Porosity enhancement in β nucleated isotactic polypropylene stretched films by thermal annealing

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Microporous polymer membranes were fabricated by extrusion, thermal annealing, and subsequent biaxial stretching of β nucleated isotactic polypropylene. Fabrication conditions were optimized based on prior studies so that the influence of annealing on the precursor film crystallinity and the pore formation in such films upon stretching could be investigated. Annealing perfected the crystalline structure of these materials, as evidenced by thermal and x-ray techniques. A mechanism detailing the annealing and pore formation process during biaxial stretching is presented. An appropriate metric was developed to relate the crystallinity of the precursor films to the porosity of the films after biaxially stretching. The porosity developed in biaxially stretched films increased substantially when its precursor was annealed near the melting temperature of β crystalline material, enabling the production of high permeability microporous membranes.

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1. Introduction

Microporous polymer membranes are of interest in many industrial applications. Since nitrocellulose micro- and ultrafiltration membranes were first commercialized in the 1920s [1], many types of microporous polymer membranes have been produced. Such membranes have been studied for use in filtration applications [1,2], gas exchange [3], membrane distillation [4], for use in bioreactors [5], as battery separators [6,7], and as porous supports for gas separation and desalination membranes [1,8,9], which were first made possible by the Loeb-Sourirajan phase separation process [10]. This study examines extruded β nucleated isotactic polypropylene (β-iPP) films that have been annealed and biaxially stretched to induce pore formation. The aim of this research is to develop a methodology by which these films may be coextruded in a multilayered configuration [11,12] with alternating layers of porous precursors and nonporous materials. These films may then be stretched to form a composite membrane (i.e., a nonporous thin membrane supported on a porous support) with useful properties. One potential use of this approach would be to prepare membranes for modified atmosphere packaging applications, which is being studied concurrently [13,14]. This approach has the additional advantage of avoiding expensive and environmentally hazardous solvent-based processes, which are the current industry standard for the production of composite membranes [1,8,9].

There are several pathways to produce isotropic porous films using solvent-free stretching methods. This process generally begins with the formation of a two-phase structure, and is followed by a stretching step which imposes stress on the interface [15]. For example, polypropylene can be blended with inorganic fillers such as CaCO3 and then stretched, causing cavitation through delamination of filler from the matrix. The number of pores and their sizes can be controlled by varying particle loading, particle size, and stretching conditions [16,17]. Perhaps the best-known microporous stretched film is the original Gore-Tex, a highly porous membrane produced by rapid stretching of polytetrafluoroethylene at high temperatures [18]. Other innovations in this area are isotactic polypropylene (iPP) and polyethylene (PE) microporous membranes produced by Celgard employing a “dry stretch” technique, patented by Celanese in the late 1960s [19–21] and commercialized in 1974 [22]. The extrusion, film take-up and annealing conditions for iPP prior to this “dry stretch” must be closely controlled to ensure that the film becomes highly oriented prior to crystallization. In iPP, this results in films with a stacked lamellar α crystalline structure that exhibit higher porosity and permeability upon...
stretching compared to films with spherulitic α structures [23–26]. In addition to iPP and PE, other semicrystalline polymers that can form highly oriented stacked lamellar crystalline structures such as polyoxymethylene [27,28] and isotactic poly(4-methyl-1-pentene) [29,30] have been reported. Those studies were performed to determine the extrusion and annealing conditions required to create polymer precursors that successfully generate microporous membranes using the “dry stretch” technique. The challenges of forming structures amenable to pore formation during stretching of a melt-extruded multilayered film have led to other approaches for iPP films, one of which is the stretching of extruded β-iPP films.

Isotactic polypropylene is a polymorphic semicrystalline polymer, manifesting crystalline modifications of the α, β and γ form [31,32]. Polymer films containing the first two modifications can be stretched under appropriate conditions to generate porosity, making these crystal forms of interest in this study [3,23]. Both α and β crystals exist in a β₁ helical conformation, but the α form packs into a monoclinic unit cell while β packs in a hexagonal unit cell [33,34]. The β₁ form is considered a metastable phase, due to its tendency to transform to α when exposed to mechanical or thermal stimulation [33,35]. One reason for the instability of the β₁ form and the difficulty to isolate and thus characterize the material is that β-iPP crystallizes with a frustrated helical packing, wherein the different azimuthal orientation of the helices ensure that at least one of the three helices in the packing is in an energetically unfavorable position [34,35]. For this reason, a nucleating additive is required to obtain any significant quantity of the β form, and iPP tends not to remain in that form [35]. Additionally, many β nucleators also serve as nucleators for the α phase [35,36]. From a practical perspective, any system designed to take advantage of the properties of β-iPP must also account for the presence of α-iPP.

The crystallinity of β-iPP precursor films is critical to porosity formation in the film upon stretching. This study examines porous films produced from melt-extruded β-iPP precursors and builds upon previous work in this area [37–39]. For example, Chu et al. produced β-iPP films crystallized in a hot press at a fixed temperature [3,40,41]. The film crystallinity was measured, then the samples were uniaxially or biaxially stretched to induce pore formation. A pore formation mechanism was proposed, and porosity, pore size distribution and gas permeability of the stretched films were measured. Several examples of melt-extruded biaxially stretched β-iPP microporous films are taught in the patent literature [42–45]. However, none of the previously mentioned studies examined the effect of annealing on β crystal structure and the resulting pore formation. A large body of work exists discussing the effect of annealing on β-iPP, primarily in the context of modifying the mechanical properties [46–50]. Compared to neat iPP, β-iPP generally exhibits greater toughness, higher impact strength, lower yield strength and reduced modulus across a variety of different iPP resin grades, nucleator types, and processing conditions [48,51]. Impact strength in particular is greatly enhanced when samples are annealed [49]. Of particular relevance to stretching annealed β-iPP films is an observed increase in resistance to necking, resulting in more homogeneous deformation [50]. Changes in mechanical properties upon annealing would likely affect the behavior of the films when stretched, including the extent of pore formation.

2. Experimental

2.1. Materials selection

Three grades of iPP were included in this study. Dow H700-12, with an ASTM D1238 melt flow index (MFI) of 12 g/10 min, Exxon 2252 (MFI = 3.5), and Exxon 1572 (MFI = 2.1) were selected as the model iPP materials, and they were received in pellet form. A highly active [48,52] β nucleating agent for iPP, quinacridone quinone (QQ), was purchased from Sigma–Aldrich and was used without further modification. The chemical structures of the polymer and nucleating agent are presented in Fig. 1.

2.2. Film preparation

A master batch of each iPP grade containing 0.5 wt.% QQ was prepared by melt blending at 190 °C using a Haake Rheomix 600 twin screw extruder and pelletizing the extrudate. These pellets were then mixed with additional iPP in the hopper before film extrusion to reach the desired concentration of 0.1 wt.% QQ. This two-step process ensured good control over the QQ content in the β-iPP films, as well as a uniform distribution of the QQ β nucleator in the iPP.

