Gas permeability of melt-processed poly(ether block amide) copolymers and the effects of orientation

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1. Introduction

Recent interest in the permeation properties of polymers has developed due to the need for more energy efficient and environmentally friendly gas separation methods. Poly(ether block amide) (PEBA) copolymers, in particular, have generated interest as a result of the permeation selectivity of polar to non-polar gases. A high CO2 gas selectivity is desirable in applications such as post-combustion carbon capture, purification of hydrogen, and natural gas sweetening, as well as for CO2/O2 control in modified atmosphere packaging [1–3]. In this last application, a high flux, in addition to high CO2/O2 selectivity, is necessary to be effective, which is provided by the amorphous soft block content of many PEBA copolymers.

PEBA copolymers are a useful and diverse set of thermoplastic elastomers used in applications requiring good permeation, abrasion resistance, elasticity, and toughness. Additional advantageous properties include chemical resistance, low density, fatigue resistance, and good low temperature performance. PEBA copolymers have traditionally been used in toughness applications (e.g., running shoes, ski boots, and golf ball cores) and recently as high permeability materials [4,5]. PEBA copolymers with high polyether content have generated interest for use in permeation driven applications due to their relatively high gas flux, a result of the copolymer architecture and morphology, and good selectivity for separations where CO2 (or other acid gases) is one of the components [6].

The potential use of PEBA copolymers in permeation based applications arose from the ability to maintain beneficial poly(ethylene oxide) (PEO) gas selectivity properties while avoiding common PEO limitations of water sensitivity, low permeability (due to high crystallinity levels), and low melting temperature. PEO is known for its unique separation properties of polar (or quadrupolar) gases from mixtures with non-polar gases, and it demonstrates an affinity for CO2, contributing to high CO2 permeability and selectivity [7,8,11]. Many applications that can take advantage of the high CO2 selectivity contain water vapor in the gas streams, rendering PEO less useful as a gas separation membrane.

One approach has been to crosslink PEO to reduce water sensitivity and improve mechanical properties; however, moisture continues...
to have an effect [9]. Current gas separation membrane applications require that the membrane materials possess high selectivity as well as moisture resistance and relatively high flux [10]. Toward a solution to water sensitivity, PEBA and other polyether based copolymers can provide reasonable gas flux, CO₂ gas selectivities, and water resistance [11–14].

Copolymers have unique and beneficial properties which arise from the nature of the individual polymer components and the interactions between them. The copolymer architecture, morphology, and composition directly relate to observed macro-scale properties. PEBA copolymers are microphase separated thermoplastic elastomers, in which the polyether blocks often exist above their melting point and act as soft blocks within the copolymer, while the polyamide hard blocks act as physical crosslinks [13,15,16]. PEBA acquires mechanical strength from the hard polyamide blocks while elasticity and relatively high permeation are a result of the polyether soft blocks [17].

The combination of permeation and elastomeric properties provides the opportunity to explore how orientation and permeability are interrelated for PEBA copolymers. Previous studies focused on structural changes occurring as a result of orientation, usually explored with the aid of x-ray scattering and atomic force microscopy [18,19]. Until now, the effect of uniaxial orientation on the permeation properties of PEBA has not been studied, most likely owing to the fact that most PEBA membranes are cast from solution directly onto porous substrates rather than being extruded [4,5]. This study will further explore the effects of mechanical orientation on PEBA copolymer structure and morphology by comparing oxygen and carbon dioxide permeation, as well as x-ray scattering and differential scanning calorimetry, of as-extruded and uniaxially oriented PEBA extruded thin films.

2. Materials and methods

Poly(ether block amide)s that are part of the PEBAX xx33 series were purchased from Arkema in pellet form. The PEBAX xx33 grades are a series of copolymers consisting of poly(tetramethylene oxide) (PTMO) and polyamide-12 (PA-12) with the xx denoting the shore D hardness [20]. Until now, the effect of uniaxial orientation on the permeation properties of PEBA has not been studied, most likely owing to the fact that most PEBA membranes are cast from solution directly onto porous substrates rather than being extruded [4,5]. This study will further explore the effects of mechanical orientation on PEBA copolymer structure and morphology by comparing oxygen and carbon dioxide permeation, as well as x-ray scattering and differential scanning calorimetry, of as-extruded and uniaxially oriented PEBA extruded thin films.

