STRUCTURAL PHENOMENA OF MULTILAYERED POLYMERIC FILMS

by

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*We also certify that written approval has been obtained for any proprietary material contained therein.
DEDICATION

To my parents, Dr. Shih-Yaw Lai and Ming Chu Chen Lai.
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CHAPTER 1: It is widely thought that confinement of an amorphous polymer alters the chain mobility, which affects the temperature and intensity of the glass transition. The present study sought to determine whether the same effects extend to semicrystalline polymers. Confinement was achieved by forced assembly of hundreds of alternating layers of poly(ethylene oxide) (PEO) with either poly(ethylene-co-acrylic acid) or polystyrene. The confinement gradually reduced the intensity of the PEO $\beta$-relaxation as the layer thickness decreased from the microscale to the nanoscale. By considering the changes in crystalline morphology that accompanied layer confinement, it was possible to completely account for the reduction in relaxation intensity using standard mechanical models. The viscoelastic behavior of the amorphous phase was satisfactorily represented by a modified standard linear solid (SLS). The amorphous and crystalline contributions were combined using a combination of parallel and series coupling in accordance with the Takayanagi model. No adjustment in the viscoelastic parameters of the modified SLS was required, indicating that there was no significant change in amorphous chain dynamics even in layers as thin as 45 nm.

CHAPTER 2: The effect of confinement on the deformation behavior of poly(ethylene oxide) (PEO) was studied using melt processed coextruded poly(ethylene-co-acrylic acid) (EAA) and PEO multilayer films with varying PEO layer thicknesses from 3600 nm
down to 20 nm. The deformation mechanism was found to shift as layer thickness was decreased between 510 nm and 125 nm, from typical axial alignment of the crystalline fraction, as seen in bulk materials, to non-uniform micro-necking mechanisms found in solution-grown single crystals. This change was evaluated via tensile testing, wide angle X-ray diffraction (WAXD), atomic force microscopy (AFM), and differential scanning calorimetry (DSC). With the commercially-relevant method of melt coextrusion, we were able to overcome the limitations to the testing of solution-grown single crystals and the artifacts that occur from their handling, and bridged the gap in knowledge between thick bulk materials and thin single crystals.

CHAPTER 3: The interdiffusion of two materials used to fabricate polymeric gradient refractive index (GRIN) lenses was examined by varying contact time during multilayer film coextrusion composed of alternating poly(methylmethacrylate) (PMMA) and poly(styrene-co-acrylonitrile) with 17 mol% acrylonitrile (SAN17). The model applied successfully described their interdiffusion, and a reasonable mutual diffusion coefficient of $7.0 \times 10^{-13}$ m$^2$/sec was determined. Atomic force microscopy confirmed good agreement between modeled profiles and actual layer structure, and optical properties were investigated. Films with contact times of $\leq 160$ seconds exhibited multiple refractive indices, while films with longer contact times, showed single refractive indices that followed an additive line. Though a single additive value requires layers $\leq$ a quarter-wavelength of light, these films exhibit such behavior with thicknesses 5x greater than expected, though layer resolution is still present. Using the model profiles, it was determined that only a 1% reduction in material purity is required to reduce the effective layer thickness.
PART I: Mechanical Properties of Confined Semi-Crystalline Polymers
CHAPTER 1

Effect of Confinement on the Relaxation Behavior of Poly(ethylene oxide)

1.1 Introduction

The viscoelastic behavior of polymers in ultrathin films, at interfaces, and in physical confinement becomes of increasing technological and theoretical interest as applications move toward the micro- and nano-scales. To date, research has focused primarily on the glass transition \( T_g \) of amorphous polymers in thin and ultrathin (>10 nm) films.\(^1\)\(^-\)\(^2\) A sizable body of work convincingly demonstrates a substantial influence of the air-polymer and substrate-polymer interfaces. The presence of a free surface, for example in free-standing thin films or on a coated non-interacting substrate, generally results in a decrease in \( T_g \) due to the enhanced segmental mobility.\(^3\)\(^-\)\(^4\) The magnitude of the effect depends on the polymer, but is up to 35 °C in polystyrene (PS).\(^5\) The decrease in \( T_g \) can be eliminated, and even reversed to an increase in the \( T_g \), if the polymer interacts with the substrate.\(^6\)

The dynamics of polymer chains confined within small pores has been studied primarily to address questions concerning the length scale that controls the molecular motions of the glass transition. For these studies, the required dimension of the confinement is less than 20 nm. The confinement is imposed by imbibing the polymer into a nanoporous inorganic glass,\(^7\)\(^-\)\(^9\) or intercalation in a layered silicate.\(^10\) As with thin films, confinement and substrate interactions produce opposing effects. The confinement effect leads to an acceleration of the segmental dynamics (confinement effect) compared to the bulk. The molecular dynamics of the confined glass is also influenced by surface
interactions (adsorption effect), which generally retard relaxation processes. Thus, there is a counterbalance between confinement and adsorption effects.

There is little information available on the viscoelastic behavior of confined semicrystalline polymers. Rigid confinement at a size scale below 20 nm appears to inhibit crystallization of polymers that would normally crystallize in the bulk.\textsuperscript{9} However, crystallization proceeds readily when the confinement occurs at a size scale equal to or larger than the lamellar thickness, approximately 20 nm, or in supported ultrathin films with a free surface.\textsuperscript{11} A decrease in the $T_g$ of poly(L-lactic acid) films below a thickness of 50 nm was interpreted in terms of a disentanglement effect near a noninteracting surface.\textsuperscript{12} Rigidly confined thin films without a free surface can be fabricated by microlayer coextrusion.\textsuperscript{13-14} As the thickness of a confined poly(ethylene oxide) (PEO) layer decreases from the microscale to the nanoscale, the morphology systematically changes from three-dimensional spherulites to two-dimensional discoids to ‘in-plane’ lamellar stacks.\textsuperscript{15} Finally, when the confinement occurs on the 25 nm size scale of the usual lamellar thickness, the PEO layers crystallize as single lamellae with large aspect ratio that resemble large single crystals.\textsuperscript{16} However, it is not known how the confinement affects the amorphous phase.

