the blends. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1941–1949, 1999

**Key words:** polyamide 6; polypropylene; permeation; blends; compatibilization

## INTRODUCTION

Packaging applications require good barrier properties as a means of achieving a long shelf life for a product. However, when using for packaging a single polymer, it is difficult to attain all together the properties required: so, a polymer with good oxygen barrier properties may show poor water barrier properties, while another polymer may present an opposite behavior.

In this context, polyolefins and polyamides can be usefully melted together to obtain blends, in which the properties of the former component can be combined with those of the latter.[1–3] For instance, the properties of insensitivity to moisture and impact strength on one side and the barrier property vs oxygen on the other side can be exploited.

Unfortunately, polyolefins and polyamides are not miscible, so that a third component—a compatibilizer—has to be added in order to improve their interfacial adhesion and to enhance the material homogeneity. In this way, the properties of the compatibilized blends can become better than those of the uncompatibilized ones.

Functionalized polypropylene compatibilizers are popular third components used for improving both adhesion and mixing in polypropylene/polyamide system. Compatibilizing agents for these blends have been developed by grafting maleic anhydride onto polypropylene chains, where the amount of grafted anhydride can be varied.[4] In polypropylene/polyamide blends, the polypropylene grafted maleic anhydride compatibilizer forms a chemical linkage through the reaction of anhydride groups with the polyamide end groups. Consequently, a graft copolymer with segments of polypropylene and polyamide is formed *in situ* at the interface.[5] The graft copolymer improves the inter-

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facial compatibility, associating the different segments with their respective components.

In the present work, polypropylene/polyamide 6 blends prepared with and without compatibilizer have been considered. The characterization of these blends was previously[1,2] made using several techniques such as differential scanning calorimetry (DSC), scanning electron microscopy (SEM), wide angle x-ray diffusion (WAXD), interfacial tension measurements and mechanical tests.

The aim of this work has been to study how oxygen permeation parameters, like permeability $P$, diffusion $D$, and solubility $S$ coefficients, depend on the composition of compatibilized and unmodified polypropylene/polyamide blends. Also, the effect of the compatibilizer amount and the influence of the temperature on the transport parameters have been investigated.

## EXPERIMENTAL

### Materials

The polymers employed in this work were as follows: Daplen KFC 2206, manufactured by Petrochemie Danubia, which is a polypropylene containing 6% by weight of ethylene as random comonomer (PP); Grilon F 34, manufactured by EMS Chemie, which is a polyamide 6 (PA6); and Orevac CA 100, manufactured by ELF Atochem, which is a polypropylene grafted with 1% by weight of maleic anhydride (OR).

### Development of the Blends

The polymer films were prepared by calendering the melt-blended mixture of PP, PA6, and OR extruded from their powders; blending was made in a Gimac single-screw micro-extruder with five zones kept at 260°C and with a screw speed of 38–48 rpm. Before mixing in a one-step process, the components were separately ground and sieved (20 mesh) and PA6 was dried for 105 min at 105°C. After calendering, the materials were dried in a vacuum desiccator. The weight composition of the plain and compatibilized PP/PA6 blends were 100/0, 90/10/0, 90/10/1 80/20/0, 80/20/2, 70/30/0, 70/30/3 60/40/4, and 50/50/5. We are also examined a cast film of pure PA6 prepared in an industrial extruder. The PA6 was extruded at 260°C and quenched in a cold air stream.

### Thermal Determinations

The degree of crystallinity of the various components was studied by differential scanning calorimetry (Perkin Elmer DSC-4), measuring the melting enthalpies of the single polymers in the blends. The specimens (8–10 mg), encapsulated in aluminum pans, were heated at a scanning rate of 20°C/min. All the experiments were performed under a constant flow of dry nitrogen. The fusion enthalpies $\Delta H_{f,PP}$ or $\Delta H_{f,PA}$ were measured and the crystallinity degrees $x_{c,PP}$ and $x_{c,PP}$ were calculated by the following equations:

$$x_{c,PP} = \Delta H_{f,PP}/\Delta H^\circ_{f,PP} \qquad x_{c,PA} = \Delta H_{f,PA}/\Delta H^\circ_{f,PA}$$

where $\Delta H^\circ_{f,PP}$ (50.0 cal/g)[6,7] and $\Delta H^\circ_{f,PA}$ (55.0 cal/g)[6-9] are the fusion enthalpies of completely crystalline PP and PA, respectively.

