Gas transport in coextruded multilayered membranes with alternating dense and porous polymeric layers

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Abstract

Multilayered gas separation membranes with alternating layers of β crystalline polypropylene and PEBAX copolymers were produced via coextrusion and biaxial stretching for potential applications in modified atmosphere packaging. The number of layers and PEBAX compositions were varied to study the effect of various membrane configurations on pore formation in the polypropylene layers, which ideally serve as a mechanical support for the selective PEBAX layers. Gas permeabilities of multilayered films were compared to control PEBAX films using a simple model, which allowed inferences about the completeness of pore formation to be drawn. Preliminary results show that increasing the layer count degrades membrane throughput and separation capability, while varying PEBAX composition results in a tradeoff between these properties.

1. Introduction

1.1. Composite membranes by multilayered coextrusion

In composite membranes, a thin skin layer determines separation performance, but that layer must be supported by a substrate material that provides both mechanical integrity and little resistance to mass transfer, which implies that it must be both porous and much thicker than the skin layer. These membranes have typically been produced by a solution-based phase inversion process, or by laminating more than one previously fabricated material together. A Celgard trilayer membrane, for instance, is fabricated by lamination [1]. Before extruded composite membranes can be produced, the production and properties of a compatible support layer must be developed. Studies of β-IPP isotropic films were undertaken for this purpose. Extruded β-IPP films, which become porous upon stretching [2,3], were produced. The aim of this part of the research is to develop a methodology by which these films may be coextruded in a multilayered configuration [4,5] with alternating layers of porous precursors and nonporous materials. These films may then be stretched to form the final composite membrane. Stand-alone β-IPP films made from resins with different values of melt flow index (MFI) were used to explore pore formation while ensuring future rheological compatibility with other polymers during coextrusion. If useful composite membranes can ultimately be produced in this way, thus displacing solvent-based membrane production [6–8], large environmental and economic benefits could be realized. This work extends our prior study [9] by developing a fundamental model for transport through such membranes.

1.2. Multilayered coextrusion

Extruded polymer films made from two or more polymers arranged in a periodic layered structure can be produced by a technique pioneered by Dow Chemical Co. called multilayer coextrusion [10]. This technology is currently being advanced by the Center for Layered Polymeric Systems (CLiPS) NSF Science and Technology Center, which made this study possible. Several studies of transport in multilayered materials have been undertaken in the areas of barrier materials [11–13], breathable films [5], and modified atmosphere packaging [14–17].

1.3. Polymers exhibiting high CO₂ solubility

Polymers containing polar structural units (e.g., carbonates, acetates, nitriles, and ether oxygens) have the potential to exhibit favorable thermodynamic interactions with quadrupolar CO₂ [18]. These interactions are manifested as increased solubility of CO₂ in
the polymer relative to equivalent structures without such polar groups and can enhance solubility selectivities of CO$_2$ over nonpolar light gases [19]. In particular, polymers with structures containing polar ether oxygens have been widely shown to exhibit this property [20–23]. For membrane applications where high CO$_2$ solubility or CO$_2$ solubility selectivity will result in desirable transport properties, the incorporation of ether oxygen linkages into the polymer is an obvious route to improved performance. Rubbery polymers containing ether oxygens are of particular interest, because the solubility selective behavior provided by the ether oxygens can offset the weak size-sieving behavior characteristic of rubbery polymers while retaining their high permeability. In fact, so-called “reverse selective” membranes that exhibit higher permeabilities to gases with larger kinetic diameters (e.g., CO$_2$) over those with smaller diameters (e.g., H$_2$, H$_2$) are only possible when polymer solubility behavior is the controlling factor [18,24].