In the bulk, it is generally observed that crystallization has the effect of broadening, weakening and shifting the $T_g$ to higher temperatures. The increase in $T_g$ of 10-20 ºC is due to restricted amorphous chain mobility imposed by connectivity to the rigid crystals. Preventing the normal isotropic spherulitic organization by confining crystallization to two dimensions may affect the dynamics of the non-crystalline chain segments. In this work, we advance some results showing the impact of confined
crystallization on the glass transition and mechanical stress-strain properties of PEO. For this purpose, PEO was coextruded as microlayer and nanolayer films with up to 1025 layers of PEO alternating with poly(ethylene-co-acrylic acid) (EAA) or PS. The number of layers was adjusted in order to achieve individual layer thicknesses ranging from a few microns to 45 nm. With little or no crystallinity, EAA and PS were suitable substrates for assessing the effect of PEO crystallization habit on the mechanical relaxation behavior. Conventional experimental methods were used and the results were amenable to analysis with standard mechanical models.
1.2 Materials and Methods

The poly(ethylene oxide) (PEO) was Polyox WSR-N80 with a molecular weight of ~200,000 g/mol, crystallinity of about 70%, and melting point of 65°C. The confining layers were polystyrene (PS), Styron 666, or an ethylene-co-acrylic acid copolymer (EAA), Primacor 1410. The PS had a glass transition temperature at 100 °C. The EAA had 9.7% acrylic acid, about 30% crystallinity with a melting temperature at 99 °C. The polymers were obtained from The Dow Chemical Company. The resins used in this study were previously found to be immiscible in melt blends.\(^{17}\)

Films with 33, 257, and 1025 alternating PEO and PS or EAA layer with 50/50 (vol/vol) composition were produced through the continuous coextrusion process described previously.\(^{13-14,16,18}\) Varying the number of layers allowed for a large range of layer thicknesses. The overall film thicknesses ranged from 50 to 130 μm, which corresponded to individual PEO layer thicknesses from 45 nm to 3700 nm. There was some variation in layer thickness\(^ {15}\) however, any effect of layer thickness was averaged out in measurements of the bulk properties. The films were kept dry in a desiccator with molecular sieves before all testing.

The crystallinity was measured using differential scanning calorimetry (DSC). Thermograms were obtained on a Perkin Elmer (Boston, MA) Series 7 DSC at a heating/cooling rate 10 °C min\(^{-1}\). The weight fraction PEO crystallinity was converted to volume fraction according to

\[
V_c = \frac{\rho_a W_c}{\rho_a W_c + \rho_c (1 - W_c)}
\]

(1.1)

where, \(V_c\) is the volume fraction crystallinity, \(W_c\) is the weight fraction crystallinity, \(\rho_c\) is the crystalline phase density (1.239 g/cm\(^3\)), and \(\rho_a\) is the amorphous phase density (1.124
The volume crystallinity was 73% for the PEO control and 71% for all layered films.

Dynamic mechanical testing was performed on a Polymer Laboratories (Boston, MA) MkII dynamic mechanical thermal analyzer in tension. Rectangular samples with dimensions of 35 mm by 8 mm (n = 3) were cut from the extruded films along the extrusion direction along the same line. Thickness was measured using a digital micrometer, and width was measured with a digital caliper. The length to be tested in the DMTA was set to 13 mm for every sample. Each rectangular sample was tested at 1 Hz, strain of 11 μm, from -110 °C to 100 °C, heating at 3°C min⁻¹. Experiments were stopped when the displacement exceeded 1500 μm.

The stress–strain behavior in uniaxial tension was measured with ASTM D1708 microtensile specimens cut from the extruded EAA/PEO films along the extrusion direction. Specimens were stretched in an MTS (Eden Prairie, MN) Alliance RT30 mechanical testing machine at a strain-rate of 5% min⁻¹ at a temperature of -10 °C, right between the β-relaxation peak temperatures of PEO and EAA. Engineering stress and strain were defined conventionally. The tensile modulus was taken at 1% strain.

To change the crystalline structure of the PEO layers, the films were heated to a temperature above the melting temperature of PEO, but below the softening temperature of the confining layer, and quenched. The films were sandwiched with aluminum foil and the edges sealed with super glue. They were immersed in a hot oil bath at 70-75 °C for EAA/PEO or 85-90 °C for PS/PEO for 10 minutes to melt the PEO layer within the rigid confinement of the PS or EAA layers. The PEO was recrystallized by rapidly transferring...
the masked samples to liquid nitrogen and holding them there for 15-20 minutes. The aluminum masking was removed for further characterization.

The WAXD measurements were performed using a rotating anode X-ray generator (RU 300, 12 kW, Rigaku, Woodlands, TX). The PD and ND WAXD patterns were collected with the monochromatic X-ray beam parallel to the plane of the film (PD). The collimated beam size was ~0.5 mm. The 2D patterns were collected with a Bruker AXS (Madison, WI) HI-STAR area detector. The sample-to-detector distance was 74 mm and the diffraction angle was calibrated using a CaF$_2$ standard.
1.3 Results and Discussion

1.3.1 Dynamic Mechanical Behavior

The DMTA tan δ curves for PS/PEO and EAA/PEO layered films, and their controls are plotted in Figure 1.1. The intense β-relaxation at -45 °C corresponded to the PEO glass transition. The intensity was reduced in films with thick 3.7 micron layers due to the 50/50 composition. As the PEO layers became thinner, the intensity diminished further, even though the composition and crystallinity remained constant. The observed temperature of the relaxation remained relatively unchanged at -41 to -43 °C, only 3-5 °C higher than for the PEO control, and the peak width appeared unaffected. The EAA exhibited a β-relaxation peak at 25 °C that corresponded with the glass transition reported for an EAA of similar comonomer content. This relaxation peak intensity also decreased as the layers became thinner. The peak gradually shifted to lower temperatures, by about 10 °C.