### Morphological Determinations

Blend morphology was investigated by SEM: film samples were cryogenically fractured perpendicular to the extrusion direction [i.e.. Fig. 1(a)]. Alternatively, other samples (i.e., Fig. 2) was obtained from cryogenical delamination of the film: the delamination is a well-known phenomenon that heterogeneous film shaped blends present when they are subjected to mechanical stress.

The surfaces of the fractured specimens were coated with gold to avoid charging an electron beam. The Philips Model 515 scanning electron microscope operated at 9.4 kV.

### Treatment of Polymers with Selective Solvents

PA6-containing materials were treated with formic acid to remove the polyamide fraction not bound to the compatibilizer in order to evidence the phase discontinuity in compatibilized blends. The film samples were fractured, then treated in a formic acid solutions (88% w/w) for 24 h, and finally dried. Formic acid solution at lower concentration (61% w/w) was employed in some case in order to reduce the solvent capacity. In other samples, to evidence the shape of PA6 dispersed particles, the PP matrix was dissolved by treatment with toluene vapor at boiling point.

### Permeation Measurements

The determination of the transport coefficients of oxygen through the polymer films was made at atmospheric pressure by the differential perme-
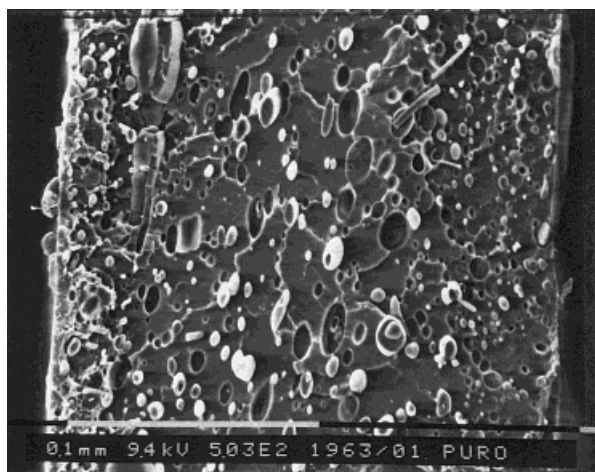
(a)
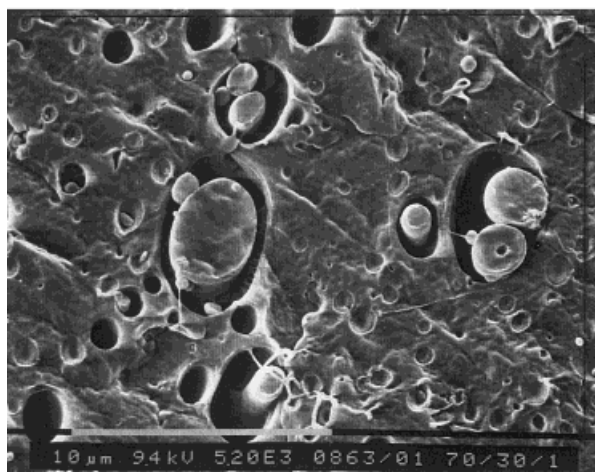
(b)

**Figure 1** SEM micrographs of cryogenically fractured surface perpendicular to extrusion direction: (a) 70/30/0 PP/PA6/OR blend; (b) 70/30/3 PP/PA6/OR blend, treated with 61% formic acid. Magnification: scale bar 0.1 mm and 10 $\mu$m, respectively.

ation method, using a Perkin Elmer Autosystem gas chromatograph, equipped with a thermal conductivity detector. The carrier gas was helium and the solid phase was 60/80 molecular sieve 5A. The design and operation of the apparatus used for the oxygen transport have been described in detail elsewhere.[10] The temperature range considered for the measurements of permeability ($P$) was from 12 to 29°C. From the same runs the diffusion coefficients ($D$) were determined by the time-lag method. The solubility coefficients $(S)$ were calculated from the formal relation $S = P/D$. No separate solubility measurements were made.