## Table 1

<table>
<thead>
<tr>
<th>PEBAX grade</th>
<th>Mol% PTMO</th>
<th>Tₘ PTMO (°C)</th>
<th>Tₘ PA-12 (°C)</th>
<th>PEBAX %Xc⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>2533</td>
<td>86</td>
<td>6</td>
<td>138</td>
<td>1-</td>
</tr>
<tr>
<td>3533</td>
<td>75</td>
<td>5</td>
<td>142</td>
<td>1.1</td>
</tr>
<tr>
<td>4033</td>
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<tr>
<td>5533</td>
<td>47</td>
<td>7</td>
<td>160</td>
<td>7.7</td>
</tr>
<tr>
<td>6333</td>
<td>37</td>
<td>7</td>
<td>169</td>
<td>10.7</td>
</tr>
<tr>
<td>7033</td>
<td>25</td>
<td>3</td>
<td>171</td>
<td>14.2</td>
</tr>
<tr>
<td>7233</td>
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<td>2</td>
<td>170</td>
<td>17.5</td>
</tr>
<tr>
<td>PA-12</td>
<td>0</td>
<td>4</td>
<td>175</td>
<td>23.4</td>
</tr>
</tbody>
</table>

⁴ PEBAX %Xc calculated at room temperature (21 °C).
using a Nicolet Nexus 870 with a Continuum microscope attachment and a Germanium crystal in the ATR mode. Each block in the PEBA copolymer has a distinct peak in the FTIR spectrum that does not overlap with the other component, allowing for direct correlation to composition, Fig. 1. The PTMO blocks exhibit an ether peak at 1100 cm\(^{-1}\) not seen in PA-12, while the PA-12 exhibits a carbonyl peak at 1640 cm\(^{-1}\) [21,22]. Composition was calculated based on these two peak heights by the following:

\[
\% \text{ PTMO} = \left( \frac{h_{1100}}{h_{1100} + h_{1640}} \right) \times 100
\]

where \(h_{1100}\) is the PTMO ether peak height, while \(h_{1640}\) corresponds to the PA-12 carbonyl peak height. Peak height was determined after establishing a baseline and measuring from the baseline to the peak maximum [23]. With increasing PTMO content, a clear increase was observed in the 1100 cm\(^{-1}\) peak with a simultaneous decrease in the 1640 cm\(^{-1}\) peak. The PEBA copolymer composition was observed to range from 20 mol% to 86 mol% PTMO, Table 1.

Seven PEBA grades in the xx33 series were extruded at 190 °C using a 14" film die inline with a film casting roll at 55 °C to produce monolith films 25–50 μm in thickness. PEBAX 4033 films were 45–50 μm while all other films were 25–30 μm. Thicker PEBAX 4033 films were used due to thinner films breaking at very low strains.

Fig. 4. Stress–strain behavior of extruded, 30 μm thick, PEBAX xx33 series films.

Fig. 5. WAXS reflection patterns of as-extruded unoriented PEBAX films. (a) 2533, (b) 3533, (c) 4033, (d) 5533, (e) 6333, (f) 7033, (g) 7233, (h) PA-12.
possibly a result of extrusion induced orientation of the PA-12, which is partially observed in the 50 μm film WAXS patterns in Fig. 5.

Uniaxial orientation of film samples with a gage length of 2.5 cm was conducted with an MTS Alliance RT/30 testing machine. Samples with dimensions of 7 cm × 4 cm were cut from the extruded films with the smaller dimension parallel to the extrusion direction. Films were oriented along the extrusion direction at room temperature (21 °C) with a strain rate of 50% min⁻¹ to maximum strains of 100, 150, 200, 300, and 400%. While in tension at each strain, the oriented samples were constrained in the stretched state by applying a self-adhesive aluminum mask to both sides of the film. The aluminum mask possessed a 5 cm² hole in the center for permeation and wide angle x-ray scattering measurements. Additionally, a series of the oriented samples were allowed to elastically recover by removing the applied stress before being adhered to the aluminum mask.