Dow H700-12 β-iPP films were extruded at a temperature of 210 °C, while films of the lower MFI Exxon grades were extruded at 250 °C. To promote the formation of β-iPP by controlling the extruded film cooling rate, and thus crystallization behavior, the iPP was coextruded with a low density polyethylene (LDPE) sacrificial surface layer on each side of the iPP layer. This approach reflects guidance from a prior study which showed that in injection molded tensile bars, the core of the bar had a significantly higher β fraction due to its slower cooling rate [49]. Each multilayered film was extruded from a 14” film die in series with a chill roll operated at a constant temperature of 95 °C in close proximity to the die. Melt flow rates and roll take-up speeds were controlled and uniform between samples so that nominal film thicknesses of 100 μm and consistent crystallization conditions upon film cooling were achieved. Control iPP films were of translucent opacity and white coloration, while the β-iPP films were of translucent opacity and became yellow in color due to the addition of QQ.

Test samples 8.5 × 8.5 cm in size were cut from the center of the extruded film for consistency of thickness, and the LDPE sacrificial layer was carefully peeled away to obtain β-iPP films. Each of the three grades of β-iPP films were subjected to three different thermal annealing treatments to produce 9 unique precursor films varying in both iPP MFI and thermal history. After conditioning the films for at least 2 h at room temperature (23 °C), films were maintained at 23 °C or annealed in an oven in air at either 130 °C or 140 °C for 30 min. The oven was allowed to equilibrate for several hours before annealing, and samples were placed in the same location. Previous studies demonstrate that any structural changes in films of the thickness used in this study are complete by the end of a 30 min annealing process [50,53]. The samples were free-standing during heat treatment, and were allowed to cool to room temperature with an open oven door. Control iPP films were maintained at room temperature after extrusion. All precursor films were stored in sealed plastic bags at room temperature until they were stretched or characterized.

The nomenclature for films produced in this study is as follows. For β-iPP precursor films, the sample code is [MFI]M-[Tanneal]-A-P, where 12M-23A-P refers to a precursor film with an iPP MFI of 12 and an annealing temperature of 23 °C. Selected characteristics of β-iPP precursor films produced for this study are displayed in Table 1. For biaxially stretched films, the sample code is [MFI]M-[Tanneal]-[A-Tstretch]-S, where 3.5M-140A-100S refers to a stretched film whose precursor had an iPP MFI of 3.5, an annealing temperature of 140 °C, and a stretching temperature of 100 °C. Each of the β-iPP precursor films was biaxially stretched to generate porosity, as demonstrated in several other studies [3,38–40,54]. A Brückner Karo IV biaxial stretching device with temperature control was used to produce porous stretched films from the precursor films. Films in this study were stretched to an elongation of 100% in the machine and transverse directions simultaneously at
a rate of 100% s\(^{-1}\) and at a temperature of 100 °C. The exposure of as-extruded samples to this temperature in the biaxial stretcher occurs for only 1–2 min, minimizing any effect of thermal annealing. Stretched films were stored in sealed plastic bags at room temperature until they were characterized.

### 2.3. Differential Scanning Calorimetry (DSC)

Thermal analysis of precursor and stretched samples was performed using a TA Instruments Q100 DSC. The DSC was calibrated for temperature using an indium standard. Measurements were taken on samples weighing around 7 mg, which were sealed in aluminum pans and purged with nitrogen gas during experiments. First heating scans were performed using a heating rate of 20 °C/min from 40 to 100 °C, and then heating from 100 to 200 °C at 10 °C/min. Samples were then cooled from 200 to 40 °C at 20 °C/min, and second heating scans were performed using the same procedure as first scans. The initially faster heating rate was used to expedite the experiment and to limit the amount of time precursor films would spend under conditions not found in the biaxial stretching step.

The fraction of a particular crystalline iPP modification (\(X_i\)) in a given sample was calculated using the equation

\[
X_i = \frac{\Delta H_i}{\Delta H_0^0}
\]

where \(\Delta H_i\) is the heat of fusion measured for an endotherm in a given sample corresponding to one of three crystalline iPP modifications (\(\alpha, \beta_1\), or \(\beta_2\)), and \(\Delta H_0^0\) is the heat of fusion for a completely crystalline material of a particular modification. As reported elsewhere [55,56], \(\Delta H_0^0 = 177.0 \text{ J/g}\) and \(\Delta H_0^0 = 168.5 \text{ J/g}\), with \(\Delta H_0^0\) used to characterize melting in both \(\beta_1\) and \(\beta_2\) endotherms. The sample crystallinity (\(X_c\)) was then determined as follows:

\[
X_c = X_{\alpha} + X_{\beta_1} + X_{\beta_2}
\]

Stretched film properties are dependent upon the fraction of precursor \(X_c\) that is in the \(\beta_1\) or \(\beta_2\) form, and this point will be discussed in more depth later.

### 2.4. X-ray diffraction (XRD)

XRD experiments were performed on precursor and stretched samples 3 × 3 cm in size using a Scintag X1 diffractometer using CuK\(\alpha\) radiation with \(\lambda = 0.154 \text{ nm}\). Scans were run in the range \(2\theta = 10–30°\) at a rate of 4°/min with an angle increment of 0.04°. The software package Jade (Materials Data Inc.) was used to generate best fits to peak areas, and accounted for background scatter.

A widely used measure of the \(\beta\) crystalline content in iPP materials is the Turner-Jones parameter, \(K_{\beta,H}\) [32]. This parameter can be determined from XRD scans with the equation

\[
K_{\beta,H} = \frac{H(300)_{\beta}}{H(300)_{\beta} + H(110)_{\beta} + H(040)_{\beta} + H(130)_{\beta}}
\]

where \(H(300)_{\beta}\) is the intensity of the equatorial \(\beta\) diffraction peak and \(H(110)_{\beta}, H(040)_{\beta}\), and \(H(130)_{\beta}\) are the intensities of the equatorial \(\alpha\) diffraction peaks. A related parameter [57,58] using the areas corresponding to these peaks rather than their intensities will also be used in this study, and will be referred to as \(K_{\beta,A}\). This parameter is only a relative measure of the amount of \(\beta\) material in a sample, and it should not be taken to represent the absolute quantity of \(\beta\) material [59]. Only equatorial peaks are used in this analysis because the (111)\(_{\alpha}\) and (301)\(_{\beta}\) peaks are found near the same 2\(\theta\) value, and their inclusion would make determination of relative \(\alpha\) and \(\beta\) content difficult [60]. Sample crystallinity, \(X_c\), can also be estimated from the ratio of crystalline peak area to the total peak area [60].

The relative size of the largest dimension of the \(\beta\) crystal, \(D_{300}\), can be estimated based on the peak broadening associated with the (300)\(_{\beta}\) peak. This estimate is based on the Scherrer equation [40,61] as follows:

\[
D_{300} = \frac{\lambda}{B_{300} \cdot \cos(\theta)}
\]

In this equation, \(\lambda\) is the X-ray wavelength, \(B_{300}\) is the (300)\(_{\beta}\) peak width at half the maximum intensity, and \(\theta\) is half the scattering angle.

### 2.5. Film density and porosity determination

Densities of precursor and stretched films were measured using the density kit for a Mettler Toledo Excellence balance. Pure water was used as the liquid medium for measurement. Samples were measured for wet and dry weight in triplicate and densities were calculated from these weights based on Archimedes’ principle.