## RESULTS AND DISCUSSION

The permeability and the solubility coefficients at 23°C of the considered blends are reported in Figures 3 and 4, respectively, as functions of the volume fraction of the dispersed phase (PA6). The very low value of $P$ for pure PA6 indicates that its contribution to the transport properties of the material is almost negligible. Thus, the decreasing trend in Figure 3 reflects the decreasing amounts of PP in the plain as well as in the compatibilized blends. The inspection of the same figure also reveals that the transport parameter is higher for the compatibilized blend than for the unmodified ones, so evidencing that a more extended dispersion favors the permeability. Accordingly, the gap between the two curves increases with the increase of the amount of compatibilizer OR, since the ratio OR/PA6 has been kept constant.

Figure 3 also reports the curves corresponding to

$$P = P_{PP}(1 - \Phi_{PA6})/(1 + \tfrac{1}{2}(L/W)\Phi_{PA6}) \qquad (1)$$

where $P_{PP}$ is the permeability of pure PP, $\Phi_{PA6}$ is the volume fraction of PA6 in the blend, and $L/W$ is the ratio between length and thickness of the hypothetical uniformly dispersed plates of PA6 in the PP matrix. This equation, proposed for filled polymers with platelike particles,[11] can be employed in the present case since the permeability
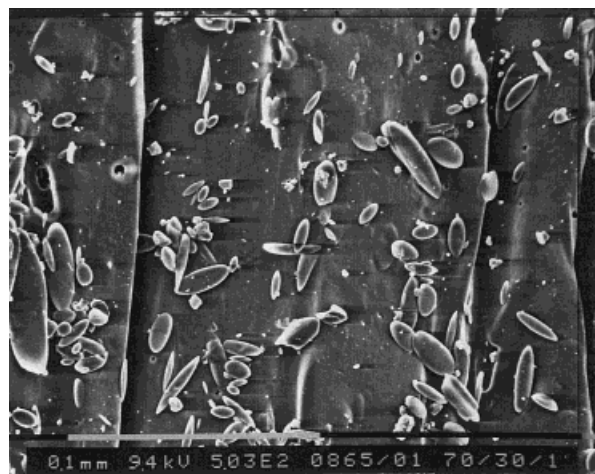


**Figure 2** SEM micrograph of surface of 70/30/0 PP/PA6/OR blend, treated with toluene vapor. Magnification: scale bar 0.1 mm.
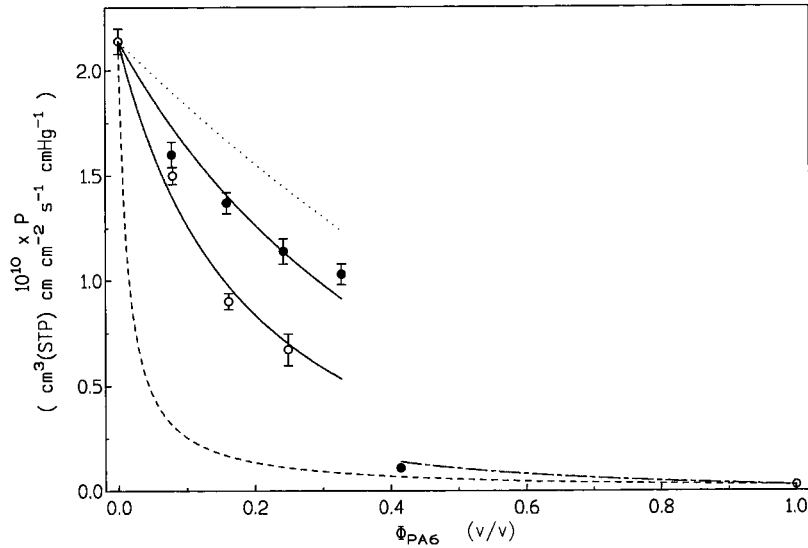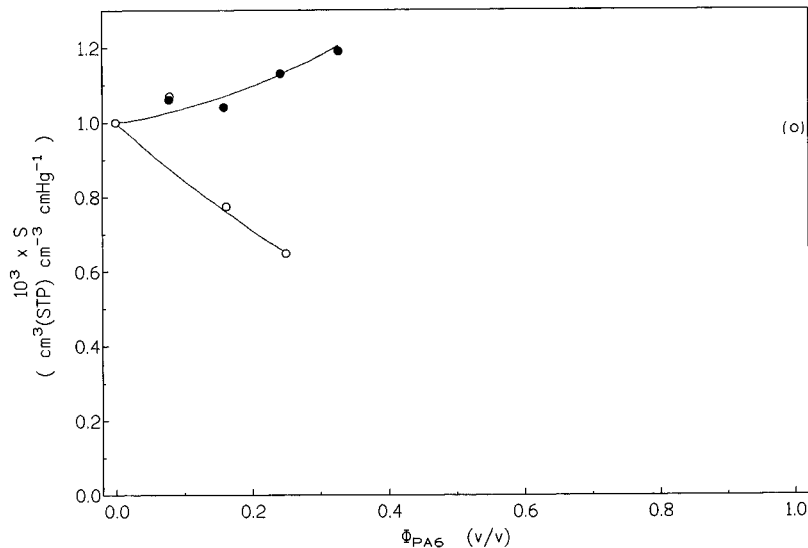
**Figure 3** Oxygen permeability coefficients ($P$) of plain ($\bigcirc$) and compatibilized ($\bullet$) PP/PA6 blends at 23°C vs PA6 volume fraction ($\Phi_{PA6}$). Compatibilizer OR/PA6 ratio: 1/10 by weight. For other curves, see text.

