
LIST OF FIGURES

FIGURE		PAGE
2.1	Schematic of the types of row structure with the respective extrusion condition and the main features of the PE WAXS patterns. ³³	10
2.2	Tensile curves of hard elastic Celcon (POM) and non-hard elastic film obtained at -190°C . ³⁶	12
2.3	SEM micrograph of a microporous film cross-section displaying uniform microporosity throughout the film cross-section.	15
2.4	Schematic depicting spherulitic impingement and radial growth rings. ⁵²	17
2.5	Schematic depicting a spherulite with twisting lamellae emanating from the spherulitic center. ⁵⁰	17
2.6	Schematic diagrams representing crystallization regimes I, II, and III where “i” is the stem nucleation rate and “g” is the substrate completion rate.	18
2.7	Schematic representation of the shish-kebab morphology. ³³	22
2.8	Scheme depicting the intermediate orientations between predominant “c”-axis and “c”/“a”-axis orientation in terms of increasing diameter between row nucleating crystals. ⁷⁹	27
2.9	Plot of intensity of a dilute solution between crossed polarizers, i.e. birefringence, as a function of strain rate, where $M_1 > M_2 > M_3$, showing that the critical strain rate is dependent upon mol wt. ⁶²	30
2.10	A “phase diagram” of the development of connectivity as a function of concentration and strain rate, displaying ϵ_c and the ϵ_n for monodisperse ($M_w/M_n = 1$) a-PS in decalin soln. ⁶²	32
2.11	Schematic of tubular film process and key components.	37
2.12	H_v SALS patterns of a) tubular extruded iPP film and b) stirred solution grown shish-kebob morphologies. ¹¹⁰	40
2.13	PB-1 tubular films a) surface replication of the sheaf-like structures, b) SALS H_v pattern of the PB-1 film, and c) proposed model accounting for these structures. ³⁷	41
2.14	Dielectric (D) and mechanical (M) α_c relaxation distribution times for similar PE specimens at 50°C . ¹¹³	45

2.15	DMA $\text{Tan}\delta$ response of a PMP (-●-) slow cooled and (-●-) quenched compression molded samples as a function of temperature using a heating rate of $2^\circ\text{C}/\text{min}$ at 1Hz.	48
2.16	$\text{Tan}\delta$ response of Delrin 100 POM (-■-) slow cooled and (-□-) quenched compression molded samples as a function of temperature using a heating rate of $2^\circ\text{C}/\text{min}$ at 1Hz.	50
2.17	Semicrystalline polymers that possess and do not possess an α_c relaxation relative to their ability to ultradraw. Reproduced from K. Schmidt-Rohr.	54
2.18	Chain length profile and cross-sections of the trans-planar zigzag conformation of PE, the 3/1 helical conformation of i-PP, and the 7/2 helical conformation of PMP. ¹⁷³	56
2.19	Specific volume dependence on temperature for crystalline and amorphous phases of PMP: (O) amorphous, (Δ) crystalline. ¹⁷³	57
2.20	Coordinate system used to define the tetragonal unit cell with respect to a given set of orthogonal axes.	60
2.21a	WAXS photograph of a melt extruded PMP precursor. MD direction shown.	62
2.21b	Schematic depicting the WAXS diffraction pattern for an oriented melt-extruded PMP film with the azimuthal diffraction angle (Ψ_{hkl}) for the (200) reflection defined.	62
2.22a	WAXS photograph of POM precursor. Note the indication of preferential “a”-axis orientation in the meridional region of the (100) scattering reflection. The MD direction is shown.	70
2.22b	Schematic depicting the WAXS diffraction pattern for an oriented melt-extruded POM film with the azimuthal diffraction angle (Ψ_{hkl}) for the (100) reflection defined.	70
3.1	Schematic depicting the tubular extrusion setup utilized in this study with some processing parameters indicated.	84
3.2	Coordinate system used to define the tetragonal unit cell with respect to a given set of orthogonal axes.	87
3.3	AFM phase images of the resin A PMP films a) A1, b) A2, c) A3, and d) A4. The machine direction is labeled MD. Images are $3\mu\text{m} \times 3\mu\text{m}$.	90
3.4	FE-SEM micrographs PMP resin A films a) A1, b) A2. The MD is labeled.	92