Precursor film densities were also estimated from DSC and XRD measurements, since both experiments yielded crystalline \(\alpha\) and \(\beta\) content as well as amorphous content. These estimates were based on the equation

---

Table 1

<table>
<thead>
<tr>
<th>Sample code</th>
<th>iPP grade</th>
<th>MFI (g/10 min)</th>
<th>Annealing treatment</th>
<th>(\rho) (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>12M-23A-P</td>
<td>Dow H700-12</td>
<td>12</td>
<td>23 °C</td>
<td>0.900 ± 0.002</td>
</tr>
<tr>
<td>3.5M-23A-P</td>
<td>Exxon 2252</td>
<td>3.5</td>
<td>23 °C</td>
<td>0.994 ± 0.004</td>
</tr>
<tr>
<td>2.1M-23A-P</td>
<td>Exxon 1572</td>
<td>2.1</td>
<td>23 °C</td>
<td>0.902 ± 0.003</td>
</tr>
<tr>
<td>12M-130A-P</td>
<td>Dow H700-12</td>
<td>12</td>
<td>130 °C/30 min</td>
<td>0.904 ± 0.003</td>
</tr>
<tr>
<td>3.5M-130A-P</td>
<td>Exxon 2252</td>
<td>3.5</td>
<td>130 °C/30 min</td>
<td>0.906 ± 0.002</td>
</tr>
<tr>
<td>2.1M-130A-P</td>
<td>Exxon 1572</td>
<td>2.1</td>
<td>130 °C/30 min</td>
<td>0.907 ± 0.001</td>
</tr>
<tr>
<td>12M-140A-P</td>
<td>Dow H700-12</td>
<td>12</td>
<td>140 °C/30 min</td>
<td>0.902 ± 0.002</td>
</tr>
<tr>
<td>3.5M-140A-P</td>
<td>Exxon 2252</td>
<td>3.5</td>
<td>140 °C/30 min</td>
<td>0.905 ± 0.003</td>
</tr>
<tr>
<td>2.1M-140A-P</td>
<td>Exxon 1572</td>
<td>2.1</td>
<td>140 °C/30 min</td>
<td>0.902 ± 0.004</td>
</tr>
</tbody>
</table>
\( \rho_{\text{PP}} = X_a \cdot \rho_a + X_b \cdot \rho_b + (1 - X_a) \cdot \rho_a \)  
\( (5) \)

where \( \rho \) is density, and the subscripts “iPP” and “a” refer to bulk iPP material and amorphous phase, respectively. Densities of amorphous, \( \alpha \), and \( \beta \)-iPP material have been reported to be 0.852, 0.936, and 0.922 g/cm\(^3\), respectively [62].

The bulk porosity, \( \Phi \), of the stretched film was determined by tracking the reduction in density upon stretching a given precursor film. Porosity was calculated as follows:

\[ \Phi = 1 - \frac{\rho_{\text{stretch}}}{\rho_0} \]  
\( (6) \)

where \( \rho_{\text{stretch}} \) is the stretched film density and \( \rho_0 \) is the precursor film density.

2.6. Scanning Electron Microscopy (SEM)

Surface SEM was performed to examine pore formation resulting from stretching precursor films. Stretched films of 30–70 \( \mu \)m in thickness were sputter-coated with ~10 nm of iridium and images of representative areas were captured on a Zeiss SEM.

2.7. Capillary Flow Porometry (CFP)

Analytical services were provided by LabQMC, who used a Quantachrome Porometer 3Gzh for CFP to determine the size distribution of through-pores in stretched film samples. Dry stretched films were wetted with a proprietary fluorinated hydrocarbon (Porofil) having a low surface tension and vapor pressure, then placed into the CFP device. Differential air pressure, \( \Delta p_{\text{air}} \), was applied to the film until the force applied was great enough to overcome the capillary force in the largest pore (the bubble point) and expel the liquid. As pressure was further increased, the flow of air through the porous film was monitored, and liquid was expelled from decreasingly small pores until either all pores were dry or the pressure limit of the device had been reached. The accessed through-pore diameter, \( D_{\text{pore}} \), was calculated using the equation for capillary pressure [63]

\[ D_{\text{pore}} = \frac{4 \cdot \gamma_{\text{liq}} \cdot \cos(\theta_{\text{liq}})}{\Delta p_{\text{air}}} \]  
\( (7) \)

where \( \gamma_{\text{liq}} \) is the surface tension of Porofil and \( \theta_{\text{liq}} \) is the contact angle of the Porofil on the stretched film. \( D_{\text{pore}} \) values greater than 18 nm could be detected using this method.

2.8. Gas permeability

The permeability of pure \( \text{N}_2 \) gas through stretched films was measured using a device that applies a constant pressure driving force to the film and permits the measurement of the gas flow through the film [64]. The gas permeability, \( P_{\text{gas}} \), was calculated using a standard definition of permeability [65]. Gas permeability is in units of Barrer, where 1 Barrer = 10\(^{-10}\) cm\(^3\) (STP) \cdot cm/(cm\(^2\) \cdot s \cdot cm Hg).

3. Results and discussion

3.1. \( \beta \)-Crystallinity in precursor and stretched iPP films

Thermal analysis of precursor and stretched \( \beta \)-iPP films was performed by DSC. These experiments provided insight about the populations of crystals in a given film as they melted during the scan. The evolution of the crystalline material in precursor films for each of the three annealing conditions was tracked, and further changes in the crystalline material were observed as the films were stretched. Several key properties arising from the crystallinity of the precursor films are presented in Table 2.

Heat flows measured during first heating DSC scans of precursor films are presented in Fig. 2. In each precursor film scan, distinct melting peaks for \( \beta_1 \), \( \beta_2 \) and \( \alpha \) endotherms were observed. Double \( \beta \) peaks, seen in the form of \( \beta_1 \) and \( \beta_2 \) endotherms, are typical of polymorphic \( \beta \)-iPP. These peaks occur when the polymer has been crystallized at temperatures below 125 °C, and are due to the instability of the \( \beta_1 \) crystals formed at high cooling rates and their propensity to recrystallize to \( \beta_2 \) [66–68]. This phenomenon has also been seen to occur during nonisothermal crystallization [57], as is used in this study.

Melting peak temperatures for \( \beta_1 \) material in the precursor films increased with increasing annealing temperature, as shown in Table 2. The nonisothermal crystallization of \( \beta \)-iPP was achieved with temperatures at or above the chill roll temperature of 95 °C, and films were cooled to room temperature before characterization. Thus, the critical temperature of recooling (100–110 °C) [47] was reached in all samples. This temperature is defined as that below which \( \alpha \) nuclei are formed in the \( \beta \) phase, resulting in \( \alpha \) recrystallization during the \( \beta \) melting. This bears mentioning here, because recooled samples that are then annealed below the melting temperature of the \( \beta_1 \) material exhibit greater stability and a correspondingly higher melting point for the \( \beta_1 \) material [48], consistent with observations in this study. At a given annealing temperature, melting peak temperatures observed were about 2 °C lower in 12 MFI iPP precursors than in the two lower MFI iPP precursors. Few studies examine the effect of iPP homopolymer MFI on \( \beta \) crystal melting peak temperature, but two related papers by Varga et al. show that a 5.5 MFI iPP has a melting temperature about 1 °C lower than that of a 0.76 MFI iPP [66,67]. This result was obtained under controlled crystallization conditions, contrasting with crystallization during extrusion and chill roll take-up used in this study. Precursor annealing temperature did not influence the melting peak temperatures of \( \beta_2 \) (\( T_m = 150 \) °C) or of \( \alpha \) (\( T_m = 166 \) °C) material, but 12 MFI iPP precursors exhibited a peak at about 165 °C, roughly 1 °C lower than the two lower MFI iPP precursors. The lower melting temperatures observed in the 12 MFI iPP can be attributed to the reduced chain entanglement that accompanies lower molecular weight. Observed melting temperatures were consistent with similar materials previously studied [58,69].