of dispersed PA6 phase is negligible, on the condition that an average value of $L$ is considered.

According to eq. (1), the permeability of the PP/PA6 blends here considered is given by the permeability of pure PP multiplied by its volume fraction and divided by term $[1 + \frac{1}{2}(L/W)\Phi_{PA6}]$. This term is an approximated estimate[11,12] of the tortuosity factor ($\tau$), i.e., of the factor that take

into account that an impermeable dispersed phase imposes a more tortuous path upon the steady-state permeation of a penetrant across the polymer film. The $\tau$ is defined as the ratio of the effective path length required for permeation divided by the actual film thickness. In the above term, $L$ is taken to be parallel to the composite surface.



**Figure 4** Oxygen solubility coefficients ($S$) of plain ($\bigcirc$) and compatibilized ($\bullet$) PP/PA6 blends at 23°C vs PA6 volume fraction ($\Phi_{PA6}$). Compatibilizer OR/PA6 ratio: 1/10 by weight.

**Table I  Values of the Form Factor *L/W* for Experimental Data at 12, 23, and 29°C**

| $T$(°C) | Unmodified Blends | | Compatibilized Blends | |
|---|---|---|---|---|
| | *L/W* | *r* | *L/W* | *r* |
| 12 | 11.8 | 0.99 | 5.19 | 0.98 |
| 23 | 10.4 | 0.99 | 3.51 | 0.99 |
| 29 | 10.7 | 0.99 | 3.38 | 0.99 |
| Mean | 11.0 | | 4.03 | |

The calculated upper curve in Figure 3, drawn for $L/W = 1$, corresponds to the model of completely dispersed spheres of PA6 in the PP matrix. For the compatibilized and unmodified blends, the best fittings of the theoretical model on the experimental data at 12, 23, and 29°C have given the values of *L/W* reported in Table I, from which mean values of 4.0 and 11.0 can be obtained. The value of *L/W* for the unmodified blends is in line with the results shown in Figure 1(a) and 2. The latter figure allows to evidence the length of the PA6 domain that cannot be observed in the fractured samples; in the present case the PP matrix is dissolved by toluene and the micrograph evidence domains of PA6 deposed on remaining film. They reveal the presence of large domains of PA6 oriented to the extrusion direction, with their flat surfaces parallel to the film and with shapes in rough agreement with the value $L/W = 11$.

For the compatibilized blends ($L/W = 4$), no experimental verify has been possible. However, the compatibilizer effect appeared to generate a general rounding off of the PA6 dispersed particles, as can be observed comparing the fractured surfaces of the unmodified blends [Fig. 1(a)] with those of the compatibilized ones (Fig. 5).