3.5	TEM micrographs of RuO ₄ stained PMP resin A films a) A1, b) A2. The MD is labeled .	93
3.6	WAXS photograph of an oriented PMP film with X-ray beam parallel to film MD isotropic crystal orientation with respect to the ND of the film.	96
3.7	WAXS photographs of resin A PMP films a) A1, b) A2, c) A3, and D) A4. The machine direction is labeled MD. Arrows in fig. 3.7a indicate the scattering reflection corresponding to the (200) set-of-planes.	97
3.8	DSC heating scans of PMP films (-■-) A1, (-●-) B1, and (-Δ-) C1 utilizing a heating rate of 30°C/min.	98
3.9	WAXS patterns of resin B PMP films a) B1 b) B2, c) B3 and d) B4. The MD is labeled.	100
3.10	AFM phase images of resin B PMP films a) B1 and b) B2. The MD is labeled. Images are 3μm x 3μm.	101
3.11	AFM phase images of resin C PMP films a) C1 and b) C2. The MD is labeled. Images are 3μm x 3μm.	103
3.12	WAXS photographs of resin C PMP films a) C1 b) C2, c) C3, and d) C4. The MD is labeled.	104
3.13	DSC heating scans of the PMP resins utilized in this study (-■-) resin A, (-●-) resin B, and (-Δ-) resin C. A heating rate of 30°C/min was employed.	108
3.14	Complex viscosity versus frequency for resins (-■-) A, (-●-) B, and (-Δ-) C from this study obtained via dynamic oscillatory shear measurements at 265°C. A table of the CY parameters is included.	110
4.1	Tan δ for PMP films (-■-) A1, (-●-) B1, and (-Δ-) C1. This data was obtained utilizing a heating rate of 2°C/min and a frequency of 1.0 Hz.	123
4.2	DSC heating scan of PMP resin A where a heating rate of 30°C/min was employed.	124
4.3	WAXS photographs of A1 films a) precursor, b) free-annealed at T _a = 205°C for t _a = 20min, c) 3 % tension T _a = 205°C for t _a = 20min, d) 15% tension T _a = 205°C for t _a = 20min. MD direction shown.	126
4.4	Crystalline orientation (<i>f_c</i>) of the A1 films dependence upon annealing tension level and T _a for a t _a of 20min: (-■-) T _a = 205°C, (-●-) T _a = 180°C, (-▲-) T _a = 160°C, (-▼-) T _a = 145°C.	127

4.5	Crystalline orientation (f_c) of the A1 films dependence upon annealing tension level and t_a for a T_a of 205°C: (-■-) tension of 15%, (-●-) tension of 9%, (-▲-) tension of 3%, (-▼-) free-annealed .	128
4.6	The dichroic ratio (D) for the A1 films dependence upon annealing tension level and t_a for a T_a of 205°C: (-■-) tension of 15%, (-●-) tension of 9%, (-▲-) tension of 3%, (-▼-) free-annealed (tension of 0%).	129
4.7	The FTIR spectra of the parallel and perpendicular scans for the 918cm ⁻¹ band obtained on the A1 precursor.	130
4.8	AFM phase images of the A1 free-annealed films with t_a equal to 20min. a) $T_a = 180^\circ\text{C}$, b) $T_a = 205^\circ\text{C}$, and c) $T_a = 215^\circ\text{C}$. The MD is labeled. The images are 3 μm x 3 μm .	132
4.9	AFM phase images displaying the influence of tension during annealing on the morphologies of selected A1 films where $T_a = 205^\circ\text{C}$ & $t_a = 20\text{min}$. a) 3% tension, b) 9% tension, and c) 15% tension.	134
4.10	TEM micrographs of RuO ₄ stained A1 films where $T_a = 205^\circ\text{C}$ & $t_a = 20\text{min}$. a) 9% tension and b) 15% tension. The MD is shown.	136
4.11	DSC heating scans of the A1 precursor and annealed films ($T_a = 205^\circ\text{C}$ for $t_a = 20\text{min}$): (-■-) precursor, (-●-) free annealed, and (-▲-) 15% tension utilizing a heating rate of 30°C/min.	139
4.12	DSC heating scans of the B1 precursor and annealed films ($T_a = 205^\circ\text{C}$ for $t_a = 20\text{min}$): (-■-) precursor, (-●-) free annealed, and (-▲-) 15% tension utilizing a heating rate of 30°C/min.	140
4.13	Tan δ as a function of temperature for the A1 precursor and annealed films ($t_a = 20\text{min}$): (-■-) precursor, (-●-) $T_a = 160^\circ\text{C}$, and (-▲-) $T_a = 205^\circ\text{C}$. This data was obtained utilizing a heating rate of 2°C/min and a frequency of 1.0 Hz.	141
4.14	Tan δ for the A1 precursor and annealed films ($T_a = 205^\circ\text{C}$ and $t_a = 20\text{min}$): (-■-) precursor, (-●-) free-annealed, (-□-) 3% tension, (-▲-) 9% tension, and (-▼-) 15% tension .	142
4.15	Effect of annealing temperature on the Gurley number for A1 and A2 stretched films.	145
4.16	Effect of annealing time on the Gurley number for A1 and A2 stretched films.	146
4.17	Effect of tension level during annealing on the Gurley number for A1 and A2 stretched films.	148