A linear relationship between relaxation intensity and the log of the nominal PEO layer thickness can be seen in Figure 1.2 for both PS/PEO and EAA/PEO films. The intensity was taken at the peak maximum after the baseline was subtracted. Comparing the PEO in the two systems, it can be seen that the peak was about twice the intensity in EAA/PEO films as in PS/PEO films of similar PEO layer thickness. In the EAA/PEO system, the β-relaxation intensity of the EAA layers decreased in parallel with the PEO relaxation.

It is significant that changes in the relaxation peak intensities were observed in relatively thick layers. This characteristic, together with the negligible changes in peak
temperature and peak width, suggested that the intensity changes were not a substrate
effect. An alternative explanation was needed to account for both the decrease in the PEO
β-relaxation and the parallel decrease in the β-relaxation of the confining EAA layers.
For this purpose, we considered the stress distribution within the PEO layers and also the
stress distribution between the PEO layers and the confining layers. Previously it was
established that without a change in the crystallinity, the morphology of the PEO layer
changed from isotropic 3-dimensional spherulites to 2-dimensional discoids and finally to
highly oriented, in-plane lamellae as the confined PEO layer thickness decreased from
the microscale to the nanoscale.\textsuperscript{15} As the PEO lamellae lengthened and became more
aligned in the loading direction, it is proposed that the load was redistributed with
increased load carried by the crystalline phase. Because less of the load was born by the
amorphous phase, the intensity of the amorphous phase β-relaxation was reduced.
Furthermore, the reinforcing effect of the long, oriented lamellae increased the
modulus of the PEO layers in the loading direction of the dynamic mechanical
experiment. This reduced the load on the unoriented confining layers of the parallel
construction and the intensity of the EAA β-relaxation correspondingly decreased. The
confining PS layers did not have any relaxations in the temperature range examined.

\subsection*{1.3.2 Modeling the Two-Phase Structure of PEO}

The semicrystalline PEO layers are considered to consist of a crystalline phase
dispersed in a continuous amorphous matrix. The 2-phase structure is modeled as a series
combination of a discontinuous amorphous part and a crystalline part assembled in
parallel with a continuous amorphous part, \textbf{Figure 1.3a}, according to the Takayanagi
configuration\textsuperscript{22-23} The relative contributions of the series and parallel components are
adjusted to accommodate thickness-dependent morphology changes, which are assumed to occur only in the PEO layers and not in the confining layers. Subsequently, the layered film is constructed as a parallel arrangement of oriented semicrystalline PEO layers and isotropic confining layers.

The crystalline phase has dimensions \( a \) and \((1-b)\), with an area \(a(1-b)\) equal to the crystalline volume fraction \(V_c\). The total amorphous phase with volume fraction \(1-V_c\) is equal to the total area of the two amorphous parts \(1-a+ab\). As the layer thickness decreases, the morphology change is represented by changes in the parameters \(a\) and \(b\) of the model. This is represented schematically in Figure 1.3b. The spherulitic morphology of thick PEO layers resembles that of the PEO control, represented by a thicker discontinuous amorphous phase, and a thinner continuous amorphous phase. Reducing the layer thickness aligns the PEO lamellae along the direction of the layers, increasing \(1-b\), and decreasing \(a\). In the thinnest layers, the lamellae approach a parallel configuration, with a single continuous crystalline part in parallel with a continuous amorphous part.

The elastic modulus in the 2-phase Takayanagi model is expressed by: \(^{22-23}\)

\[
E_{PEO} = a \left[ \frac{b}{E_{am}} + \frac{(1-b)}{E_c} \right]^{\gamma} + (1-a)E_{am}
\]

\(\text{(1.2)}\)

where \(E_{PEO}\) is the elastic modulus of the PEO layer, \(E_{am}\) is the modulus of the amorphous part, and \(E_c\) is the modulus of the crystalline part. The area of the crystalline region \(V_c\) can be expressed in terms of \(a\) and \(b\)

\[
a = \frac{V_c}{(1-b)}
\]

\(\text{(1.3)}\)

\textbf{Equation 1.2} can be simplified to a single unknown
The modulus of the control films determined at ambient temperature followed well with literature values.\textsuperscript{24-25} However, for this study, the tensile modulus of the EAA/PEO films was measured at -10 °C, which was intermediate between the β-relaxations of PEO and EAA where the loss was lowest. Because the modulus decreased rapidly between -10 °C and ambient temperature, the values obtained at -10 °C were substantially higher than the usual ambient temperature values. The results for EAA/PEO films and the controls at -10 °C are reported in Table 1.1. The changes in the modulus of layered films were attributed to the PEO layer only. The modulus of the EAA layers was assumed to remain constant based on the previous finding that layer thickness affected the orientation of the PEO layers, but not of the low crystallinity EAA layers.\textsuperscript{16} The extracted PEO modulus increased with the PEO layer thickness logarithmically, Figure 1.4. In the thinnest layers, the modulus was about 3x that of the control. As the layer thickness increased, the modulus decreased, approaching that of the control in the thickest layers, Table 1.1.

To determine the parameters $a$ and $b$, $E_{am}$ was assumed to be equivalent to a typical rubbery modulus of 15 MPa,\textsuperscript{25-26} and $E_c$ was assigned a reported value of 4.6 GPa.\textsuperscript{27} Applying equation 1.4, $b$ was varied to match the measured PEO modulus, and $a$
was then calculated using \textbf{equation 1.3}. The results are summarized in \textbf{Table 1.1}. As expected, $b$ decreased, approaching zero, in the thinnest layers.

\textbf{1.3.3 Dynamic Response of PEO}

To model the dynamic response in the $\beta$-relaxation region, the PEO was considered to consist of an elastic crystalline phase and a viscoelastic amorphous phase, Figure 1.5. The temperature-dependent response of the amorphous phase was elicited using a modified standard linear solid (SLS) model in which the dashpot of the classical Zener model is replaced with a springpot.\textsuperscript{28} In the model, a series combination of a spring with glassy modulus $E_1$ and a spring pot is combined in parallel with a spring with rubbery modulus $E_2$. At lower temperatures, the amorphous phase is in the glassy state and there is no response from the springpot due to its high viscosity. The model response is governed primarily by $E_1$ as $E_2<<E_1$. At higher temperatures, well above the $\beta$-relaxation, the spring-pot is fluid and the model response is governed by the rubbery modulus $E_2$. In the region of the $\beta$-relaxation, the viscosity of the spring-pot determines the model response.