The lowest curve in Figure 3 corresponds to the permeability trend calculated for coextruded structures of PP and PA6, i.e., for films consisting of two separate sheets of PP and PA6, according to[13]:

$$1/P = \Phi_{PA6}/P_{PA6} + (1 - \Phi_{PA6})/P_{PP} \qquad (2)$$

This trend, in absence of any dispersion of PA6 in PP matrix, represents, to a certain extent, the counterpart of the highest curve. Eventually, on the right side of Figure 3, a curve has been drawn according to the Maxwell equation[12]:

$$P = P_{PP}\frac{P_{PA6} + 2P_{PP} - 2\Phi_{PA6}(P_{PP} - P_{PA6})}{P_{PA6} + 2P_{PP} + \Phi_{PA6}(P_{PP} - P_{PA6})} \qquad (3)$$

This equation applies for spheres of PP dispersed in a PA6 matrix, —namely, after the phase inversion occurring for $\Phi_{PA6} > 0.4$. In this case, the permeability of the dispersed phase cannot be neglected. The last curve shows that the decrease of permeability induced by the phase inversion is as marked to reach values close to those of the coextruded films.

A further comment on the results shown in Figure 3 regards the slight but regular deviation of the experimental data of the compatibilized blends with respect to the corresponding optimized curve. Such a deviation is likely attributable to a decrease of the form factor *L/W* with the increase $\Phi_{PA6}$. Thus, a decrease of the *L/W* value from 5.95 to 2.44 has been evaluated on going from 90/10/1 to 60/40/4 PP/PA6/OR blends. However, also the increase of the blend viscosity[14] with the PA6 content can play an important role in modifying the film morphology.

As to Figure 4, the oxygen solubility coefficients of the compatibilized blends appear to be progressively increasing with $\Phi_{PA6}$ or more correctly, with the content of OR (the OR/PA6 ratio has been kept constant). However, the oxygen solubility coefficients of the unmodified PP/PA6 blends decrease when $\Phi_{PA6}$ increases. Since the oxygen solubility is much lower in PA6 than in PP, it can be inferred that in the former case the
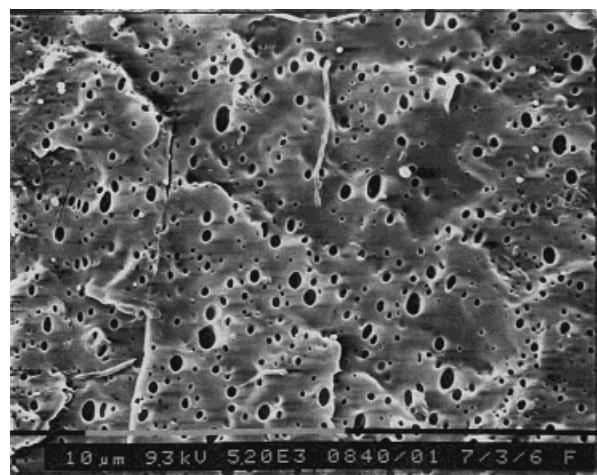


**Figure 5**  SEM micrograph of cryogenically fractured surface perpendicular to extrusion direction of 70/30/6 PP/PA6/OR blend, treated with 88% formic acid. Magnification: scale bar 10 $\mu$m.

**Table II   Experimental Fusion Enthalpies ($\Delta H_f$) and Crystallinity Degree ($x_c$) of PP and PA6 in PP/PA6/OR Blends**

| PP/PA6/OR (Weight Ratio) | $\Delta H_{f,PP}$ (kJ g$^{-1}$) | $x_{c,PP}$ | $\Delta H_{f,PA6}$ (kJ g$^{-1}$) | $x_{c,PA6}$ |
|---|---|---|---|---|
| 100/0/0 | 78.1 | 0.373 | | |
| 90/10/0 | 75.7 | 0.362 | 66.1 | 0.287 |
| 90/10/1 | 70.0 | 0.334 | 61.1 | 0.266 |
| 80/20/0 | 72.2 | 0.345 | 80.8 | 0.351 |
| 80/20/2 | 69.1 | 0.330 | 59.9 | 0.261 |
| 70/30/0 | 70.1 | 0.335 | 77.4 | 0.336 |
| 70/30/3 | 75.7 | 0.362 | 72.4 | 0.315 |
| 60/40/4 | 64.0 | 0.306 | 67.4 | 0.292 |
| 0/100/0 | | | 58.2 | 0.253 |