-
- 4.18** AFM images of stretched A1 membranes where $T_a = 205^\circ\text{C}$ & $t_a = 20\text{min}$. a) free, b) 3% tension, c) 9% tension, and d) free but at higher magnification than a. The MD is labeled. 149
- 4.19** SEM micrograph of the cross-section of the A1 membrane produced using the main annealing/stretching condition. 151
- 4.20** Effect of the cold stretch parameters (T_{cs} and %CS) on the Gurley number for A1 stretched films (-■-) $T_{ca} = 40^\circ\text{C}$, (-●-) $T_{cs} = 70^\circ\text{C}$, (-▲-) $T_{ca} = 80^\circ\text{C}$, and (-∇-) $T_{ca} = 90^\circ\text{C}$. 153
- 4.21** AFM height (left) and phase (right) images for the stretched membrane A1- $T_{cs}90\text{C}$. The MD is labeled. Images are $5\mu\text{m} \times 5\mu\text{m}$. 154
- 4.22** AFM images for an A1 stretched membrane where the standard hot stretch step was not used. The MD is labeled. Images are $5\mu\text{m} \times 5\mu\text{m}$. 157
- 4.23** Effect of the hot stretch parameters (T_{hs} and %HS) on the Gurley number for A1 stretched films (-■-) $T_{ca} = 120^\circ\text{C}$, (-●-) $T_{ca} = 160^\circ\text{C}$, and (-▲-) $T_{ca} = 180^\circ\text{C}$. The other annealing/stretching parameters remained constant with the standard condition. 158
- 4.24** AFM height (left) and phase (right) images displaying the influence of total extension level (%TS) during stretching on A1 membrane morphology: a) %TS = 100% and b) %TS = 180%. 161
- 4.25** Effect of the percent the film is allowed to relax from the %TS after hot stretching on the Gurley number for A1 stretched films. The other annealing/stretching parameters remained constant with the standard condition. 162
- 4.26** AFM phase images of the a) B1 and b) C1 stretched films produced utilizing the main annealing/stretching condition. The MD is labeled. Images are $5\mu\text{m} \times 5\mu\text{m}$. 163
- 4.27** Gurley number dependence on cold stretch extension level (%CS) for A1 stretched films using $T_{ha} = 180^\circ\text{C}$. 168
- 5.1** Schematic depicting the tubular extrusion setup utilized in this study with some processing parameters indicated. 180
- 5.2** Coordinate system used to define the hexagonal unit cell with respect to a given set of orthogonal axes. 183
- 5.3** Second heating scans of POM (-□-) resin D, (-●-) resin E, and (-Δ-) resin F utilizing a heating rate of $30^\circ\text{C}/\text{min}$. 188

5.4	WAXS of an oriented POM film with the X-ray beam parallel to the film MD.	189
5.5	WAXS photographs of resin D POM films a) D2, b) D3, c) D4, and d) D5. The MD is labeled. Arrows in figure (a) indicate the reflection corresponding to the (100) set-of-planes.	192
5.6	The measured total birefringence (Δ_T) plotted against the crystalline orientation (f_c) measured from WAXS.	193
5.7	AFM phase images of resin D POM films a) D2, b) D3, c) D4, and d) D5. The MD is labeled. Images are each $3\mu\text{m} \times 3\mu\text{m}$.	195
5.8	H_V SALS photographs of resin D POM films a) D2, b) D3, c) D4, and d) D5. The MD is labeled.	199
5.9	Oriented fan model of Hashimoto and coworkers where angle γ is half the aperture angle of the fan. The MD is along the Z-axis. ¹²	200
5.10	AFM height images of POM resin D films a) D2 and b) D5. The MD is labeled. Images are each $30\mu\text{m} \times 30\mu\text{m}$.	202
5.11	WAXS photographs of resin E POM films a) E2 and b) E4. The MD is labeled.	204
5.12	AFM phase images of the resin E POM films a) E2 and b) E4. The MD is labeled. Images are $3\mu\text{m} \times 3\mu\text{m}$.	205
5.13	H_V SALS photographs of resin E POM films a) E2 and b) E4. The machine direction is labeled.	207
5.14	AFM height micrographs of POM resin E films a) E2 and b) E4. The MD is labeled. The images are $10\mu\text{m} \times 10\mu\text{m}$.	208
5.15	WAXS photographs of resin F POM films a) F1, b) F2, c) F3, and d) F4. The MD is labeled.	210
5.16	AFM phase images of the resin F films in order of decreasing f_c values a) F1, b) F2, c) F5, d) F3, and e) F4. The MD is labeled. Images are each $3\mu\text{m} \times 3\mu\text{m}$.	212
5.17	H_V SALS photographs of resin F POM films arranged according to decreasing f_c or Δ_T a) F1, b) F2, c) F5, d) F3, and e) F4. The machine direction is labeled.	215
5.18	AFM height images of the resin F POM films a) F1 and b) F2. The MD is labeled. Images are each $30\mu\text{m} \times 30\mu\text{m}$.	219
5.19	The slit-smear SAXS spectra from the highest oriented POM films (-□-) D2, (-●-) E2, and (-Δ-) F2.	220