Several approaches are available to produce membranes made of rubbery polymers containing ether oxygens [19]. Poly(ethylene oxide) (PEO), poly(tetramethylene oxide) (PTMO), or other structures with ether oxygen linkages can be synthesized and cast from solution as membranes. These polyethers (PE) tend to have high crystallinity, and therefore exhibit low gas permeability [25,26]. PEO is also soluble in water, greatly limiting the range of applications for which it would be well-suited as a membrane [27,28]. Furthermore, the mechanical properties of PEO are quite poor [5]. The high crystallinity and water solubility of these materials can be addressed by crosslinking the polymer network after casting from solution, an approach which has been extensively studied previously for PEO [29–31]. An intriguing method to exploit the properties of PE units in gas separation membranes that has been widely used since the mid-1990s is to synthesize block copolymers composed of a “soft” polyether (PE) block and a second “hard” structural block. PEO-based materials with “hard” polyimide [20,32], polyamide [33,34], polyester [35,36], and polyurethane [22,32] segments have all been prepared and characterized with respect to their CO$_2$, N$_2$, and other light gas permeation properties. PTMO-based materials along these lines have been studied concurrently. This class of materials exhibits significantly better mechanical properties than solution-cast polyethers or their crosslinked derivatives, and depending upon the hard block, such copolymers may also be melt extruded. A commercially available line of polyether-block-polyamide (PE-b-PA) segmented copolymers, sold under the name PEBAX, possess these excellent processing characteristics and still retain an enhanced solubility selectivity toward CO$_2$.

Due to the lower solubility selectivities arising from a lower concentration of ether oxygens, PTMO-b-PA materials tend to exhibit lower permeselectivities for CO$_2$ over light gases compared to PEO-b-PA materials. The PTMO-based materials exhibit higher permeabilities, which could make them useful for high throughput applications [33,37]. Research on PEO and PTMO-based materials has primarily been directed toward hydrogen purification, natural gas sweetening, and flue gas CO$_2$ recovery [18]. There are interesting possibilities in several other areas, including modified atmosphere packaging (MAP). To provide the optimal environment for produce such as apples and pears using MAP, a high CO$_2$/O$_2$ selectivity polymeric membrane is necessary [38].

2. Materials and methods

2.1. Extruded PEBAX single layer films

2.1.1. Materials selection

The properties of a commercially available series of polyether-block-amide (PE-b-PA) copolymers produced by Arkema, Inc., PEBAX, were studied. Because PEBAX is commercially available, the large quantities required for extrusion were readily available in pellet form. The structures of the polymer blocks and that of the copolymer are presented in Table 1.

All grades of PEBAX used in this study contain a Nylon-12 (PA12) polyamide block. Grades containing poly(tetramethylene oxide) (PTMO) (1041, 1205, 2533) polyether blocks were obtained. The nomenclature for films produced in this study is as follows. [wt.% PE][PE]-PA12 is the sample code, where, for example, 80PTMO-PA12 is a PEBAX film containing 80 wt.% of the polyether PTMO, and the polyamide block is PA12 (as it is for all samples in this study). Basic properties of these polymers are presented in Table 2.

A related study [14,39] performed by research collaborators used the PEBAX xx33 series, which were block copolymers with a Shore D hardness of “xx” and contain PTMO polyether blocks.

2.1.2. Film preparation

Pelletized PEBAX was spread out on trays in a vacuum oven and dried at 100 °C for at least 6 h. Both the polyamide and the polyether blocks in PEBAX are somewhat hydrophilic, resulting in water uptake that could generate water vapor in the extruder at high temperature and lead to problems with film quality and consistency. The drying step is, therefore, necessary to ensure that as little water remains in the polymer as possible prior to extrusion. Each grade of pelletized PEBAX was placed in a hopper and fed into the extruder. The extrusion temperature for each grade was 190 °C, and a 14° film die was used to extrude a uniform film onto a chill roll at 55 °C. The melt pump rate was set at a fixed value between grades, and the chill roll take-up rate was set to produce films between 25 and 40 μm in thickness. Films were un wound from the roll and wound onto wax paper to prevent self-cling. The wound rolls were stored at room temperature until needed for further characterization. All films were clear in appearance, with visible extrusion die lines present on all samples. Films with higher polyether block contents were tackier than those with lower contents. For all samples, the film and away from die lines.

2.1.3. Elemental analysis

Analytical services provided by Galbraith Labs were used to determine the nitrogen content of PEBAX copolymers. As outlined