OR effect prevails over the PA6 effect, while the opposite occurs in the latter. The OR effect is reasonably associated with the increase of the amorphous phase due to the graft polymer, which leads to an enhancement of the oxygen solubility. The increase of the amorphous phase in the presence of OR is evidenced by the results reported in Table II in terms of the lowering of the crystallization degree, as determined by DSC measurements, on going from plain to compatibilized blends. Apart from one case, a unique trend can be observed, but we cannot exclude also a morphological effect due to the compatibilization. Such an increase of the amorphous phase could be also invoked to explain the enhancement of permeability in the presence of OR, since it is known

that the transport phenomena take place in the amorphous region. On the other hand, the permeation values normalized to the PP amorphous fraction ($P'$, Table III), determined as

$$P' = [P/(1 - x_{c,PP}]$$
$$\times [(w_{PP} + w_{OR} + w_{PA6})/(w_{PP} + w_{OR})] \quad (4)$$

where $w_{PP}$, $w_{PA6}$, and $w_{OR}$ represent the weight fraction of the pure polymer in the blend. The $P'$ values have not been found to be constant, as it should be expected if the extent of the amorphous region were the only factor governing the permeability. On the contrary, $P'$ values have been

**Table III   Complete Set of Permeability ($P$), Diffusion ($D$), and Normalized Permeability ($P'$) Coefficients at 12, 23, and 29°C**

| PP/PA6/OR (Weight Ratio) | $P$ $\left(\dfrac{cm^3 (STP) \cdot cm}{cm^2 \cdot s \cdot cm\ Hg}\right)$ | | | $D \times 10^7$ (cm$^2$s$^{-1}$) | | | $P'$ $\left(\dfrac{cm^3 (STP) \cdot cm}{cm^2 \cdot s \cdot cm\ Hg}\right)$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | 12°C | 23°C | 29°C | 12°C | 23°C | 29°C | 12°C | 23°C | 29°C |
| 100/0/0 | 1.23 | 2.14 | 3.12 | 1.16 | 2.14 | 2.75 | 1.96 | 3.41 | 4.98 |
| 90/10/0 | 0.841 | 1.50 | 2.16 | 0.765 | 1.39 | 1.56 | 1.46 | 2.61 | 3.76 |
| 90/10/1 | 0.816 | 1.60 | 2.30 | 0.828 | 1.51 | 2.20 | 1.36 | 2.66 | 3.83 |
| 80/20/0 | 0.490 | 0.902 | 1.35 | 0.581 | 1.17 | 1.25 | 0.935 | 1.72 | 2.58 |
| 80/20/2 | 0.682 | 1.37 | 1.99 | 0.635 | 1.32 | 1.77 | 1.27 | 2.54 | 3.69 |
| 70/30/0 | 0.338 | 0.678 | 0.916 | 0.515 | 1.05 | 1.43 | 0.726 | 1.55 | 1.97 |
| 70/30/3 | 0.612 | 1.14 | 1.71 | 0.532 | 1.01 | 1.38 | 1.35 | 2.52 | 3.78 |
| 60/40/4 | 0.555 | 1.03 | 1.54 | 0.485 | 0.869 | 1.32 | 1.30 | 2.41 | 3.61 |
| 50/50/5 | | <0.11 | 0.180 | | na | na | | <0.303 | 0.50 |
| 0/0/100 | 1.06 | 1.91 | 2.67 | 0.839 | 1.47 | 2.20 | 1.65 | 2.29 | 4.15 |
| 0/100/0 | 0.0177 | 0.0286 | 0.0352 | 0.0132 | 0.0292 | 0.0433 | | | |
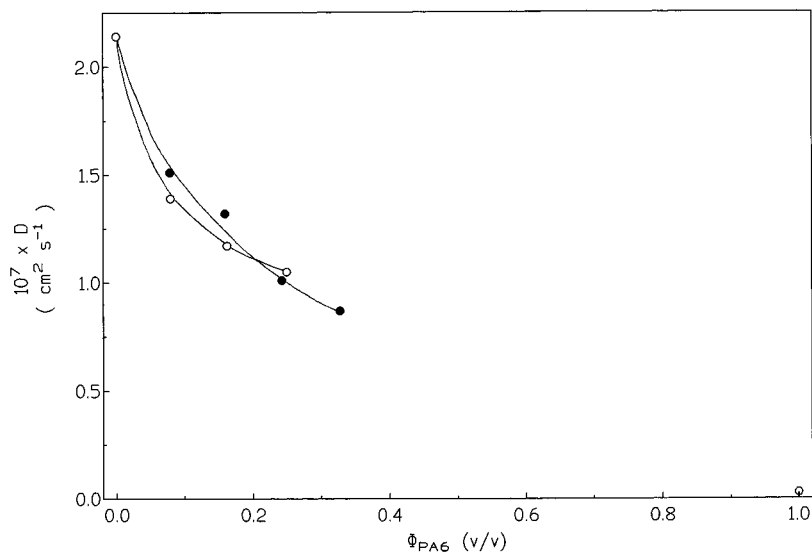
**Figure 6**   Oxygen diffusion coefficients ($D$) of plain ($\bigcirc$) and compatibilized ($\bullet$) PP/PA6 blends at 23°C vs PA6 volume fraction ($X_{PA6}$). Compatibilizer OR/PA6 ratio: 1/10 by weight.