The storage and loss moduli for the modified SLS model are described by:\textsuperscript{26}

\begin{align*}
E'_{\text{SLS}}(T) &= E_1 - \frac{(E_1 - E_2) \left[ 1 + (\omega\tau(T))^4 \cos\left(\frac{A\pi}{2}\right) \right]}{\left[ 1 + (\omega\tau(T))^4 \cos\left(\frac{A\pi}{2}\right) \right]^2 + \left[ (\omega\tau(T))^4 \sin\left(\frac{A\pi}{2}\right) \right]^2} \\
E''_{\text{SLS}}(T) &= \frac{(E_1 - E_2) \left[ 1 + (\omega\tau(T))^4 \sin\left(\frac{A\pi}{2}\right) \right]}{\left[ 1 + (\omega\tau(T))^4 \cos\left(\frac{A\pi}{2}\right) \right]^2 + \left[ (\omega\tau(T))^4 \sin\left(\frac{A\pi}{2}\right) \right]^2}
\end{align*}
where, $E_1$ and $E_2$ are the moduli of the amorphous glass and the rubber, respectively. These were varied within a range of typical values for a glass (400-1500 MPa), and a rubber (1-50 MPa). The testing frequency $\omega$ was 1Hz. The springpot parameter $A$ can take values between 0 and 1. The temperature dependent relaxation time spectrum $\tau(T)$ is expressed as

$$\tau(T) = \tau_0 \left( \exp \left( \frac{E_\sigma}{kT} \right) \right)^Z \quad (1.8)$$

The $Z$ exponent is calculated from

$$Z(T) = \frac{T(T^*-T_0)}{T^*(T-T_0)} \quad (1.9)$$

where $T^*$ is the melting temperature, $T_0$ is a temperature below the glass transition, and $k$ is the Boltzmann’s constant, $1.38 \times 10^{-23}$ (m$^2$ kg s$^{-1}$ K$^{-1}$).

The effect of the springpot parameters on the relaxation characteristics of the modified SLS model was examined. Decreasing $A$ broadened the relaxation and decreased the intensity of the loss modulus and tan $\delta$ peaks, Figure 1.6a. The pre-exponential factor $\tau_0$ in the expression for $\tau(T)$ affected the transition temperature, as well as the distribution, although $\tau_0$ did not affect the distribution as strongly as the $A$ parameter did, Figure 1.6b. Decreasing $E_\sigma$ shifted the relaxation to lower temperatures and slightly narrowed the relaxation, although the effect was small compared to that of the other two parameters. Varying $T_0$ shifted the peak position in the dynamic response.

The modified SLS model for the PEO amorphous phase was combined with the crystalline phase of elastic modulus $E_3$ as shown in Figure 1.5. Expressions for the storage and loss moduli of the Takayanagi model were taken from the literature: $^{29}$
Substitution of equations 1.10 and 1.11 gave the temperature dependent response as

\[
E'_\text{PEO}(T) = (1 - a)E'_{am} + \frac{a[E'_{am}E'_c - E''_{am}E''_c][(1 - b)E'_{am} + bE'_c]}{[(1 - b)E'_{am} + bE'_c]^2 + [(1 - b)E''_{am} + bE''_c]^2}
+ \frac{a[E'_{am}E'_c + E''_{am}E''_c][(1 - b)E''_{am} + bE''_c]}{[(1 - b)E'_c + bE'_c]^2 + [(1 - b)E''_{am} + bE''_c]^2}
\] (1.10)

\[
E''_\text{PEO}(T) = (1 - a)E''_{am} + \frac{a[E'_{am}E'_c - E''_{am}E''_c][(1 - b)E''_{am} + bE''_c]}{[(1 - b)E'_c + bE'_c]^2 + [(1 - b)E''_{am} + bE''_c]^2}
- \frac{a[E'_{am}E'_c + E''_{am}E''_c][(1 - b)E''_{am} + bE''_c]}{[(1 - b)E'_c + bE'_c]^2 + [(1 - b)E''_{am} + bE''_c]^2}
\] (1.11)

Substitution of equations 1.10 and 1.11 gave the temperature dependent response as

\[
E'_\text{PEO}(T) = (1 - a)E'_{SLS}(T) + \frac{a[E'_{SLS}(T)E_j][(1 - b)E'_{SLS}(T) + bE_j]}{[(1 - b)E'_{SLS}(T) + bE_j]^2 + [(1 - b)E''_{SLS}(T)]}^2
+ \frac{a[E''_{SLS}(T)E_j][(1 - b)E''_{SLS}(T)]}{[(1 - b)E'_j + bE'_j]^2 + [(1 - b)E''_{SLS}(T)]^2}
\] (1.12)

\[
E''_\text{PEO}(T) = (1 - a)E''_{SLS}(T) + \frac{a[E''_{SLS}(T)E_j][(1 - b)E'_{SLS}(T) + bE_j]}{[(1 - b)E'_{SLS}(T) + bE_j]^2 + [(1 - b)E''_{SLS}(T)]^2}
- \frac{a[E'_{SLS}(T)E_j][(1 - b)E''_{SLS}(T)]}{[(1 - b)E'_j + bE'_j]^2 + [(1 - b)E''_{SLS}(T)]^2}
\] (1.13)

The crystalline modulus \( E_j \) was assigned a value of 4.6 GPa, taken from the literature.\(^{27}\)