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Structure of PEBAX copolymers and constituent blocks.</th>
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<tbody>
<tr>
<td>Polymer</td>
<td>Structure</td>
</tr>
<tr>
<td>PEBAX block copolymer</td>
<td><img src="Image" alt="PEBA Block Structure" /></td>
</tr>
<tr>
<td>Polyiminio(1-oxido-decamethylene)]</td>
<td>Polyiminio(1-oxido-decamethylene)</td>
</tr>
<tr>
<td>(PA – Nylon-12[PA12]</td>
<td>Poly(imino(1-oxido-decamethylene)]</td>
</tr>
<tr>
<td>Poly(tetramethylene oxide)</td>
<td>Poly(tetramethylene oxide)</td>
</tr>
<tr>
<td>(PE – PTMO)</td>
<td>(PTMO)</td>
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</tbody>
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<table>
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<th>Table 2</th>
<th>Selected characteristics of PEBAX copolymers.</th>
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<tr>
<td>PEBAX Grade</td>
<td>PE block</td>
</tr>
<tr>
<td>---------</td>
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</tr>
<tr>
<td>1041</td>
<td>PTMO</td>
</tr>
<tr>
<td>1205</td>
<td>PTMO</td>
</tr>
<tr>
<td>2533</td>
<td>PTMO</td>
</tr>
</tbody>
</table>

Values from Arkema Product Literature.
previously [40], since the polyamide blocks present in PEBAX are the only part of the structure containing nitrogen, analyses for nitrogen can be used to calculate the weight fraction of the polyamide block, PA12 in this case, and thus the polyether block weight fraction by difference. Transport properties in this class of materials are largely determined by the polyether content. The calculation of PA12 weight fraction is performed as follows:

$$\omega_{PA12} = \frac{MW_{PA12}}{MW_{PA12} / N}$$

(3.1)

where $MW_{PA12}$ is the molecular weight of a PA12 repeat unit (197 g/mol), $MW_N$ is the molecular weight of elemental nitrogen (14 g/mol), and $\omega_N$ is the measured weight fraction of nitrogen from elemental analysis.

2.1.4. Film thickness determination

The thicknesses of extruded PEBAX films were determined using a Mitutoyo handheld micrometer. Prior to permeation testing, thickness measurements at five equally spaced points on the exposed membrane area were performed and averaged.

2.1.5. Gas permeability

A constant volume, variable pressure system [41] was used to measure the permeability of extruded PEBAX membranes. These measurements were performed over a variety of upstream applied pressures of CO2, O2, and N2, and at temperatures ranging from 5 to 35 °C. The system was operated by evacuating the volume downstream of the membrane in the permeation cell using a vacuum pump and applying a fixed test gas pressure to the upstream face of the membrane. The temperature of the membrane was controlled using a water bath, and the temperature of the downstream volume was enclosed in an insulated box fixed at 35 °C. Once enough time passed for the gas flux through the membrane to reach steady state, the line to the vacuum pump was closed. The rate of pressure increase in the downstream volume was monitored and used to calculate the number of moles of gas transported through the membrane per unit time using the ideal gas law. This technique is not dependent upon proper calibration of detector-based systems like Mocon devices. In all cases, the driving force did not change significantly during the course of the experiment because the upstream ballast volume was large, and the pressure of the downstream volume never exceeded 10 torr, which was a small fraction of the pressure in the upstream. This information was then coupled with membrane thickness and area to calculate the permeability of the test gas at a fixed temperature and upstream pressure [42]. Permeability in this study is reported in Barrer, where 1 Barrer = $10^{-10}$ cm$^3$(STP) cm/(cm$^2$ s cmHg).

Because of the potential for CO2 to plasticize membranes, which leads to increased gas permeability and decreased gas pair selectivity, the gases were tested in the following order: N2, O2, CO2.

2.2. Coextruded multilayered β-iPP/PEBAX films

2.2.1. Materials selection

A grade of iPP (Dow H7012-35RN) with lower viscosity (MFI = 35) than the iPP samples considered in prior studies [16,17] and the highest permeability PEBAX sample, PEBAX 2533, were selected for the coextrusion of multilayered films. The iPP was β nucleated with 0.1 wt.% quinacridone quinone to promote the formation of β crystalline structures amenable to pore formation. This grade of iPP was selected to ensure a viscosity match between the β-iPP and PEBAX 2533 during coextrusion.

2.2.2. Film preparation

The multilayered membranes characterized in this project were coextruded at Case Western Reserve University (Cleveland, OH). The coextrusion device is capable of splitting and stacking flows of polymer melt an arbitrary number of times using layer multiplication elements to create as many layers as desired. It is typical to produce multilayered films with hundreds or even thousands of layers at layer thicknesses as thin as 100 nm. A schematic of this approach is shown in Fig. 1 [43].