found to be parallel to $P$ previously described, so morphology seem to be prevailing in determining the transport phenomena.

It must be noticed that the gap here observed between compatibilized and plain blends in terms of $S$ values appears to be much less marked when the diffusion phenomenon is considered (Fig. 6).

The trend of permeability as a function of OR/PA6 ratio for 70/30 PP/PA6 blends at 12, 23, and 29°C is shown in Figure 7: a regular increase of permeability is observed up to OR/PA6=0.20, according to analogous literature data.[15] The subsequent decrease of $P$, in the 70/30/10 PP/PA6/OR blend, might be associated with its unexpected "core-shell" morphology [Fig. 1(b)], absent in the other blends: such behavior is reasonably induced by the high OR content.[4]

The complete set of permeation and diffusion data obtained in this work is reported in Table III.
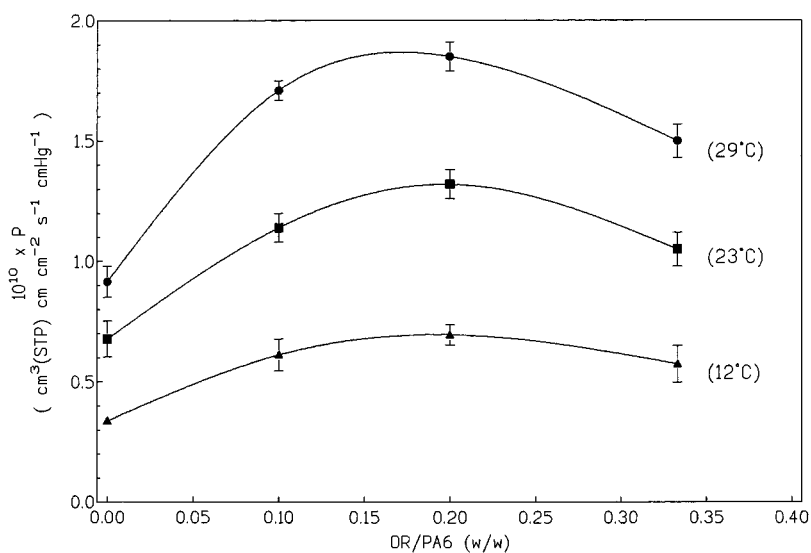


**Figure 7**   Effect of the compatibilizer (OR) content on the oxygen permeability coefficient ($P$) at various temperatures of 70/30 PP/PA6 blends.

**Table IV    Temperature Coefficients of *D* and *S* of Unmodified and Compatibilized Blends**

| PP/PA6/OR (Weight Ratio) | $E_D$ (kJ mol$^{-1}$) | $D_0$ (cm$^2$ s$^{-1}$) | $\Delta H_s$ (kJ mol$^{-1}$) | $S_0 \times 10^5$ $\left( \dfrac{\text{cm}^3 \text{ (STP)}}{\text{cm}^3 \cdot \text{cm Hg}} \right)$ |
|---|---|---|---|---|
| 100/0/0 | 36.5 | 0.581 | 2.26 | 268 |
| 90/10/0 | 31.2 | 0.0415 | 8.1 | 3230 |
| 90/10/1 | 40.7 | 2.35 | 2.91 | 338 |
| 80/20/0 | 34.1 | 0.105 | 8.06 | 2390 |
| 80/20/2 | 37.3 | 0.432 | 1.27 | 181 |
| 70/30/0 | 43.5 | 4.79 | −1.30 | 37.2 |
| 70/30/3 | 40.3 | 1.27 | 2.63 | 343 |
| 60/40/4 | 41.5 | 1.87 | 1.00 | 175 |
| 0/0/100 | 39.9 | 1.69 | −.0977 | 84.4 |
| 0/100/0 | 49.9 | 1.83 | −24.7 | 0.00420 |