Permeability measurements were conducted on PEBAX films with different thermo-mechanical histories: (1) as-extruded, (2) in tension, (3) elastically recovered, and (4) after annealing while in tension. The O₂ and CO₂ permeabilities were measured using MOCON OX-TRAN 2/20 and PERMATRAN-C 4/40 permeation instruments. Testing was done at 23 °C and 0% humidity with a sample test area of 5 cm² for all samples. The O₂ and CO₂ test gases were used at 2% concentration in nitrogen to prevent sensor saturation due to high flux values.

Thermal analysis was done under nitrogen using a Perkin Elmer DSC-7. The heating scans ranged from −60 to 200 °C at a rate of 10 °C min⁻¹ with sample sizes of 4–6 mg. For all figures containing DSC thermograms, only the first heating scan is shown.

Wide angle x-ray scattering (WAXS) was conducted with an x-ray generator (MicroMax-002, Rigaku, Woodlands, TX) equipped with two laterally graded multilayer optics in a side-by-side arrangement, giving a highly focused parallel beam of monochromatic CuKα radiation (λ = 0.154 nm). The monochromatic x-ray beam, operated at 45 kV and 0.88 mA, was collimated using three pinholes; the diameter of the x-ray beam at the sample position was ~700 μm. The images were collected using Fujiﬁlm magnetic imaging plates, which were processed by a Fujifilm FLA-7000 image plate reader. Measurements were conducted in the normal direction (ND) under vacuum and at room temperature (21 °C) on PEBAX films with the following thermo-mechanical histories: (1) as-extruded, (2) in tension, (3) elastically recovered, and (4) after annealing while in tension. As-extruded, unoriented samples were exposed for 7 h while the oriented samples were exposed for 15 h. PEBAX has a relatively low crystallinity, necessitating the long exposure times to achieve strong reflection patterns. Additionally, the oriented films required extended exposure times relative to the controls due to a reduction in thickness during orientation, which results in less scattering.

3. Results and discussion

3.1. Unoriented PEBAX copolymer films

To determine and understand the changes that occur upon orientation of PEBAX copolymers, as-extruded unoriented films were initially studied. As-extruded films exhibited an interesting trend in the O₂ and CO₂ permeabilities over the range of PEBAX copolymer compositions. As the amount of PTMO increased, permeability increased exponentially, as shown in Fig. 2. The dramatic increase in permeability was a result of low copolymer crystallinity and increased PTMO soft block content, which exists above its melting temperature, facilitating a less tortuous, high permeability pathway for gas to diffuse through the film. Additionally, while both O₂ and CO₂ permeabilities increase exponentially, CO₂ increases at a faster rate, which was evident in the CO₂/O₂ gas selectivity, Table 1. Many polymers exhibit a CO₂/O₂ gas selectivity of approximately four [24], while the PEBAX copolymers exhibit selectivity values ranging from 4 to almost 10. PEBAX grades with greater than approximately 47% PTMO showed a consistently high selectivity of about 9, probably due to most of the gas transport occurring through the polyether soft blocks, which have an affinity for CO₂. From literature, the increased selectivity has been attributed to the polyether blocks having an affinity, or increased solubility, toward CO₂ molecules [12–14].

The thermal properties of PEBAX copolymers provide insight into the observed permeation trend. At room temperature, the PTMO exists above its melting temperature (Tₘ = 15 °C) [13] while the polyamide-12 (PA-12) exists below its glass transition temperature (Tₛ = 50 °C). PEBAX is a microphase separated thermoplastic elastomer as seen by DSC. In DSC thermograms of 25 μm extruded films for each grade in the xx33 series, two distinct peaks were seen in the first heating scans of grades with at least 70% PTMO, Fig. 3. As the amount of PTMO was increased, the melting peak of the PTMO blocks shifted to higher temperature, at the same time, the PA-12 melting peak diminished and showed a shift to
lower temperature, Table 2. With lower PA-12 content, the overall crystallinity significantly decreased and the copolymer became mostly amorphous, particularly in the materials with the highest polyether content, which also exhibited the highest permeability and selectivity values. Crystallinity for all PEBAX copolymers was calculated at room temperature, which only accounts for the PA-12 crystallinity due to the PTMO having a melting point below room temperature. PA-12 crystallinity was determined assuming that the heat of fusion for PA-12 is 246 J/g and the total PEBAX crystallinity was calculated by accounting for the composition of PA-12 in the specific copolymer [13].