In this study, the coextruder was fitted with an ABA feedblock, producing 2($n$+1) + 1 layers. These multilayer films were produced at compositions of 10 and 30 vol.% PEBAX. These low concentrations of PEBAX were selected to minimize the total thickness of the layer (or layers) intended to provide the most resistance to mass transfer. Two different layer configurations were examined:

1. 3-layer films, with two layers of PEBAX sandwiching a single β-iPP layer;
2. 17-layer films, with nine layers of PEBAX sandwiching eight β-iPP layers.

In the first case, the ABA feedblock was used to directly produce a 3-layer film. In the second case, three layer multiplication elements (i.e., $n = 3$ in Fig. 1) were used in concert with the ABA feedblock to increase the number of layers of PEBAX present. It was hypothesized that increasing the number of layers might decrease the possibility that defects in any given layer would significantly diminish the separation performance of the composite membrane. The nomenclature for these films is $[Layers]L$-[vol.% PEBAX], where, for example, 3L-10 is a multilayered film with three total layers and 10 vol.% PEBAX in the film. Films were extruded at 190 °C, like the PEBAX single layer films, and at a nominal total sample thickness of 100 μm.

Test samples 8.5 × 8.5 cm in size were cut from the center of the extruded film for consistency of thickness, and they were subjected to biaxial stretching at 100 °C and 100% s$^{-1}$. Films of the 3L-10, 3L-30, 17L-10, and 17L-30 types were simultaneously stretched at a draw ratio of 2.0 in both the machine and transverse directions. 3L-10 films underwent thermal annealing at 140 °C for 30 min and were stretched at a draw ratio of 2.0 for comparison to as-extruded films.

2.2.3. Film thickness determination

Multilayer film thicknesses were determined as described for single layer PEBAX films. The total thickness of a single component is estimated to be the volume fraction of that component multiplied by the multilayered film thickness. To estimate the thicknesses of single layers in the films, the total thickness of a single component is divided by the number of layers of that component.

2.2.4. Gas permeability

Extruded PEBAX films were measured for gas permeability using two rapid screening techniques. Films were masked using a...
method similar to that presented previously [9], and they were then measured for O$_2$ permeability using a Mocon Ox-tran device. For CO$_2$ permeability, a Mocon Permatran-C device was used. These permeation systems use coulometric or infrared detection techniques [44,45], respectively. A test gas is flowed past the upstream face of the membrane, and a sweep gas carries the permeate from the downstream face of the membrane to the detector. The system is operated at atmospheric pressure, so the permeability of membranes cannot be tested at higher partial pressures.

3. Results and discussion

3.1. Permeability of single layer PEBAX films

The permeability of PTMO-based PEBAX grades (28PTMO—PA12, 52PTMO—PA12, 80PTMO—PA12) was measured at 35 °C as a function of transmembrane pressure. These results are presented in Fig. 2.

None of these PTMO-based grades exhibited measurable dependencies of permeability on transmembrane pressure. This is typical of gases that are present in low concentrations in rubbery polymers [24,46], although plasticization occurs in rubbers when exposed to high-sorbing gases such as CO$_2$ at higher pressures [24,46,47]. Because the intention of this study was to determine the properties of these materials for MAP applications, high applied pressures that result in high gas concentrations are not likely to be encountered. In each PEBAX grade, the permeability was highest for CO$_2$, significantly lower for O$_2$, and lower still for N$_2$. This is consistent with prior results for PEBAX [33,34,37,48], and it reflects the fact that CO$_2$ is a smaller gas than O$_2$, which, in turn, is smaller than N$_2$ [24,49]. This gives CO$_2$ a diffusivity selectivity advantage over the other gases. More significantly, as was discussed previously, CO$_2$ is much more soluble than either gas in this class of materials. The permselectivity of these PEBAX grades also shows little dependence on transmembrane pressure, and as can be deduced from the permeability results, CO$_2$/N$_2$ selectivities are higher than CO$_2$/O$_2$ selectivities. In the case of 28PTMO—PA12, both selectivities were slightly elevated at the highest transmembrane pressure. The permeability measurements show a small increase in CO$_2$ permeability and a small decrease in O$_2$ and N$_2$ permeability relative to values measured at lower pressures. One explanation consistent with these findings is that there was an undetected leak into the downstream, elevating the apparent flux at lower pressures. Because the change in measured permeability with applied pressure is quite small and is comparable to the measurement uncertainty, it is reasonable to refrain from making conclusions about the relationship between these variables over this range of pressure.