The sizes of the \( \beta_1 \), \( \beta_2 \) and \( \alpha \) endotherms associated with the melt-recrystallization processes occurring during the first heat were used to calculate most of the properties in Table 2. Because of the melt-recrystallization that occurs in polymorphic \( \beta \)-iPP during the heating scan, the calculated crystallinity, \( X_c \), may not be equal to the crystallinity of the precursor film just after the annealing step. It is more useful to observe the crystallinities \( X_i \) individually to track

<table>
<thead>
<tr>
<th>Sample code</th>
<th>T_m(°C)</th>
<th>( X_c )</th>
<th>( X_{\text{DSC}} )</th>
<th>( X_{b/\alpha} )</th>
<th>( \Phi_\beta )</th>
<th>( P_{\text{gas}} ) (g/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>12M-21A-P</td>
<td>141.8</td>
<td>0.65</td>
<td>0.50</td>
<td>0.249</td>
<td>0.158</td>
<td>0.902</td>
</tr>
<tr>
<td>1.5M-21A-P</td>
<td>143.8</td>
<td>0.61</td>
<td>0.47</td>
<td>0.298</td>
<td>0.176</td>
<td>0.899</td>
</tr>
<tr>
<td>2.1M-21A-P</td>
<td>143.6</td>
<td>0.58</td>
<td>0.43</td>
<td>0.299</td>
<td>0.169</td>
<td>0.897</td>
</tr>
<tr>
<td>12M-130A-P</td>
<td>143.3</td>
<td>0.62</td>
<td>0.48</td>
<td>0.342</td>
<td>0.207</td>
<td>0.900</td>
</tr>
<tr>
<td>12M-130A-P</td>
<td>144.9</td>
<td>0.60</td>
<td>0.46</td>
<td>0.378</td>
<td>0.219</td>
<td>0.898</td>
</tr>
<tr>
<td>2.1M-130A-P</td>
<td>144.6</td>
<td>0.58</td>
<td>0.42</td>
<td>0.374</td>
<td>0.213</td>
<td>0.898</td>
</tr>
<tr>
<td>12M-140A-P</td>
<td>143.7</td>
<td>0.66</td>
<td>0.49</td>
<td>0.371</td>
<td>0.240</td>
<td>0.903</td>
</tr>
<tr>
<td>3.5M-140A-P</td>
<td>145.9</td>
<td>0.73</td>
<td>0.50</td>
<td>0.430</td>
<td>0.307</td>
<td>0.908</td>
</tr>
<tr>
<td>2.1M-140A-P</td>
<td>145.1</td>
<td>0.70</td>
<td>0.48</td>
<td>0.409</td>
<td>0.279</td>
<td>0.906</td>
</tr>
</tbody>
</table>
changes in β-IPP materials as they are annealed. A quantity analogous to $K_{\beta, A}$ for XRD measurements can be defined as follows:

$$K_{\beta, DSC} = \frac{X_{\beta} + X_{\beta_2}}{X_c}$$

which is meant to provide a measure of the relative content of β-crystalline material in the film [70]. A technique employing simultaneous DSC and XRD of polymorphic β-IPP has been previously performed to decouple melting and crystallization of the α and β crystalline material [69,71], but the results of this study can be interpreted using simpler techniques. As the annealing temperature is increased, there is no apparent trend in either the calculated precursor $X_c$ or $K_{\beta, DSC}$, although there is a slight increase in $X_c$ at an annealing temperature of 140 °C. The most apparent effect of increasing the precursor annealing temperature was an accompanying enlargement of the $\beta_1$ endotherm and a decrease in $\beta_2$ endotherm size. The size of the $\alpha$ endotherm remained relatively constant across all annealing treatments, likely due to the ability of the $\beta$ crystals to melt and then recrystallize to $\alpha$ phase crystals in samples cooled below the critical temperature of recrystallization [47]. This effect is especially pronounced when the sample undergoes crystallization at a large supercooling [48,72,73], and in this study, crystallization was performed at a large supercooling and the final crystallization temperature was below the critical temperature of recrystallization. Recrystallization may mask any change in the amount of $\alpha$ material present prior to annealing. The slight increase in calculated $X_c$ at an annealing temperature of 140 °C results from a greater increase in $\beta_1$ endotherm size than the corresponding decrease in $\beta_2$ endotherm size.

The evolution of the $\beta$ endotherms as annealing temperature increases proceeds in the following way. Initially, a low temperature “shoulder” in the endotherm develops as the $\beta_1$ melting peak is approached, and it is accompanied by both an increase in peak heat flow and area in the $\beta_1$ region and a decrease in $\beta_2$ peak heat flow and area. When annealing temperature is further increased, the shoulder develops at temperatures closer to the $\beta_1$ melting peak, and it eventually disappears as it is incorporated into an increasingly smooth $\beta_1$ endotherm. The $\beta_2$ endotherm concurrently decreases in size and becomes a shoulder to the $\beta_1$ endotherm. Similar behavior has been reported previously, and it can be reasonably characterized as the perfection of the $\beta$ crystal structure [49]. The $\beta_1$ endotherm grows due to an increased size and quantity of $\beta$ crystals, and the $\beta_2$ endotherm decreases in size due to the higher melting point of the $\beta_1$ endotherm and the resulting smaller window to recrystallize to the $\beta_2$ form [50]. The melting peak elevation of the $\beta_1$ endotherm provides additional evidence for the growth of $\beta$ crystals upon annealing.

In the case of films annealed at 130 °C, the onset temperature of the shoulder peaks differs from one film to the next, with a range of about 125—131 °C. The onset temperature is related to the annealing temperature [53], which could indicate that the true annealing temperature deviates from the reported temperature. Since the deviation is small, we believe the results are not significantly affected.

Precursor films extruded from 12 MFI iPP showed less development of the $\beta$ endotherms than the higher MFI precursor films at all annealing temperatures. In the case of the 12M-140A-P film, the annealing temperature was sufficiently close to the peak melting temperature of the $\beta_1$ endotherm ($T_m(\beta_1) = 141.8$ °C) that the development of larger $\beta$ crystals with higher melting temperatures may have been impeded. A less perfected crystal structure compared to lower MFI films may explain the remaining shoulder at a temperature below the $\beta_1$ melting peak as well as the more pronounced $\beta_2$ endotherm in the 12M-140A-P film.

Contrary to other studies that examine similar extruded β-IPP materials [39], the precursor film density calculated from an additive model of the constituent phases based upon crystalline contents determined by DSC, $\rho_{DSC}$, which is shown in Table 2, differs by less than one percent from precursor density measured directly. Thus, for the materials examined in this study, the simple model of material composition involving only amorphous and $\alpha$ and $\beta$ crystalline material is consistent with the actual material composition. Because of the possibility of “double counting” crystalline material as it recrystallizes to both the $\alpha$ and $\beta$ phases, these values should be considered less reliable than those obtained by XRD.