The influence of PEBAX copolymer composition was also apparent in the mechanical behavior. Stress–strain curves for the high PTMO grades showed a very broad curve with no distinct yield point, indicative of low crystallinity and an elastomeric behavior, Fig. 4. The polyether soft blocks allow the films to stretch to high strains, up to 400% for PEBAX 2533, providing the possibility of high alignment and orientation of the polymer chains. The low PTMO containing grades showed stronger yield points and higher moduli, shown in the Fig. 4 inset, and additionally tended to fracture at lower strains, closely representative of PA-12, which prevented high orientation levels.

WAXS patterns of the as-extruded unoriented films showed the mostly amorphous structure of PEBAX. With increasing PA-12 content, a PA-12 crystal reflection appeared overlapping the amorphous PTMO halo as well as at the meridian in the center of the WAXS pattern, Fig. 5. Similar patterns have also been observed by Wilkes [32]. The PA-12 blocks show broad reflection arcs, due to slight orientation resulting from the film extrusion conditions; however, they were assumed to have no effect on the permeability.

3.2. Uniaxially oriented PEBAX copolymer films

From the mechanical characterization of the xx33 PEBAX series, it was observed that several of the high polyether content copolymers exhibited an elastomeric behavior and fairly high fracture strains. Until now, the effect of strain induced orientation on the permeability properties of PEBAX has not been studied, likely owing to the fact that most PEBAX membranes are cast from solution [18]. In addition, previous studies focused on structural

![Fig. 7. WAXS reflection patterns of uniaxially oriented PEBAX films in tension. (a) 2533, (b) 3533, (c) 4033, and (d) 5533 at 200% strain. (e) 6333, (g) 7233, and (h) PA-12 at 150% strain, while (f) 7033 is at 100% strain.](attachment:fig7.png)
changes occurring as a result of orientation, usually characterized by WAXS and SAXS, without relating the changes in the structure to a measurable property [25].

Gas permeability is an important property that directly responds to changes in polymeric structures, specifically upon orientation and changes in crystallinity of the polymer chains [26–29]. To determine the influence of mechanical orientation on PEBAX copolymers, gas permeability was measured for the xx33 series PEBAX films while in tension at varying strains, presumed to be an oriented state.

Upon uniaxial orientation, 86% PTMO (PEBAX 2533) down to 47% PTMO (PEBAX 5533) copolymers showed a significant and linear decrease in permeability at increasing strains. For PEBAX 2533, both the O₂ and CO₂ permeabilities decreased by 3.5× between the unoriented control and the 400% strain film, Fig. 6. Because a similar decrease in permeability occurred for O₂ and CO₂, there was no change in the CO₂/O₂ selectivity. The significance of the permeability decrease in each grade was highly dependent on the copolymer composition. A smaller decrease in permeability occurred with lower PTMO soft block content, Table 3. Copolymers containing less than approximately 37% polyether showed no measurable property [25].

To verify that the permeability decrease was caused by a change in the PTMO blocks, WAXS patterns were obtained for all films while in tension. A definitive difference was observed in the oriented films as compared to the as-extruded films. The high PTMO copolymers, which showed the largest permeability decrease, exhibited two strong equatorial reflections where previously only an amorphous polyether halo existed, Fig. 7. These reflections lessen in intensity as the PTMO content decreased, while the broad PA-12 reflections at the equator and the meridian intensified. It is evident from the new reflections that PTMO could be crystallizing during orientation.

In the past, authors have shown that soft, elastomeric polymers could strain crystallize when a large strain was applied. Strain induced crystallization occurred when the polymer chains were highly oriented and aligned, allowing for easier chain packing [25,30]. Natural rubber and some copolymers, such as PEBAX, have previously exhibited this property [31,32]. Also, polymer crystals are generally considered to be impermeable and have the ability to slow down or block the gas diffusion pathway through the bulk film [27–29]. Considering possible strain induced crystallization and the generally impermeable nature of polymer crystals, in combination with the permeation and WAXS data presented, the PTMO in PEBAX copolymers undergo strain induced crystallization, which increases the tortuosity of the gas diffusion pathway and reduces the permeability. Strain induced crystallization of the PTMO would produce smaller changes in permeability as the concentration of PTMO was decreased, due to fewer PTMO crystals to block the gas flow, as was observed over the range of copolymer compositions presented.