5.20	Complex viscosity versus frequency for resins (-□-) D, (-●-) E, and (-Δ-) F. A table of the CY parameters and the RSP value are also included.	222
6.1	Tan δ as a function of temperature for POM films (-□-) D2 and (-●-) F2 with their corresponding γ and α_c relaxations labeled.	235
6.2	Slit-smear intensity for precursor F1 and F1 free-annealed films as a function of annealing temperature for $t_a = 20$ min: (-■-) precursor, (-●-) $T_a = 110^\circ\text{C}$, (-□-) $T_a = 130^\circ\text{C}$, (-○-) $T_a = 145^\circ\text{C}$.	237
6.3	Long spacing (ℓ) for free-annealed F1 films as a function of annealing time (x-axis) and temperature: (-■-) $T_a = 85^\circ\text{C}$, (-●-) $T_a = 110^\circ\text{C}$, (-□-) $T_a = 130^\circ\text{C}$, (-○-) $T_a = 145^\circ\text{C}$, and (-▲-) $T_a = 150^\circ\text{C}$.	238
6.4	Breadth, $\Delta\omega$, of the SAXS peak for free-annealed F1 films as a function of annealing time and temperature: (-■-) $T_a = 85^\circ\text{C}$, (-●-) $T_a = 110^\circ\text{C}$, (-□-) $T_a = 130^\circ\text{C}$, (-○-) $T_a = 145^\circ\text{C}$, and (-▲-) $T_a = 150^\circ\text{C}$.	239
6.5	Slit-smear intensity for precursor D1 and D1 free-annealed films as a function of annealing temperature for $t_a = 20$ min: (-■-) precursor, (-●-) $T_a = 120^\circ\text{C}$, (-□-) $T_a = 145^\circ\text{C}$, (-○-) $T_a = 155^\circ\text{C}$, and (-▲-) $T_a = 160^\circ\text{C}$.	242
6.6	DSC heating scans of the F1 precursor and F1 free-annealed films for $t_a = 20$ min: (-■-) precursor, (-●-) $T_a = 110^\circ\text{C}$, (-○-) $T_a = 145^\circ\text{C}$, and (-▲-) $T_a = 150^\circ\text{C}$ utilizing a heating rate of $30^\circ\text{C}/\text{min}$.	243
6.7	The T_m and X_c results for the F1 films as a function of t_a : (-■-) and (-□-) $T_a = 110^\circ\text{C}$; (-●-) and (-○-) $T_a = 145^\circ\text{C}$.	244
6.8	AFM images of F1 films free-annealed for 20min a) $T_a = 145^\circ\text{C}$ and b) $T_a = 110^\circ\text{C}$. The MD is labeled. Phase images are $3\ \mu\text{m} \times 3\ \mu\text{m}$.	247
6.9	AFM images of F1 films annealed for 20min under tension a) 3% tension, $T_a = 145^\circ\text{C}$; b) 3%, 110°C ; c) 15%, 145°C ; and d) 15%, $T_a = 110^\circ\text{C}$. The MD is labeled. Images are each $3\ \mu\text{m} \times 3\ \mu\text{m}$.	248
6.10	SAXS for F1 annealed films under tension: (-■-) $T_a = 145^\circ\text{C}$, $t_a = 20$ min, 15%; (-●-) $T_a = 145^\circ\text{C}$, $t_a = 20$ min, 3%; (-□-) $T_a = 110^\circ\text{C}$, $t_a = 20$ min, 15%; (-+-) $T_a = 110^\circ\text{C}$, $t_a = 5$ min, 15%; (-○-) $T_a = 110^\circ\text{C}$, $t_a = 20$ min, 3%.	250
6.11	WAXS of the F2 films with tension $T_a = 145^\circ\text{C}$ for $t_a = 20$ min: a) free annealed, b) 3% tension, c) 9%, and d) 15%. The MD is labeled.	252
6.12	Effect of annealing temperature on the Gurley number for F1 and F2 stretched films. The other annealing/stretching parameters remained constant with the standard condition.	255