Values for \( a \) and \( b \) were taken from Table 1.1. The melting temperature \( T^* \) was 338 – 340 K (65-67 °C) for PEO. The other input values of \( A \), \( \tau_o \), \( E_{ao} \), and \( T_o \) for the modified SLS model were adjusted through an iterative process to optimize the fit of the combined model response to the experimental PEO control in relaxation distribution, height, and position. Adjusting \( A \) and \( \tau_o \) allowed for good control of the peak height through \( A \), while
maintaining the distribution through \( \tau_0 \). The activation energy \( E_a \) for the PEO \( \beta \)-relaxation was varied within a set of literature values, 25-147 kJ/mol.\textsuperscript{30-31} Lower \( E_a \) values shifted the relaxation to lower temperatures and narrowed it slightly. In conjunction with \( \Lambda \) and \( \tau_0 \), \( E_a \) was used to fit the position, shape, and height of the model response, although the effect of \( E_a \) was small compared to that of the other two parameters. The temperature \( T_0 \) was varied to shift the peak position. After the best fit was obtained, a baseline of \( 1 \times 10^8 \) Pa was added to the loss modulus to match the experimental baseline. Finally, \( \tan \delta \) was extracted from the fits of \( E' \) and \( E'' \).

The fits of the model to the experimental data for storage modulus, loss modulus, and \( \tan \delta \) of the PEO control are shown in Figure 1.7 (a-c). The storage modulus agreed very well with the experimental data in the transition region. The loss modulus, after shifting the baseline, almost completely emulated the experimental data through the transition. The \( \tan \delta \) response was in very good agreement with the experimental curve, with very similar peak temperature, shape and height. The resulting optimized input values for the PEO control are given in Table 1.2. These input values were utilized to describe the PEO layer in subsequent calculations of the layered systems.

1.3.4 Dynamic Response of the Layered Systems

The PS/PEO system was modeled by combining the two-phase PEO model in parallel with a spring to represent the PS layers, Figure 1.8a. The PS elastic spring modulus \( E_4 \) was taken as the measured storage modulus of the glassy PS control, \( 1.85 \times 10^9 \) Pa. A baseline of \( 4-6 \times 10^7 \) Pa was added to the calculated loss modulus. The shift was about half that used for fitting the PEO control. The layered model response closely
mimicked the experimental results, Figure 1.8 (b-c). Most importantly, the model reproduced the decrease in the PEO β-relaxation intensity with decreasing layer thickness. The response calculated for a PEO layer with the Takayanagi parameters (a and b) of the control is included as the solid line in Figure 1.8c. It shows that a noticeable confinement effect is predicted even in the thickest PEO layers. The model also reproduced the experimental storage and loss moduli fairly well. Some inconsistencies may have resulted from the sensitivity of these measurements to the specimen dimensions.

The confining EAA layers of the EAA/PEO films also displayed a β-relaxation at about 27 °C that exhibited a parallel decrease in intensity with the PEO layers. The viscoelastic response of the EAA layers was represented with a modified SLS element. In this case, the low level of crystallinity was omitted from the model. The input values were chosen to match the storage and loss moduli in the β-relaxation region, Table 1.3. The optimized input values gave good agreement with the experimental storage and loss moduli, as shown in Figure 1.9 (a-b). The resulting tan δ response fit the β-relaxation peak in shape and position, although the intensity was somewhat higher, Figure 1.9c.

The modified SLS model for EAA was combined in parallel with the PEO model as shown schematically in Figure 1.10a. The PEO loss modulus response was shifted by 4-6 × 10^7 Pa to match the experimental baseline. The model successfully reproduced the trends observed in the experimental data, as seen in Figure 1.10 (b-c). In particular, the model reproduced the decreases in both β-relaxations with decreasing layer thickness. There was good correlation in the peak intensities for the PEO layers. The experimental EAA intensities were higher than predicted, probably due to the rapid increase of damping as the temperature approached the melting region of PEO.
1.3.5 Effect of Lamellar Orientation

The model was further tested by melting the highly oriented, in-plane PEO lamellae and quenching the film to obtain a different PEO crystallization habit. The wide-angle X-ray diffraction pattern in the extrusion direction confirmed a change in the lamellar orientation in the EAA/PEO films with 125 nm layer thickness, Figure 1.11. The PEO (120) reflections appeared as equatorial arcs in the pattern of the extruded film, indicating that the PEO lamellae were oriented parallel to the layer plane. In the quenched film, appearance of the PEO (120) reflections in a four-point pattern indicated that PEO crystallized as short lamella that were preferentially oriented perpendicular to the layer plane. In this orientation, the short lamellae would have been highly interconnected by amorphous tie chains and the reinforcing effect of the crystals would have been similar to that in the isotropic spherulite.

Figure 1.12 compares the 1% tensile modulus of the PEO layers with in-plane and on-edge PEO crystal orientation. In contrast to the extruded films, the modulus of the quenched PEO layers did not change with the layer thickness. The quenched films exhibited slightly higher crystallinity than the extruded films, about 78% compared to 71% for the extruded films, which accounted for the slightly higher modulus of the thickest PEO layers. Because the quenched PEO layers were similar in crystallinity and modulus regardless of the thickness, it followed that the Takayanagi parameters (a and b) were constant, independent of layer thickness. Then, according to the stress distribution model demonstrated for the extruded films, the dynamic mechanical behavior of the quenched films should not depend on layer thickness.
The storage modulus, loss modulus, and tan $\delta$ of the quenched PS/PEO and EAA/PEO films are shown in Figure 1.13 (a-b). It can be seen that the quenched films exhibited almost identical storage modulus, loss modulus, and tan $\delta$ regardless of the layer thickness. Eliminating the layer thickness effect by removing the in-plane orientation of the PEO lamellae supported the hypothesis that the large reduction of the $\beta$-relaxation intensity seen in the extruded films was due to the gradual change in crystallization habit as the layer thickness decreased from spherulites with nearly isotropic lamellar orientation to large, highly oriented in-plane lamellae.
1.4 Conclusions