First heating scans on biaxially stretched films corresponding to the precursor films discussed above are also presented in Fig. 2. Very
weak (if any) $\beta_1$ melting peaks and strong $\alpha$ melting peaks were observed. Compared to precursor films, the melting peak temperatures of the $\beta_1$ and $\alpha$ endotherms were depressed by about 1 °C. Previous studies show that mechanical deformation of $\beta$-iPP can destroy $\beta$ crystals [37,40,48,68,72], or have both a destructive and transformative effect. A reduction in crystal size resulting from these processes may account for the observed decrease in melting peak temperatures upon stretching. The change in size of these endotherms is also consistent with these crystal phase rearrangements.

In films where the precursor was stretched without further precursor annealing, no $\beta_1$ endotherm was detectable, while higher temperature annealing of precursors resulted in a small amount of residual $\beta$ material appearing in the $\beta_1$ endotherm. Thus, the $\beta$ material was indeed either destroyed or transformed, and this process occurred to a greater extent when the $\beta$ crystals had been less perfected through the annealing process. The size of the $\alpha$ endotherm was increased upon stretching in all cases, which is possibly evidence of either a strain-induced transformation from $\beta$ to $\alpha$, recrystallization to $\alpha$ during the scan, or both. The onset of the $\alpha$ endotherm also occurred at a lower temperature than in precursor films. The lower temperature onset could indicate either a lower melting temperature for some of the newly formed $\alpha$ crystals or the formation of a small $\beta_2$ endotherm that cannot be distinguished from the $\alpha$ endotherm.

Low $\beta$ nucleator concentration is one potential cause of the instability that results in double peaks observed in the precursor first heating scans [67]. Second heating scans of both precursor and stretched samples (not shown) were nearly identical to one another, featuring a single large $\beta$ endotherm at about 150 °C and a diminished $\alpha$ endotherm at about 166 °C. The single $\beta$ endotherm observed in the second heat scan demonstrates that the crystallization process, not the nucleator concentration, most likely contributes to the double $\beta$ peaks in the first scans [74]. Crystallization conditions induced by the extrusion and annealing process always led to double peaks and were a significant factor influencing the performance of the porous films produced by stretching in this study.

Characteristic reflections of $\alpha$ and $\beta$ crystals in precursor films and stretched films were generated by using XRD techniques frequently employed for characterization of similar $\beta$-iPP materials [32,40,59,75]. Compared to DSC analysis, XRD permits the quantification of crystalline material without thermal transitions as confounding factors. Solvent extraction and depolarized light intensity methods have also been used [59] to quantify $\beta$ content, but these were not considered here because they are time-consuming techniques, and are not as prevalent in the literature as XRD. The effect of annealing on precursor film crystalline content and the effect of the stretching process on the crystalline material can then be more clearly understood relative to DSC alone. Table 3 summarizes some of the key properties calculated from diffraction patterns of precursor films.

### Table 3

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$D_{002}$ (nm)</th>
<th>$X_e$</th>
<th>$K_{B1}$</th>
<th>$K_{B2}$</th>
<th>$rho_{002}$ (g/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12M-23A-P</td>
<td>41</td>
<td>0.68</td>
<td>0.99</td>
<td>0.98</td>
<td>0.900</td>
</tr>
<tr>
<td>3.5M-23A-P</td>
<td>42</td>
<td>0.68</td>
<td>0.99</td>
<td>0.95</td>
<td>0.900</td>
</tr>
<tr>
<td>2.1M-23A-P</td>
<td>42</td>
<td>0.70</td>
<td>0.99</td>
<td>0.95</td>
<td>0.902</td>
</tr>
<tr>
<td>12M-130A-P</td>
<td>45</td>
<td>0.64</td>
<td>0.97</td>
<td>0.93</td>
<td>0.898</td>
</tr>
<tr>
<td>3.5M-130A-P</td>
<td>43</td>
<td>0.72</td>
<td>0.98</td>
<td>0.91</td>
<td>0.903</td>
</tr>
<tr>
<td>2.1M-130A-P</td>
<td>44</td>
<td>0.74</td>
<td>0.97</td>
<td>0.91</td>
<td>0.904</td>
</tr>
<tr>
<td>12M-140A-P</td>
<td>48</td>
<td>0.71</td>
<td>0.97</td>
<td>0.90</td>
<td>0.903</td>
</tr>
<tr>
<td>3.5M-140A-P</td>
<td>46</td>
<td>0.73</td>
<td>0.93</td>
<td>0.86</td>
<td>0.904</td>
</tr>
<tr>
<td>2.1M-140A-P</td>
<td>53</td>
<td>0.71</td>
<td>0.95</td>
<td>0.89</td>
<td>0.903</td>
</tr>
</tbody>
</table>

Diffraction peaks for the MFI 2.1 precursor and stretched films are presented in Fig. 3. There were no significant differences between the patterns from these films and those from higher MFI iPP materials, so for brevity only the MFI 2.1 patterns are shown.

The $K$ value and double peak behavior can be altered by varying $\beta$ nucleator content [67,75]. One study reported a maximum in $K$ value using iPP with an MFI of 8, but this effect was observed at a very low $\beta$ nucleator loading (0.1–0.3 ppm) and a low $K$ value (below 0.6) was attained [75]. As $\beta$ nucleator content was increased, the sensitivity of $K$ to MFI decreased, consistent with another study where, at still higher nucleator content, no effect was observed [67]. In this study, the influence of iPP MFI on precursor crystallinity appears to be confined to the stability of the $\beta$ crystalline material present, since no effect on the amount of $\beta$ material or precursor $K$ value was observed in XRD experiments.

The (300)$_\beta$ diffraction peak was found at about 2$\theta = 16.1^\circ$, and the (110)$_\alpha$, (040)$_\beta$, and (130)$_\alpha$ peaks were found at 2$\theta = 14.2, 17.0$ and 18.6$^\circ$, respectively, consistent with a prior study [58]. Two metrics characterizing $\beta$ crystalline content by XRD are $K_{B1}$ and $K_{B2}$, and they are recorded for precursor films in Table 3. The former is calculated using the intensity of equatorial $\beta$ peaks in a pattern, while the latter is based on the area of those same peaks. The originally conceived [32] and most widely used $K$ value is $K_{B1}$, but for consistency with the presentation of $X_e$, which is calculated based on the ratio of crystalline peak area to total area, $K_{B1}$ will be primarily used for analysis and also presented alongside $K_{B2}$. This approach has the additional advantage of generating a broader range of $K$ values, since the peak intensity is much greater for (300)$_\beta$ than for the $\alpha$ peaks.

Studies on crystallization of $\beta$-iPP have compared the growth rates of $\alpha$ and $\beta$ crystals as a function of temperature within a temperature window of 105–140 °C, where the growth rate of $\beta$ crystals is faster than that of $\alpha$ crystals [48,72]. Crystallization behavior in $\beta$-iPP assists in rationalizing the XRD results. The two annealing temperatures selected in this study were situated in the temperature window where $\beta$ grows more rapidly than $\alpha$ to ensure...
β material remained available to induce pore formation. Precursors annealed at 130 °C correspond to samples annealed at the same temperature in another study [49] that resulted in the maximization of both the fraction of β material and impact strength. The maximum temperature where the growth of β material is preferred to α is 140 °C, so a significant loss of β material during precursor annealing is avoided if this temperature is not exceeded.