3.3. Elastically recovered PEBAX copolymer films

The previous uniaxially oriented samples were measured while in tension, showing strong orientation and strain induced crystallization of the PTMO soft blocks. Elastic recovery of strained natural rubber is known to cause strain induced crystallinity to melt upon release of the stress [31]. This phenomenon may lead one to consider whether the strain induced crystallinity in PEBAX copolymers diminishes upon recovery for any or all of the copolymers, particularly because the degree of elastic recovery varied with copolymer composition, with the high polyether containing copolymers exhibiting the most recovery, Fig. 8.

Upon measurement of the elastically recovered PEBAX film permeability, a trend similar to the permeability of films in tension was observed. The grades with greater than approximately 47% PTMO content showed a decrease in permeability with increasing residual strain, Fig. 9. The permeability of the recovered films, particularly for the 2533 and 3533 grades, was lower than the films in tension at similar strains. Even when orienting within the range of total elastic recovery, a permeability lower than that of the as-extruded films and oriented films in tension was observed. The gas flow through the high PTMO containing copolymers was continuing to be inhibited after recovery, suggesting that residual PTMO crystallization may exist in the film after elastic recovery.

Two methods were used to determine whether residual PTMO crystals were in fact present in the recovered PEBAX films and subsequently causing decreased permeability. The first method used was WAXS patterns of the recovered films, which showed dramatically different scattering than the films in tension and more closely resembled unoriented films at high PTMO content, Fig. 10. Upon recovery, the two strong equatorial PTMO reflections were
diminished to two very fine arcs and lessen as the PTMO content was decreased, evidence that residual crystals exist in films of PEBAX with greater than 47% PTMO; however, to a lesser extent than while in tension.

The second method was to use thermal analysis to extract the presence of residual PTMO crystals. In unoriented samples, the soft PTMO blocks melted below room temperature at around 7 °C and were observed only in the three highest PTMO containing copolymers. Thermograms of PEBAX films recovered from various strains, with approximately 47% PTMO and higher, were obtained and compared with the unoriented as-extruded films, Fig. 11. As the applied orientation strain was increased, a second endotherm appeared at 42 °C, along with a decrease in the PTMO melting peak at 7 °C [33,34]. It appears that the PTMO crystal morphology changed due to orientation and results in a higher melting point, present above room temperature, which allowed the crystals to remain as gas barriers in the film. Interestingly, the 42 °C endotherm is close to the reported 43–46 °C equilibrium melting temperature, T_m, for low molecular weight pure PTMO [35–37]. The T_m is achieved by extended-chain crystals that can be created through high orientation of the polymer chains, similar to the conditions described in this work.

PEBAX 2533 (86% PTMO) showed the strongest effect of orientation on the formation of the 42 °C melting peak, which corresponds to the strong PTMO crystal reflections in the WAXS patterns and the most significant drop in permeability. The presence and intensity of the new peak was less dominant as PTMO content decreased due to less PTMO available to strain crystallize during orientation. Further evidence that the additional 42 °C peak was a result of PTMO crystals came from the second heating thermograms, which showed only a PTMO melting peak at around 7 °C and no melting peak at 42 °C.

From the heats of melting, a dramatic change in the crystalline melting behavior was observed as a result of uniaxial orientation. PEBAX 2533 had a strong strain crystallized peak, particularly at 400% strain. At 400% strain, the heat of melting decreased from approximately 20.5 to 2.9 J/g for the 7 °C endotherm, while the 42 °C peak heat of melting was as high as 17.8 J/g. The effect was less evident in lower PTMO containing copolymers, however, was still present at 75% and 71% PTMO, particularly at the highest strains, Fig. 12. The decreased effect was due to a lower PTMO content, which was prevented from strain crystallizing during uniaxial orientation by the increased number of PA-12 hard blocks. During uniaxial orientation and elastic recovery, the PA-12 crystallinity remained constant with no effects of orientation on the amount of crystallinity present. However, in all cases, the increased PTMO crystallinity present at room temperature produced a more tortuous path for gas flow as compared to the unoriented films, which resulted in a substantial decrease in permeability of oriented and elastically recovered PEBAX films.