6.13	AFM phase images of the resin F POM stretched films a) F1-T _a 110C, b) F1-T _a 145C (standard condition), c) F1-T _a 150C, and d) 2μm x2μm image of b). The MD is labeled.	256
6.14	Effect of annealing time on the Gurley number for F1 and F2 stretched films. The other annealing/stretching parameters remained constant with the standard condition.	258
6.15	Effect of tension level during annealing on the Gurley number for F1 and F2 stretched films. The other annealing/stretching parameters remained constant with the standard condition.	260
6.16	AFM images of the resin F POM stretched films: a) 3% tension & b) 15% tension. The MD is labeled. The images are each 2μm x 2μm.	261
6.17	Effect of the T _{cs} and %CS on the Gurley number for F1 stretched films (-■-) T _{ca} = 35°C, (-●-) T _{ca} = 50°C, and (-▲-) T _{ca} = 70°C. The other annealing/stretching parameters remained constant with the standard condition.	263
6.18	Effect of the T _{hs} and %HS on the Gurley number for F1 stretched films (-■-) T _{hs} = 100°C and (-●-) T _{hs} = 115°C. The other annealing/stretching parameters remained constant with the standard condition.	265
6.19	AFM image of the stretched film F1-T _a 110C,T _{hs} 145C displaying the effect on microporosity when T _{hs} > T _a . The MD is labeled.	266
6.20	AFM images of the %TS effect on F1 membrane morphology: a) %TS = 100% and b) %TS = 180%. The MD is labeled.	268
6.21	AFM image of the D1 stretched film utilizing the standard annealing/stretching condition. The MD is labeled.	270
6.22	AFM phase image of the F1 free-annealed film utilizing a T _a = 150°C for 20min. The MD is labeled, and the image is 5 μm x 5μm.	274
8.1	AFM tilted height images of blown films a) sample A, b) sample B, and c) sample C. Scales of the images are 800 nm x 40μm x 40μm.	296
8.2	General profilometry scans of blown films a) sample A, b) sample B, and c) sample C. Scales of the images are 800nm x 40μm x 40μm.	297
8.3	AFM height (left) and phase (right) images of blown films a) sample C & b) sample A. Images are 10μm (vertical) x 7μm (horizontal).	298
8.4	TEM micrographs of a) sample B and b) sample C. Note in sample C an arrow indicates the radial direction and twisting of a specific lamellae where as in sample B a more random lamellae morphology exists.	300

8.5	SALS H_v patterns of blown films a) sample A, b) sample B, c) sample C, d) sample E, e) sample F, and f) sample G. All sample to film distances are 10 cm with the exception of sample A is 5 cm.	302
8.6	SALS H_v patterns of compression molded quenched samples from resins a) A, b) B, c) C and slow cooled samples d) A, e) B, and f) C. MD direction is shown.	305
8.7	Complex viscosity versus frequency data for all the resins from this study obtained via dynamic oscillatory shear measurements.	307
8.8	WAXS photographs of blown films a) sample A, b) sample C, c) sample Z-1, and d) sample Z-2. MD direction is shown.	309
8.9	AFM phase image of blown film sample Z-2. Image is $2\mu\text{m}$ (vertical x $4\mu\text{m}$ (horizontal). MD direction shown.	310
8.10	Model illustrating the nucleation of spherulitic-like morphologies on extended chain crystal nuclei.	314
8.11	SALS H_v patterns of cast roll films with different film thickness values utilizing resin A: a) 1 mil film, b) 3 mil film, c) 5 mil film.	316
8.12	WAXS photographs of cast roll films with different film thickness values utilizing resin A: a) 1 mil film and b) 5 mil film.	317
8.13	AFM height images of sample H cast roll films blended with varying wt% resin P concentration a) 0wt% P, b) 5wt% P, c) 12wt% P, and d) 30wt% P.	320
8.14	AFM phase images of sample H cast roll films blended with varying wt% resin P concentration a) 3wt% P and b) 20wt% P.	321
8.15	WAXS photographs of sample H cast roll films blended with varying wt% resin P concentrations: a) 0wt% P, b) 5wt% P, c) 12wt% P, and d) 30wt% P.	322