One way to recast the data to explore structure–property relationships in these materials is to examine the change in transport properties with PTMO block content, which is also shown in Fig. 2.
As PTMO block content increases, the permeability of each gas increases, consistent with the picture that transport occurs primarily through the PE block in these materials. At levels of PTMO above 28%, there is little change in the selectivity of either gas pair studied as a function of PTMO content. These materials are known to have a morphology featuring an interconnected PTMO phase [50]. A recent study [14,39] on a series of similar materials shows similar behavior above 47% PTMO, but also reveals a behavior consistent with the breakup of PTMO interconnection at lower concentrations of PTMO. The permeability of CO₂ and O₂ begins to decline sharply with decreasing PTMO content below 25 wt.% PTMO, with CO₂ permeability decreasing more than that of O₂. Since CO₂ permeability is especially advantaged due to its high solubility in the PE phase of PE-b-PA materials, network breakup is an excellent hypothesis to explain the observed permeation phenomena.

3.2. Multilayered β-iPP/PEBAX films for MAP applications

Although orientation can affect the permeability of 80PTMO-PA12 by creating PTMO structures which melt at 40–45 °C [14], each multilayered film was stretched at 100 °C, preventing orientation from occurring in these films. Two variables were examined for their effects on gas transport: the number of layers, and the volume fraction of PEBAX in the film, outlined previously. All multilayered films were measured for permeability using Mocon devices.

Fig. 3 displays the O₂ throughput and the separation ability of the multilayered films. The top figure shows the performance of the multilayered films relative to the O₂ permeance target for MAP membranes. This target is 30 GPU (GPU = Barrer/μm), a permeance that permits a reasonable membrane area for standard produce package sizes [51]. All films have O₂ permeances of less than 5 GPU, while exhibiting a substantial reduction in expected permeability compared to the control PEBAX film at a given thickness. Films with 3 layers appear to attain both higher permeabilities and permeances than 17-layer films, indicating that pore formation is likely inhibited when there are a greater number of layers. In the 3-layer films, higher PEBAX content results in greater permeability in the PEBAX layers. Permeabilities are about the same in 17-layer films with different PEBAX content. This apparent increase in permeability cannot offset the reduction in total PEBAX thickness, however, because the films with lower PEBAX content exhibit higher permeance. The bottom figure displays CO₂/O₂ selectivity as a function of O₂ permeance. The films generally have much lower selectivity than single layer PEBAX films, with the effect most pronounced in films with 17 layers and films with 10 vol.% PEBAX.

These composite membranes are complex materials with internal structures that clearly vary depending upon layer count and film composition, as well as from sample to sample [9]. To better understand the performance of these materials, a model accounting for the influence of inadequate pore formation on the observed transport properties will be developed in the following section.

A simple model for gas transport through these multilayered membranes is presented in Fig. 4.

Mathematically, this model can be represented using the following three equations:

\[
P_{1,i} = \frac{l_{\text{composite}}}{(P_{\text{pp}}/P_{\text{PP}}) + (P_{\text{porous}}/P_{\text{porous}})} \approx \frac{l_{\text{composite}}}{(l_{\text{pp}}/l_{\text{PP}}) + (l_{\text{porous}}/l_{\text{porous}})}
\]

\[
P_{2,i} = \frac{l_{\text{composite}}}{(P_{\text{pp}}/P_{\text{PP}}) + (P_{\text{porous}}/P_{\text{porous}})} \approx \frac{l_{\text{composite}}}{(l_{\text{pp}}/l_{\text{PP}}) + (l_{\text{porous}}/l_{\text{porous}})}
\]

\[
P_i = e \cdot P_{1,i} + (1 - e) \cdot P_{2,i}
\]