Analysis of XRD patterns from precursor films show that the total amount of β crystalline material decreased slightly with increasing annealing temperature, while the total amount of α crystalline material increased substantially with increasing annealing temperature. This can be verified by noting that the value of $X_c$ is relatively stable as annealing temperatures are increased, while both $K_{βH}$ and $K_{βA}$ values decrease with increasing annealing temperature. The balance crystallinity must then be made up of crystalline material in the α phase. The decrease in β material observed when annealing at 140 °C is likely due to some degree of melting of β and recrystallization to α arising from the instability of low-melting β material, and exposure to an annealing temperature where the growth of β is only slightly preferred to α. A smaller change along these lines is apparent at 130 °C, where α growth is not as strongly preferred as at 140 °C.

The growth of α material with increasing annealing temperature is anticipated by the decline in β content. The amount of growth of the α content, however, is too great to be accounted for by only the transformation of β to α during annealing. The value of $X_c$ increases slightly even as $K_{βA}$ decreases, indicating an excess growth of α material that must be explained by some other mechanism. The increase in both α material and $X_c$ likely results from the transformation of semi-ordered smectic iPP to ordered α crystalline PP, which is known to occur in iPP that has been rapidly cooled and then heat treated above 80 °C [76], similar to the thermal history of samples used in this study. Precursor density values calculated from crystalline composition, $\rho_{XRD}$, are within the uncertainty of the directly measured density values.

Patterns from films biaxially stretched at 100 °C are also shown in Fig. 3. Significant α and β diffraction peaks did not change position relative to precursor film scans, but large changes in intensity were observed. For all precursors and annealing conditions, the intensity of the (300)β reflection was reduced by more than 90% after stretching. This observation, along with DSC first heat scans which show the near-complete disappearance of β1 endotherms, provides evidence supporting a large scale destruction of β material upon stretching. Prior studies show a similar large reduction in the K value of β-iPP films upon stretching uniaxially [39–41] or biaxially [3,39] under comparable crystallization conditions. The change in α material is also readily apparent, with all equatorial α reflections increasing in intensity relative to precursor films. This increase is consistent with the idea that α crystals form upon deformation of β-iPP films [41]. Additionally, the XRD measurement is not confounded by the potential recrystallization to α caused by the temperature ramp used in thermal analysis, which made it difficult to confirm the growth of α material induced by stretching.

An interesting outcome of stretching films that were annealed under different conditions is that XRD patterns of these films do not display systematic patterns based on their annealing treatment or iPP MFI. Thus, trends existing in precursor films, such as the increase in α material (or decrease in K value) with increasing annealing temperature, do not persist after stretching. There are several reasons for the inability to identify trends in post-stretch patterns. First, the α material formed during stretching is much greater in quantity than that found in precursors prior to stretching. Second, existing α material may be lost during stretching, even as new α material is formed. Third, the amount of additional α material formed is related to the existing quantity and stability of β material, which differs between films having different annealing treatments. The situation is much the same for DSC first heating scans of stretched films, although in that case there are some subtle systematic differences in the β phase resulting from precursor annealing conditions. Overall, the morphology present in extruded precursor films is disrupted by the biaxial stretching process, which simultaneously induces pore formation and thereby reduces organization of the remaining crystallinity and alters XRD reflections. Due to the difficulty of differentiating measures of crystallinity after stretching, it seems likely that the change in crystallinity during stretching or even the precursor crystallinity itself may be a more effective predictor of stretched film properties than the crystallinity of stretched films.

The annealing process has a large influence on the composition and stability of crystalline structures in β-iPP films. Fig. 4 illustrates the effect of annealing temperature on the size of β crystals in precursor films using two independent metrics. First, DSC was used to determine the peak melting temperature of the initially formed crystals in the β1 endotherm, $T_{m1}(β1)$ (Table 2). The melting temperature of crystalline polymers increases with increasing crystal size, and β crystalline material is no exception [72]. Second, XRD was used to observe the peak broadening of the (300)β reflection (Table 3), which can be related to the size of the largest dimension, $D_{300}$, of the β crystals in the sample using the Scherrer equation (Equation (4)). Compared to precursor films that have not been annealed, both $T_{m1}(β1)$ and $D_{300}$ increase with increasing annealing temperature. This increase in both measures strongly indicates that β crystals grow in size when annealed at 130 and 140 °C, which is consistent with the idea that the annealing process perfects the β crystalline material. The size of the β1 endotherm also increases with annealing, indicating that crystal growth, and not only the formation of new β crystals, is a likely driver of increased β material in annealed films. Other studies [40,61] have found $D_{300}$ values of 18–35 nm for β crystalline materials, with little effect seen for either crystallization temperature or β nucleator concentration on $D_{300}$. The observed increase in crystal size in this study is a large effect, with $D_{300}$ increasing by 10–25% over the course of annealing from an initial size of about 40 nm.

![Fig. 4. Growth of β crystal size as indicated by increase in β1 melting peak temperature determined by DSC, and the increase in the largest β crystal dimension as calculated from the Scherrer equation based on observed XRD (300)β peak broadening, both as a function of precursor film annealing temperature. Results are shown for MFI 2.1 (○), MFI 3.3 (□) and MFI 12 (▲) films. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
The general trend in \( \bar{K} \) value presented previously for DSC and XRD analyses is as follows: \( K_{\beta,DSC} \) showed no appreciable trend with precursor film annealing temperature (Table 2), and \( K_{\beta,A} \) decreased with increasing annealing temperature (Table 3). The more likely explanation for this discrepancy lies in the counting of the \( \beta_2 \) endotherm from melt-recrystallization of the initially formed \( \beta \) material during the DSC scan in the calculation of \( K_{\beta,DSC} \). Since the formation of the \( \beta_2 \) endotherm occurs due to externally imposed heating not present in XRD measurements, it is reasonable to develop a metric based on DSC measurements that only considers the initially formed \( \beta_1 \) material so that results from the two techniques may be compared on an equivalent basis. One prior metric proposed by Bai [49] with a definition nearly identical to \( K_{\beta,DSC} \) was developed to compare DSC and XRD analyses, but it was used to examine annealed \( \beta \)-iPP materials that did not exhibit double peak behavior. A comparison in this study between three measures of \( \beta \) crystallinity from DSC scans and \( K_{\beta,A} \) for all precursor films is shown in Fig. 5. The behavior of \( K_{\beta,DSC} \) is uncorrelated with \( K_{\beta,A} \), as would be expected from the prior discussion detailing the melt-recrystallization of \( \beta \) to \( \alpha \). The fraction of total crystallinity in the \( \beta_1 \) phase, \( X_{\beta_1}/X_c \), is strongly correlated with \( K_{\beta,A} \). Interestingly, it is a negative correlation, with the fraction of \( \beta_1 \) material measured growing with increasing annealing temperature while \( K_{\beta,A} \) decreases. Through the annealing process, \( \beta \) material is perfected, resulting in a growth in crystal size (Fig. 4) reflected in the growth of the \( \beta_1 \) endotherm and thus the increase in \( X_{\beta_1}/X_c \). The \( \beta \) material initially formed during the rapid cooling present in extrusion and take-up of the film is also composed of relatively small and less stable crystals, and thus is also more subject to conversion to \( \alpha \) crystalline material. The growth of some \( \beta \) crystalline material and the conversion of less stable \( \beta \) material to \( \alpha \) must proceed concurrently to explain these opposite trends and their high degree of correlation.