It is widely suggested that confinement of an amorphous polymer in thin spaces reduces the chain mobility, which is manifest as a reduction in the $\beta$-relaxation intensity. The presence of a crystalline phase imposes additional constraints on the amorphous chains due to attachment to the crystals. The present study sought to determine whether concepts developed for confined amorphous polymers extend to semicrystalline polymers. For this purpose, long range, almost defect free confinement was achieved by forced assembly of hundreds of alternating layers of PEO with a minimally interacting confining polymer. The confinement gradually reduces the intensity of the PEO $\beta$-relaxation as the layer thickness decreases from the microscale to the nanoscale. However, the effect is observed in relatively thick layers where any influence of the substrate should be negligible. By considering the previously reported changes in crystalline morphology that accompany layer confinement, it is possible to completely account for the reduction in relaxation intensity using standard mechanical models. The viscoelastic behavior of the amorphous phase is satisfactorily represented by a modified SLS model. The amorphous and crystalline contributions are combined using a combination of parallel and series coupling in accordance with the Takayanagi model. No adjustment in the viscoelastic parameters of the modified SLS model is required, indicating that there is no change in amorphous phase mobility even in layers as thin as 45 nm. The effect of the crystalline morphology is accommodated through the independently determined parameters of the Takayanagi model, which dictate an increasing contribution of parallel coupling as the layer thickness decreases. It appears that in semicrystalline polymers the constraints imposed by attachment to crystals influence the amorphous chain mobility to a greater
extent than does physical confinement. However, the situation may be different if the polymer is rigidly confined, i.e. without a free surface, at a size scale below the lamellar thickness of about 20 nm.
1.5 References


Figure 1 (a-b): Dynamic mechanical data showing large reductions in relaxation intensities with decreasing layer thickness: a) Tan δ curves of 50/50 PS/PEO and controls; b) Tan δ curves of 50/50 EAA/PEO and controls.
Figure 1.2: Comparison of relaxation intensities vs. layer thickness of EAA/PEO and PS/PEO systems.
Figure 1.3 (a-b): The mechanical model for the PEO layers: (a) The composite parallel system with the PEO layers described by the Takayanagi model; and (b) schematics showing the effect of layer thickness on the lamellar organization and the corresponding changes in the mechanical model.
Figure 1.4: The tensile modulus of PEO layers vs. nominal PEO layer thickness showing the increase in PEO modulus with decreasing layer thickness. Measurements were made on the EAA/PEO system at -10 °C and 5%/min.
Table 1.1: Tensile modulus of EAA/PEO and controls, calculated PEO layer modulus (5%/min, T = -10 °C), and input values for the Takayanagi model: PEO layer only

<table>
<thead>
<tr>
<th>Sample</th>
<th>1% Modulus (MPa)</th>
<th>1% PEO Modulus (MPa)</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>EAA Control</td>
<td>670 ± 40</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PEO Control</td>
<td>540 ± 20</td>
<td>540 ± 20</td>
<td>0.722</td>
<td>0.017</td>
</tr>
<tr>
<td>50/50 3600</td>
<td>730 ± 80</td>
<td>790 ± 120</td>
<td>0.717</td>
<td>0.010</td>
</tr>
<tr>
<td>50/50 510 nm</td>
<td>940 ± 30</td>
<td>1210 ± 70</td>
<td>0.714</td>
<td>0.005</td>
</tr>
<tr>
<td>50/50 125 nm</td>
<td>1060 ± 50</td>
<td>1450 ± 90</td>
<td>0.712</td>
<td>0.004</td>
</tr>
<tr>
<td>50/50 45 nm</td>
<td>1240 ± 50</td>
<td>1820 ± 90</td>
<td>0.711</td>
<td>0.002</td>
</tr>
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</table>

PEO $V_c = 0.71$
Figure 1.5: Combination of a modified standard linear solid model, representing the amorphous phase, with a crystalline spring according to the Takayangi model.
Figure 1.6 (a-b): Effect of input values on the SLS model response a) Springpot parameter $A$ for $\tau_0 = 1 \times 10^{-17}$ s, b) relaxation time pre-exponential factor, $\tau_0$, for $A = 0.2$
Table 1.2: Optimized input values for PEO

<table>
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<th>PEO</th>
</tr>
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<tbody>
<tr>
<td>$A_1$</td>
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</tr>
<tr>
<td>$\tau_0$ (s)</td>
<td>$10^{-30}$</td>
</tr>
<tr>
<td>$E_a$ (J/molecule)</td>
<td>$9.14 \times 10^{-20}$</td>
</tr>
<tr>
<td>$E_1$ (Pa)</td>
<td>$1.0 \times 10^9$</td>
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<tr>
<td>$E_2$ (Pa)</td>
<td>$5.5 \times 10^7$</td>
</tr>
<tr>
<td>$E_3$ (Pa)</td>
<td>$4.60 \times 10^9$</td>
</tr>
<tr>
<td>$T^*$ = $T_m$ (°C)</td>
<td>66</td>
</tr>
<tr>
<td>$T_o$ (°C)</td>
<td>-107</td>
</tr>
<tr>
<td>$\omega$ (Hz)</td>
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</table>
Figure 1.7 (a-c): Comparison of PEO model response with experimental results for the PEO control: (a) Storage modulus; (b) loss modulus; and (c) tan δ.
Figure 1.8 (a-c): Comparison of experiment and model for PS/PEO; (a) Schematic of the PS/PEO composite system; (b) experimental results; and (c) model response.
Table 1.3: Optimized input values for EAA – SLS model only