where \(P_{1,i}\) and \(P_{2,i}\) are the steady state permeabilities of gas \(i\) through the structure containing some intact nonporous PP and the structure containing no intact PP, respectively (cf., Fig. 4). This model can be understood conceptually as the transport of gas \(i\) through series resistances operating in parallel. One resistance has an area fraction of \(e\), and it is composed of a PEBAX layer of thickness \(l_{\text{PEBAX}}\) in series with an intact (i.e., nonporous) PP layer of thickness \(l_{\text{pp}}\) and a porous layer of thickness \(l_{\text{porous}}\). The other resistance has an area fraction of \((1 - e)\), and it is composed of a PEBAX layer of thickness \(l_{\text{PEBAX}}\) in series with a porous PP layer of thickness \(l_{\text{porous}}\). The total thickness is \(l_{\text{composite}}\). In both cases, the resistance of the porous layer is assumed to be negligible, leading to the approximations displayed above. The permeability of pure PEBAX at 23 °C to the relevant gases is known, and the permeability of dense
PP (assumed here to be 50% crystalline) is reported elsewhere [52]. The total thickness of PEBAX layers is known from its volume fraction in the melt and its area expansion from the drawing of the film. The model, therefore, has only two unknown parameters ($\varepsilon$ and $l_{PP}$), and it may be solved given the permeability of the composite film to two gases, CO$_2$ and O$_2$. Other models with more sophisticated treatments of the structures present in these multilayered films (i.e., the consideration of defects) would be possible if permeability data for additional gases were available. The calculated parameters for the films are shown in Table 3.

The results of evaluating the performance of multilayered films using the model are presented in Fig. 5. Performance is cast in terms of the ratio of multilayered film O$_2$ permeability to 80PTMO–PA12 permeability and in terms of multilayered film CO$_2$/O$_2$ selectivity to 80PTMO–PA12 selectivity. The ratio of $l_{PP}$ to $l_{PEBAx}$ is used to allow comparison between films with different PEBAX thicknesses, and this ratio is called $\tau$. For these materials, the maximum value of $\tau$ should be 9, which corresponds to a film with 10 vol.% PEBAX and 90 vol.% intact PP. In practice, $\tau$ was less than 0.6. If a membrane’s structure corresponds to the physical situation captured by the model, its properties must lie in the envelope defined by $\tau = 9$ and $\varepsilon = 1$, shown in Fig. 5. It is possible for a membrane with a different structure to exhibit these properties, but if the membrane properties lie outside of this envelope, its construction does not correspond to the model physics. Generally, as $\tau$ and $\varepsilon$ increase, the O$_2$ permeability of the multilayered film decreases. At a fixed value of $\varepsilon$, where $\varepsilon < 1$, CO$_2$/O$_2$ selectivity decreases as $\tau$ increases, reaches a minimum value, and then increases. When $\varepsilon = 1$, selectivity decreases as $\tau$ increases. When $\varepsilon = 0$, the selectivity is equal to that of PEBAX because the PP, being porous, contributes negligible contribution to the selectivity. At a fixed value of $\tau$, where $\tau > 0$, selectivity decreases as $\varepsilon$ increases, reflecting the increasing contribution of the low selectivity of PP to the overall selectivity of the composite structure. At $\tau = 0$, the selectivity is that of PEBAX since such a structure is composed only of PEBAX. When $\varepsilon = 1$ and $\tau$ is very large, the selectivity is equal to that of PP, reflecting the dominance of the PP transport properties on those of the composite.

**Table 3**
Model parameters for transport in multilayered β-IPP/PEBAx membranes. Each ($\varepsilon$, $l_{PP}$) pair for a given layer configuration and PEBAX content corresponds to the value for an individual sample of those specifications.

<table>
<thead>
<tr>
<th>Layer</th>
<th>$\varepsilon$</th>
<th>$l_{PP}$ (μm)</th>
</tr>
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<tbody>
<tr>
<td>3L-10</td>
<td>0.74</td>
<td>0.54</td>
</tr>
<tr>
<td>3L-30</td>
<td>0.76</td>
<td>0.33</td>
</tr>
<tr>
<td>17L-10</td>
<td>0.75</td>
<td>0.42</td>
</tr>
<tr>
<td>17L-30</td>
<td>0.74</td>
<td>0.72</td>
</tr>
</tbody>
</table>

**Fig. 4.** One potential model of gas transport in multilayered films with a dense PEBAX layer and a porous support. Interactions at the interface between PEBAX and β-IPP may result in areas where porosity is not formed in the β-IPP, forming a region of intact nonporous PP (top). Gas transport in this model occurs in parallel, with one area ($\varepsilon$) experiencing resistance to mass transfer from both PEBAX and the intact nonporous PP, and the other area ($1 - \varepsilon$) experiencing resistance only from PEBAX (bottom). The area coverage $\varepsilon$ and thickness $l_{PP}$ of intact nonporous PP are model parameters.