One shortcoming of the measure \( X_{\beta_1}/X_c \) is that \( X_c \) necessarily contains \( X_{\beta_2} \). Since the measure of \( \alpha \) crystallinity can be influenced by recrystallization to \( \alpha \) after the melting of \( \beta \) crystals in the DSC scan, a more robust measure of \( \beta_1 \) content would avoid the inclusion of \( X_c \). One possible alternative measure is the volume fraction of \( \beta_1 \) (Table 2) in the precursor films, which can be simply calculated as follows:

\[
\phi_{\beta_1} = \frac{\rho_0}{\rho_{\beta_1}} X_{\beta_1} \tag{9}
\]

This measure is also well-correlated with \( K_{\beta,A} \), so it tracks \( X_{\beta_1}/X_c \) quite closely, shown in Fig. 5. This is likely because calculated \( X_c \) does not change significantly during annealing, and it is therefore acting only as a scaling factor on \( X_{\beta_1} \). Pore formation in stretched \( \beta \)-iPP films may also be related to this quantity, which will be explored in the following section.

3.2. Pore formation by stretching in \( \beta \)-iPP films

The previous section discussed the modification of several \( \beta \)-iPP precursor film parameters (crystallinity \( X_c \), \( \beta \) fraction \( K_{\beta,A} \), size of \( \beta \) crystals \( D_{300} \)) by varying the starting iPP MFI and precursor film annealing temperature. The method by which \( \beta \)-iPP materials mechanically deform is dependent upon each phase present (\( \alpha \), \( \beta \), smectic, amorphous) and how the crystallization and annealing conditions to which they have been previously influenced influence the morphology and amount of these phases. During stretching, iPP is deformed by the separation of crystalline lamellae, by shear forces between lamellae, and by slip along the glide planes of a given lamella [51,77]. This deformation can also be accompanied by a phase transformation from \( \beta \) to \( \alpha \) [32]. The lamellar structure of \( \alpha \) crystalline material is a relatively unusual cross-hatched configuration of radial parent lamellae and tangential daughter lamellae, while the \( \beta \) form is structured more conventionally in the form of parallel, stacked lamellae [72]. The deformation modes are then influenced by these differing lamellar structures. A number of prior studies have used mechanical testing and other techniques to evaluate why \( \beta \)-iPP materials exhibit superior toughness and impact strength relative to neat iPP, and how this difference in properties is related to its deformation behavior.

One key difference between the two modifications is an increased tendency for \( \beta \)-iPP to cavitate as part of its deformation process during stretching relative to neat iPP [37,78]. This behavior is seen generally in semicrystalline polymers, and it occurs during elongation when stress transmitter density near lamellae is inadequate to cause lamellar shear, instead resulting in cavitation [79]. However, because \( \beta \)-iPP materials exhibit a phase transformation from \( \beta \) to \( \alpha \) or from \( \beta \) to smectic when stretched, the accompanying change in density was thought to be the primary cause of pore formation [37]. More recent studies found that the initial pore formation upon stretching of \( \beta \)-iPP films, which occurs before the yield point, is a result of the decoupling between \( \beta \) lamellae and weakly bound adjacent amorphous material [40,41]. This cavitation begins as lamellae separate during stretching of \( \beta \)-iPP, as the mobility of the amorphous phase is not restricted by cross-hatched \( \alpha \) structures [78]. Amorphous tie chains are also less abundant in \( \beta \)-iPP than in neat iPP, and this lack of stress transmitters facilitates the decoupling, presenting a picture in line with cavitation in other semicrystalline polymers [49]. When iPP is exposed to shear forces during drawing that occur due to the inhomogeneity of the material, interlocked \( \alpha \) lamellae resist rotation [80]. Lamellae in the \( \beta \) phase rotate perpendicular to the drawing direction as strain is increased, however, and this rotation contributes to pore formation by assisting in the separation of lamellae [41,81]. After this initial cavitation, continued drawing results in enlargement of previously formed cavities, a phenomenon reflected in prior studies [3,39]. These processes are outlined in a general schematic presented in Fig. 6.
Aside from pore formation by reorientation of existing β crystal structures, phase transformation during stretching influences the porosity of these materials. The transformation from β to α occurs after the yield point during drawing [81,82], so this process is only related to changes in porosity after it is initially generated. This transformation may be induced thermally, but only those produced by mechanical drawing are correlated with changes in porosity [40]. While the existence of the β to α transformation is apparent, its mechanism remains a contentious matter. At low temperatures, stretching results in a β to smectic transition, while at higher temperatures where α crystallization is more favored, β to α transformation occurs [41]. Both types of crystals are arranged in the same 31 helical conformation, but the β form is packed so that the chains are isochiral in each layer, while the α form is packed in a lower energy configuration with alternating chain directionality in each layer [82]. It has been proposed that this transformation can occur in the solid state at these higher temperatures during stretching, where the additional thermal energy can activate the rewinding of helices and result in direct recrystallization to α [37]. Others believe such a solid state transition is impossible, citing a lack of mobility in the ordered β structure and speculating that a pseudo-melt (decrystallization) and recrystallization to α with energy imparted from the drawing process is required [33,82]. In any case, the transformation proceeds with increasing draw ratio, beginning at the yield point and concluding when the sample fractures, in both uniaxially [39,41,82] or biaxially stretched samples [39,40]. The local densification that this transformation causes results in void formation, but that cannot entirely account for the high porosity in stretched β-iPP films since the change in density is on the order of 1% [40].

A factor that strongly influences both lamellar reorientation and phase transformation as well as the resulting pore formation is the extent of β lamellae growth in the sample. Both crystallization temperature and the subsequent annealing influence the size of β lamellae. Crystallization proceeds more slowly at elevated temperatures than when samples are quenched from the melt [41], resulting in larger lamellae. Additionally, annealing the samples at temperatures where β crystalline growth is favored over α also results in larger lamellar blocks [49]. When the lamellae are larger, they have greater thermal and mechanical stability, making it more likely that cavitation will occur as the crystals reorient and separate from the amorphous material [41]. Annealing in particular should increase the likelihood of cavitation, since crystal growth comes directly from the adjacent amorphous region, reducing tie chain density [49]. Larger lamellae also inhibit phase transformation, such that higher draw ratios are required to complete the shift to α, demonstrated by residual β material in DSC thermograms of annealed and stretched films. If this transformation can be retarded,...
by more stable \( \beta \) lamellae during stretching, there are more opportunities for cavitation by lamellar reorientation, resulting in the generation of higher porosity [41].

Based on guidance provided by previous studies that outlined how various processing conditions affected the porosity of stretched \( \beta \)-iPP films, processing of parameters were fixed at values favorable to pore formation to explore the influence of the starting iPP MFI and precursor film annealing temperature on porosity. The nonisothermal crystallization of the film during extrusion was performed at an elevated temperature to yield larger initial \( \beta \) crystals [41,42]. Precursor films were stretched biaxially because prior findings show films made with this technique have higher porosity [38,40] and higher permeability [38] than uniaxially stretched films. The biaxial draw ratio was also optimized for maximum porosity [38-40,54]. The porosity characteristics of selected microporous membranes produced in this study are recorded in Table 4.