For every blend here considered, the entropic ($D_0$) and energetic ($E_D$) parameters have been evaluated according to

$$\ln D = \ln D_0 - E_D/RT$$

The resulting values are collected in Table IV. Interestingly, there is a good linear relationship between them as is shown in Figure 8 that reports the plot of $\ln D_0$ vs $E_D$.[16] Only the pure components significantly diverge from the straight line. In general, the compatibilized blends have higher values compared with those of the unmodified ones, likely because both $D_0$ and $E_D$ are related to the cohesive energy density of the amorphous region.[17] In line with this, in the 70/30/6 PP/PA6/OR blend $E_D$ is higher than in the 70/30/3 PP/PA6/OR blend (where the content of OR is smaller). In this context, the results of 70/30/0 and 70/30/10 PP/PA6/OR blends appear to be anomalous, the former likely due to delamination phenomena occurring under the operating conditions for its preparation, the latter likely due to its unexpected morphology (probably related to an alteration in the amorphous phase nature). In Table IV
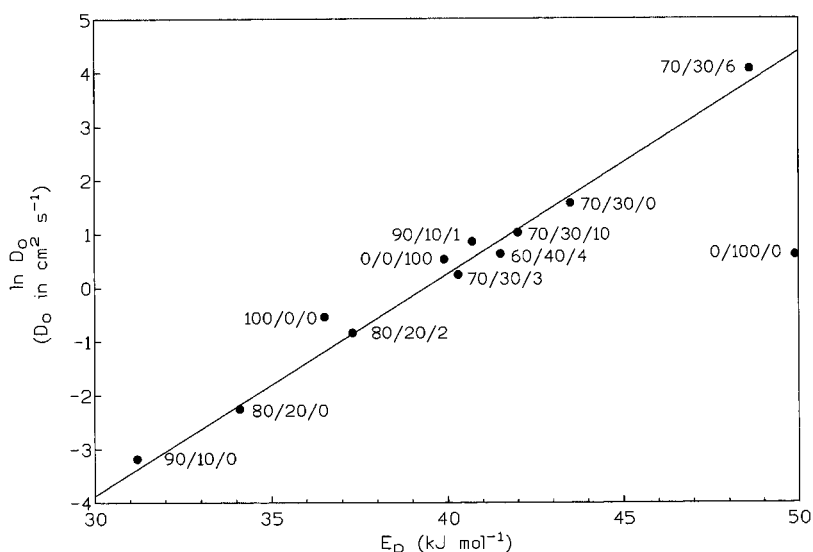


**Figure 8**    Preexponential factor $D_0$ (cm$^2$ s$^{-1}$) vs energetic parameter $E_D$ (kJ mol$^{-1}$) for PP/PA6/OR blends.

are reported the values of enthalpy of oxygen solution in the various considered blends ($\Delta H_S$) and the values of the corresponding limiting solubility ($S_0$). Apart from the same case mentioned above, the compatibilization appears to lower both these factors.

As regards pure PP and pure OR, namely a polypropylene grafted with maleic anhydride, the slightly lowering of permeability on going from the former to the latter (Table III) and the corresponding increase of $E_D$ (Table IV) are in a good agreement with the well-known behavior observed when a polar group (as the grafted maleic anhydride) is introduced in a polymer.[16]

## CONCLUSIONS

The compatibilized blends showed higher permeability coefficients compared with those of unmodified ones. From the application of a suitable model, it has been possible to explain this behavior with the shape of the dispersed PA6 particles, qualitatively confirmed by SEM investigations too.

The compatibilizer increases the permeability as long as OR/PA6 ratio 0.2; over this value, a drastic change in morphology seem to explain the surprising decrease of the permeability coefficient.

The solubility coefficients of the compatibilized blends increase as PA6 increased; this is probably related to the growth of amorphous phase fraction observed by DSC measurements. The sensible increase in $E_D$ values induced from the compatibilizer seem to indicate an increase of polarity of the amorphous phase.

So, the permeation measurements allows us to achieve important information about nature and morphology of heterogeneous membranes, though the complexity of the system does not allow to reach quantitative results.

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