**Fig. 5.** Influence of transport model parameters on the O$_2$ permeability and CO$_2$/O$_2$ selectivity, $\alpha$, of multilayered films. Results for 3L-10 (■), 3L-30 (○), 17L-10 (▲), and 17L-30 (△) films are presented.
structure when the PP composition is much larger than that of PEBAX.

These results yield physical insight into the performance differences between 3-layer and 17-layer films, as well as between films having different PEBAX content. The area coverage of dense PP, ɛ, is a more important parameter to the separation performance of these films than the thickness of that PP layer, lPP. There are more interfaces between PEBAX and PP layers (16 total) in 17-layer films than in 3-layer films (2 total). Thus, there should be more interactions per unit volume of PP in films with more layers. If interactions between PEBAX and PP layers during stretching retard pore formation, 17-layer films should have greater values of ɛ than 3-layer films and correspondingly lower selectivity. This trend is in fact observed in 17-layer films relative to 3-layer films, where every 17-layer film observed had a value of ɛ above 0.8. Additionally, when PEBAX layers are thinner, their interaction with PP should be stronger [53], potentially retarding pore formation in PP and again reducing selectivity. At a fixed number of film layers, modeling results show that films with one-third the PEBAX thickness (i.e., 10 vol.% PEBAX instead of 30 vol.% PEBAX) have higher ɛ values. This observation could indicate that the retardation of pore formation occurs more often at the interface in films with more layers. The total thickness of the PP layers, lPP, was also greater in 17-layer films than in 3-layer films, suggesting that pore formation is less efficient per PP layer in the 17-layer films. Practically, if one was to design an optimal multilayered film of this type, that film should have one separating layer and one porous layer.

Multilayered films were thermally annealed at 140 °C prior to stretching so that the benefits to pore formation in β-IPP films shown previously [16,17] might be realized. The results of this experiment are presented in Fig. 6. Compared to as-extruded films, the thickness of PEBAX in annealed films is decreased, but the O2 permeability also decreases. This results in a modest improvement in permeance relative to that of the films depicted in Fig. 3.

4. Conclusions

The permeabilities to several gases of PEBAX grades containing poly(tetramethylene oxide) (PTMO) were measured over a range of transmembrane pressures. The permeability of these materials is dependent upon the PE soft block content, with greater PE contents resulting in higher permeabilities and, to a certain extent, higher selectivities of CO2 over light gases due to CO2’s favorable interaction with ether oxygen linkages.

Multilayered films of β-IPP and the PTMO-based PEBAX were produced, and their performance was studied over a range of layer counts and PEBAX content. Generally, 3-layer films performed better than 17-layer films, and higher PEBAX content resulted in films with higher selectivities but lower permeances. Comparison of the multilayer results with those of single layer PEBAX films indicated the imperfect nature of pore formation in multilayered films, and this was modeled using two parameters with distinct physical meaning. Based on results from the model, large areas of intact, nonporous PP still existed in all of the multilayered films, inhibiting the transport properties. Thermal annealing of the multilayered films slightly improved O2 permeance.

The good pore formation of β-IPP films is mitigated by interactions at the PEBAX-PP interface. The model reveals that pore formation is inhibited in the PP over large areas, and thicknesses of several hundred nanometers of intact PP per layer remains in these areas. It is not currently known whether the presence of PEBAX is more influential on the crystallization of β-IPP or the stretching process. Fundamentally, it would be interesting to understand how pore formation is influenced by contact with different materials (e.g., thermoplastic elastomers like PEBAX, glassy polymers, or even polymers in the melt at the applied stretching temperature). Practically, this issue must be understood so that useful multilayered membranes with a porous support can be produced.

Acknowledgments

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References

Yoshino M, Ito K, Kita H, Okamoto K. Effects of hard-segment polymers on Kusuma VA, Gunawan G, Smith ZP, Freeman BD. Gas permeability of cross-
their permeability of \( \beta \)-nucleated isotactic polypropylene-stretched films by thermal annealing. Polymer 2013;54:2577–89.


Kusuma VA, Gunawan G, Smith ZP, Freeman BD. Gas permeability of cross-linked poly(ethylene oxide) based on poly(ethylene glycol) dimethacrylate and a miscible siloxane co-monomer. Polymer 2010;51:5734–43.