![Fig. 9. Oxygen permeability of PEBAX xx33 series films after elastically recovering from various strains.](image)

![Fig. 10. WAXS reflection patterns of recovered PEBAX films. (a) 2533, (b) 3533, (c) 4033, and (d) 5533 recovered from 200% strain. (e) 6333 recovered from 100% strain.](image)
Fig. 11. Thermograms of uniaxially oriented PEBAX films after elastic recovery from various stages of strain: (a) 2533, (b) 3533, (c) 4033, (d) 5533.

Fig. 12. Melting enthalpy of residual strain-induced crystallinity of PEBAX films recovered from various strains.

Fig. 13. Oxygen permeability of PEBAX 2533, 3533, and 4033 films as extruded, in tension (200%), and after annealing at 60 °C for 30 min.
3.4. Annealed PEBAX copolymer films

From the thermal analysis of recovered PEBAX films, specifically those with higher PTMO contents, an additional melting peak was observed at 42 °C due to residual strain induced crystallization. In many gas separation membrane applications, the decrease in permeation caused by residual crystallization would be an undesired consequence of orienting PEBAX. A solution for increasing the gas flux would be to incorporate a post process annealing step to eliminate the residual strain induced crystallinity without negatively affecting the membrane structure or properties.

Toward a solution to resolve the decreased permeability upon orientation, PEBAX films oriented to 200% strain were annealed at 60 °C while in tension. A temperature of 60 °C was chosen because it was well enough above the 42 °C melting endotherm of the strain induced crystallinity to ensure complete melting. Annealing above 42 °C should remove the PTMO crystallinity and thereby reduce the resistance to gas flow through the film.

The permeability of PEBAX copolymers which show effects of strain induced crystallinity was measured in tension and after annealing while in tension. As seen previously, the permeability dramatically decreased after uniaxial orientation. However, after annealing, the permeability increased to levels comparable to that of the as-extruded unoriented films, Fig. 13. The increase in permeability was a result of melting the PTMO crystals and recreating a high gas diffusion pathway through the polyether blocks.

In addition, WAXS patterns were collected at the same points at which permeability measurements were conducted to determine structural changes that occurred during orientation and after annealing. Upon annealing, the two equatorial PTMO crystal reflections, present in the oriented films, were eliminated, corresponding to the observed increase in permeability, Fig. 14. Only the highly oriented PA-12 reflections were seen after annealing of the oriented films, which have no effect on the permeability of PEBAX copolymers.

Upon examination of the permeability after annealing, the annealed films showed values slightly higher than the unoriented control films. The increase in permeability was larger than the decrease caused by uniaxial orientation, which meant that a change in the copolymer, other than melting of the PTMO, had occurred. It was possible that upon orientation, the polyamide-12 blocks had changed morphology. Uniaxial orientation of all samples was done at room temperature, well below that of the glass transition of the PA-12. During orientation, the PA-12 crystals could have been broken into small blocks as a result of the high strain used to orient the films [25,30]. Smaller PA-12 crystals would provide a less tortuous diffusion pathway, increasing the overall permeability.

4. Conclusions

Uniaxial orientation has a significant effect on the gas permeability of poly(ether block amide) (PEBA) copolymers, with up to a 3.5× decrease from the unoriented control to the 400% strain sample. The decrease in permeability was attributed to crystallinity resulting from strain-induced crystallization of the poly(tetramethylene oxide) (PTMO) soft blocks. The PTMO, usually melted at room temperature, strain crystallizes in a form that melts above room temperature (at 42 °C), which allowed for the crystals to block the flow of gas through the oriented and elastically recovered films. The diffusion path becomes more tortuous resulting in a much lower permeability. To reverse the effect of orientation on PEBA copolymers, particularly for high flux membrane applications, an annealing step was employed. Annealing melted the PTMO crystals and increased the permeation back to levels comparable to that of the unoriented as-extruded films. The ability to remove the effects of orientation in PEBA copolymers allows for a broad range of applications, particularly in extruded gas separation membranes.

Acknowledgments

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References