The most striking feature about the porosity of these films is that the strongest influence on pore formation is the precursor annealing temperature. Compared to films stretched without annealing, those annealed at 130 °C and 140 °C exhibited very large increases in porosity. This finding is reasonable because annealing affects the size of \( \beta \) lamellae and tie chain density in ways that assist pore formation [41,49]. Further, the measured porosity of 17–38% is in line with previous studies based on similar films [38-40,41]. Fig. 7 presents surface SEM of 12M-[Tanneal]A-100S films, with the associated properties presented in Table 4.

The increase in porosity with annealing temperature was most apparent in these 12 MFI \( \beta \)-iPP films. The increase cannot be explained in terms of greater relative increases in crystal size compared to lower MFI films (Fig. 4) or in terms of more extensive perfection of the crystals during annealing (Fig. 2) since the \( \beta \) endotherms are only intermediate in the transition to more stable \( \beta_1 \) compared to lower MFI films. One possible explanation for the larger increase in porosity in 12 MFI films is that the formation of crystalline structures after extrusion is not as favorable in these films as in the lower MFI films, either due to its lower molecular weight or lower extrusion temperature. This disadvantage is offset by a lower density of tie chains between the \( \beta \) crystalline and amorphous phase because of the lower molecular weight of the iPP [51]. The lower tie chain density would further decrease as the crystal structure is improved by annealing, making initial cavitation more likely and resulting in the parity of porosity between films with different MFI at the highest annealing temperature. The 2.1 and 3.5 MFI films had measured porosities similar to one another at all annealing temperatures, and like the 12 MFI films, increased in porosity with annealing temperature. Regardless of annealing temperature, the intermediate 3.5 MFI films had the highest porosity. Perhaps there is a balance between tie chain density (lower in high MFI iPP) and lamellar block size (higher in low MFI iPP) that must be struck to develop the greatest porosity.

The measured thickness of these films prior to stretching was nominally 100 \( \mu \)m, and the films were biaxially stretched to 100% elongation in the machine and transverse directions. If phase transformation, void formation or other phenomena do not influence the density of the films, the final thickness should be 25 \( \mu \)m. Accounting for both porosity and phase change in each of the stretched films, the expected final thickness should range from 30 to 40 \( \mu \)m. In all cases, the film thicknesses were greater than expected. One prior study of \( \beta \)-iPP materials [40] found a similar discrepancy between expected and measured film thicknesses, with thicknesses substantially higher than expected based on film porosity and draw ratio. This phenomenon is of limited applicability; however, because stretching was performed uniaxially with free film width, which would result in thicker films due to a reduction in width during stretching. To our knowledge, no such results have been reported for biaxially stretched films. Since the uncertainty in both film thickness and porosity is much smaller than the difference between expected and measured thickness, an alternative explanation is required.

Pore size and gas permeability for these selected films were also characterized. For the as-extruded films and some of the films annealed at 130 °C, the pore diameter was too small to measure by the technique used. One of the films annealed at 130 °C and all of the films annealed at 140 °C were found to have pores in the ultrafiltration range, with mean pore diameters between 21 and 29 nm. This size is consistent with the surface SEM images in Fig. 7. The \( N_2 \) permeability of stretched films closely tracked the porosity measured in each film, with precursor film annealing temperature again playing a key role. With one exception [39], the measured \( N_2 \) permeability of 449,000 Barrer is the highest reported for a microporous membrane of this type. The close relationship between permeability and porosity across the films indicates that the interconnectedness and size of pores are similar. A more complete discussion of the permeability of these microporous membranes will be provided in a publication to follow.

Having discussed both the porosity of stretched films and the quantity of stable \( \beta_1 \) crystalline material in the precursor films, it is now possible to demonstrate a relationship between them. Fig. 8 presents a correlation between the volume fraction of \( \beta_1 \) material in precursor films (influenced by iPP MFI, extrusion conditions and annealing temperature) and the bulk porosity of films stretched at 100 °C. A volume fraction is a more appropriate quantity to consider than a mass fraction in this case because it yields some physical insight into how much space \( \beta_1 \) crystals occupy in the bulk, and in turn, how large a volume they may cause to be converted into voids in the material. In fact, there appears to be a close correspondence between these values. Over the range of volume fractions of \( \beta_1 \) present in the precursor films, each unit increase in that value results in a unit increase in film porosity, i.e., the slope of the linear fit is close to unity. The intercept of the fit does not represent a plausible extrapolation to porosity at infinite dilution of \( \beta_1 \) content, since pore formation cannot occur by the mechanism discussed without \( \beta \) crystals present. Indeed, the requirements for pore formation absent \( \beta \) crystals in iPP are not met by films produced in this study [27-30]. It is more likely that below some critical value of \( \beta_1 \) volume fraction, zero porosity will be developed. The low porosity of the stretched film corresponding to the 12M-23A-100S precursor may indicate that its volume fraction of \( \beta_1 \) is close to that point, because it also exhibits an especially low \( N_2 \) permeability (Table 4). Precursor annealing temperature appears to be the most important factor in both volume fraction of \( \beta_1 \) and porosity, with little scatter between points representing a given annealing temperature. This general observation gives way to two exceptions,
both occurring in the 12 MFI iPP films, and these exceptions can be rationalized based on prior observations. In the case of the as-extruded film, the porosity is lower than expected due to poor crystallization conditions during extrusion. For the film annealed at 140 °C, the annealing process induced substantial growth in the lamellae, but the higher than expected porosity can be attributed to a lower tie chain density than the other films annealed under these conditions. Additionally, the greater variability in $\beta_1$ volume fraction for films annealed at 140 °C can be attributed to the fact that the annealing temperature is closer to the melt temperature of $\beta$ crystals than in the other films, permitting melt-recrystallization of $\beta$ material according to the original sizes of crystals formed during extrusion. Characterization of the volume fraction of $\beta_1$ in these materials provides a powerful tool to predict the porosity and thus performance of microporous membranes made from $\beta$-iPP.

4. Conclusions

The crystallinity of extruded $\beta$-iPP materials was influenced by the MFI of the iPP used, the extrusion conditions, and by the annealing treatment applied to the extruded films. A comparison of crystallinity in these films by DSC and XRD techniques enabled the development of metrics that can be used to predict the porosity of the films once they are biaxially stretched. The mechanism of pore formation in biaxially stretched $\beta$-iPP films was clarified schematically and used to explain pore formation in the films. The growth of stable $\beta_1$ crystals in $\beta$-iPP materials, facilitated by appropriate post-extrusion annealing, was the most important factor in creating highly porous films. Several annealing treatments can be used to successfully create microporous membranes from a variety of iPP materials with this approach, compared with the more strict processing requirements of row-nucleated materials such as Celgard. This flexibility makes $\beta$-iPP microporous films attractive in their own right or for use in multilayered composite membranes where the temperature, viscosity, or other requirements for the nonporous material limit the range of extrusion conditions that can be used.

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References


Fig. 7. SEM micrographs of representative regions in stretched films. Films were prepared from precursors extruded from $\beta$-iPP having an MFI of 12 that were subsequently annealed at 23 °C (as-extruded), 130 °C, and 140 °C for 30 min and then stretched at 100 °C.

Fig. 8. Porosity calculated from densities measured by Archimedes’ principle in biaxially stretched films as a function of $\beta_1$ crystallinity in the corresponding precursor $\beta$-iPP films. Values are plotted for precursor films of MFI 2.1 (●), MFI 3.5 (▲), and MFI 12 (▲). Uncertainties represent ±1 standard deviation. The dashed line is the least squares line to the data set. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)