<table>
<thead>
<tr>
<th>Parameter</th>
<th>EAA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2$</td>
<td>0.255</td>
</tr>
<tr>
<td>$\tau_o$ (s)</td>
<td>$10^{-28}$</td>
</tr>
<tr>
<td>$E_a$ (J/molecule)</td>
<td>$2.01 \times 10^{-19}$</td>
</tr>
<tr>
<td>$E_4$ (Pa)</td>
<td>$4.50 \times 10^8$</td>
</tr>
<tr>
<td>$E_5$ (Pa)</td>
<td>$4.50 \times 10^7$</td>
</tr>
<tr>
<td>$T^* = T_m$ (°C)</td>
<td>99</td>
</tr>
<tr>
<td>$T_o$ (°C)</td>
<td>-112</td>
</tr>
<tr>
<td>$\omega$ (Hz)</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 1.9 (a-c): Comparison of EAA model response with experimental results for the EAA control: (a) Storage modulus; (b) loss modulus; and (c) tan δ.
Figure 1.10 (a-c): Comparison of experiment and model for EAA/PEO; (a) Schematic of the EAA/PEO composite system; (b) experimental results; and (c) model response.
Figure 1.11: 2D WAXS patterns of EAA/PEO films with 125 nm layers showing a change from in-plane lamellar orientation in the as-extruded film to on-edge lamellar orientation in the quenched film.
Figure 1.12: The tensile modulus of PEO layers vs. nominal PEO layer thickness comparing the as-extruded and quenched EAA/PEO films. Measurements were made at -10°C and 5%/min.
Figure 1.13 (a-b): Tan δ curves for quenched films: (a) PS/PEO; and (b) EAA/PEO.
**Figure 1.14:** Comparison of relaxation intensities vs. nominal PEO layer thickness of as-extruded and quenched films; As-extruded: solid black symbols, Quenched: open black symbols.
CHAPTER 2

Deformation of Confined Poly(ethylene oxide) in Multilayer Films

2.1 Introduction

There has been much interest in the mechanism of plastic deformation of semi-crystalline polymers since the 1960s, when polymers were emerging as commercial products. As these types of polymers are useful for many applications, their mechanical properties are of great importance. Several studies have examined bulk materials, single crystals, and single crystal mats of polyethylene (PE), polypropylene (PP), polyesters, and polyoxymethylene (POM), with very distinct structures resulting from deformation due to the large differences in scale and crystalline orientation.\textsuperscript{1-14} However, there has been little investigation of the deformation of semi-crystalline polymers as a function of thickness spanning the thicknesses between bulk and single crystals, as it was difficult to obtain samples of various thicknesses using a single process.

A vast amount of literature on the deformation of bulk polymers exists today. It has been widely accepted that the process of deformation for bulk materials with a spherulitic morphology progresses in the following manner: 1) interlamellar deformation of the amorphous phase and elongation of amorphous tie chains, 2) shearing and tilting of lamellar chain folds where twinning and phase transformations can also occur, 3) separation of the crystalline block segments, 4) orientation of the block segments and tie chains and/or chain pullout and re-crystallization.\textsuperscript{1-8} Crystal alignment in relation to the deformation axis greatly affects the amount of interlamellar deformation and the onset time of subsequent steps. The most interlamellar deformation and voiding are observed when the crystalline lamellae are aligned perpendicular to the deformation direction,
which delays crystal shearing and tilting, and the least amount observed when the lamellae are aligned parallel to the direction of deformation.

The abundance of studies on polymeric single crystal deformation has been focused on small amounts of solution-grown samples of single crystals or single crystal mats. These single crystals were deposited on substrates, such as Mylar, which limited the studies to strains below 200%. After stretching, carbon replicas of the crystals were produced through a shadowing process, and these were imaged using electron diffraction and scanning electron microscopy (SEM). Cracks and non-uniform deformation, called micro-necking, were observed. The deformation mechanism was found to be dependent upon which crystal axis was aligned with the deformation direction in PE\textsuperscript{11-13}, POM\textsuperscript{9,10,13}, and polyesters\textsuperscript{14}. Cracks and minimal deformation were observed along one axis, while micro-necking, as well as uniform deformation, were observed along the other axis. Artifacts were often detected due to crystal slip from the substrate and to greater relaxation of the substrate than the crystal, and as a result of the replication process. Though these were important findings, the limitations to the testing of solution-grown single crystals, and the artifacts that occur from their handling, make it difficult to compare with present commercial polymers. It would be beneficial to examine these types of structures under conditions more relevant to the current processing and testing methods of semi-crystalline polymers, which often involve melt processing and larger sample volumes.

Rigidly confined thin films without a free surface can be fabricated by microlayer coextrusion with layer thicknesses from multiple microns down to nanometers.\textsuperscript{15-16} As the thickness of a confined PEO layer decreases from the microscale to the nanoscale, the
morphology systematically changes from three-dimensional spherulites to two-dimensional discoids and to ‘in-plane’ lamellar stacks.\textsuperscript{17} Finally, when the confinement occurs on the 25 nm size scale of the usual lamellar thickness, the PEO layers crystallize as single lamellae with large aspect ratio that resemble large single crystals.\textsuperscript{18} A previous study on low strain deformation of confined PEO yielded unexpected results due to the high orientation of PEO as layer thickness decreased.\textsuperscript{19} In this work, we advance our understanding, highlighting the shift in deformation mechanism as a result of PEO layer thickness. PEO was coextruded as microlayer and nanolayer films with up to 1025 layers of PEO alternating with poly(ethylene-\textit{co}-acrylic acid) (EAA). The number of layers and composition was adjusted in order to achieve individual layer thicknesses ranging from a few microns to 20 nm. Using these multilayer films, conventional experimental methods can be used to study the effect of thickness on the deformation of PEO, with the ability to stretch the PEO to high strains and image the resulting structures, which have been previously unachievable.
2.2 Experimental

The confined polymer of high crystallinity, \( \sim 70\% \), used in this study is poly(ethylene oxide) (PEO) (Polyox WSR-N80), with a molecular weight of \( \sim 200,000 \) g/mol, and melting point of 65 °C. The alternate layer that confines PEO is an ethylene-co-acrylic acid copolymer (EAA), Primacor 1410, with a melting temperature at 99 °C. All materials were obtained from Dow Chemical. The materials characteristics, melting temperature \( (T_m) \) and crystallinity \( (X_c) \), are summarized in Table 2.1.

For this study, films with 33, 257, and 1025 alternating EAA and PEO layers with EAA/PEO 50/50 (vol./vol.) composition and 1025-layer EAA/PEO 90/10 composition were produced through a continuous coextrusion process.\(^ {20-21} \) Change in the number of layers and composition allowed for a large range of layer thicknesses. The overall film thicknesses ranged from 120 to 130 \( \mu \)m, which corresponded to individual PEO layer thicknesses of 25 nm to 3600 nm. Table 2.2 summarizes the characteristics of these layered samples. Films were dried and kept stored in a desiccator with molecular sieves before all testing.

The stress–strain behavior in uniaxial tension was measured with ASTM D1708 \(^ {22} \) microtensile specimens cut from each extruded film along the extrusion direction. Three specimens of each film were stretched in an MTS (Eden Prairie, MN) Alliance RT30 at a strain-rate of 100% min\(^{-1} \) at \( T = 23 \) °C. Engineering stress and strain were defined conventionally. Tensile modulus values were taken at 1% strain. Samples for 2D WAXD were prepared by stretching 8 mm long, 2 mm wide strips to various strains: 50, 100, 150, and 250. Larger 8 mm long, 4 mm wide strips were used to obtain samples stretched to 400%. While being held in tension, the strips were clamped down in a metal holder.
before release from the MTS grips, preserving an 11 mm long strip of unrecovered sample. Though data was collected at 0, 50, 100, 150, 250, and 400% strain, we will only show raw data for 0, 150 and 400%. Raw data for 50, 100, and 250% strain are displayed in Figures 2.S1, 2.S2, and 2.S3, respectively.

Wide-angle X-ray scattering (WAXS) measurements were carried out using a Micromax002+ X-ray generator (Rigaku, Woodlands, TX), operated at 45 kV and 0.88 mA, producing a highly focused parallel beam of monochromatic Cu Kα radiation (\(\lambda = 0.154 \text{ nm}\)). Transverse direction (TD) 2D patterns were collected by aligning the incident X-ray beam parallel to the layer planes, perpendicular to the extrusion/deformation direction. Normal direction (ND) patterns of the films were obtained by aligning the incident X-ray beam perpendicular to the plane of the film. The WAXS patterns were collected using a magnetic imaging plate, which is processed using a Fujifilm PLA700 image reader after 2 hours of exposure in TD, and 17 hours of exposure in ND. The sample-to-detector distance was 150 mm and the diffraction angle was calibrated using a CaF₂ standard.

Changes in crystallinity and crystal structure due to the stretching process were measured using differential scanning calorimetry (DSC). Two first heating thermograms were obtained for each film at each strain on a Perkin Elmer Pyris 1 differential scanning calorimeter (DSC) at a heating rate of 40 °C min⁻¹, and normalized by sample weight. This fast heating rate was chosen to avoid re-crystallization of the PEO during the heating process. Calculated average crystallinity values were obtained by deconvolution of these thermograms and were corrected for weight composition. This was done by conversion of volume composition to weight composition, using the density of EAA, 0.936 g/cm³, and
the density of the PEO amorphous fraction, 1.124 g/cm³, as PEO is amorphous during the coextrusion process.23
2.3 Results and Discussion

2.3.1 Tensile Testing of Multilayered Films

Stress-strain curves of EAA/PEO and control films are shown in Figure 2.1, and the measured tensile properties are summarized in Table 3. PEO controls were extremely brittle, fracturing at (14 ± 2)% strain. EAA control films exhibited ductile behavior, with gradual yielding, and fracturing at (340 ± 18)% strain. The multilayered films retained the ductility of EAA, unaffected by the 10% or 50% volume fraction of brittle PEO, or by the scale of the layers. All layered films exhibited similar fracture strains and stresses to the EAA control. As the composition of the layered films were not the same, the PEO modulus was calculated from the composite modulus, according to the parallel model, as was done previously:19

\[
E_{PEO} = \frac{E_{\text{composite}} - E_{EAA}V_{f,EAA}}{V_{f,PEO}} \tag{1}
\]

\(E_{PEO}, E_{EAA},\) and \(E_{\text{composite}},\) are the moduli of the PEO, the EAA, and the composite, respectively, and \(V_{f,PEO}, V_{f,EAA},\) and \(V_{f,\text{composite}}\) correspond to the volume fractions of the PEO, the EAA, and the composite, respectively.

The PEO modulus increased significantly as PEO layer thickness decreased. There appeared to be no significant effect of layer thickness on yield stress, but a decrease in the yield strain was observed, with no detectable yield point when PEO layer thickness approached the thickness of a single lamella. The reinforcement was due to stress redistribution to the higher modulus aligned PEO lamellae within the layers.19 The lower yield strain observed was most likely due to a decrease in interlamellar fractions between PEO lamellae in the deformation direction as the PEO lamellae became more and more aligned in the deformation direction.
Stress-whitening was also observed in all films, regardless of layer thickness. The effect was much more pronounced in thicker layers than in thin layers. This was to be expected, as 125 nm and 25 nm layers are on the order of the quarter wavelength of visible light, which would give the films a more transparent appearance even before stretching down the layer thicknesses. The morphology differences between the different layer thicknesses also greatly affect the stress-whitening. In thick layers that contain spherulites or truncated spherulites (3600 nm and 510 nm), there are large amounts of interlamellar amorphous fractions perpendicular to the deformation axis that will stretch and result in voids that scatter light. Thin layers, however, have less interlamellar spaces due to greater orientation of the crystalline fraction, and the amorphous fraction is excluded into spaces that are also aligned with the deformation direction. After uniaxial stretching, each film was clamped at 0, 50, 100, 150, 250, and 400% strains for 2D wide-angle x-ray diffraction to determine the large-scale orientation of the crystalline fraction at each point along the stress-strain curve.

2.3.2 Wide Angle X-Ray Diffraction: Large-Scale Structural Analysis

2D WAXD patterns with the X-ray beam parallel to the layer planes, perpendicular to the deformation/extrusion axis (transverse), and perpendicular to the plane of the film (normal), were collected for each sample. PEO, at 0% strain, and EAA controls, at 0% and 400% strain, are shown in Figure 2.2. The WAXD pattern of the monoclinic crystal form of PEO had a ring at scattering angle \( \theta = 19.28^\circ \), corresponding to the reflections from (120) planes, and a second ring at \( \theta = 23.38^\circ \), containing the overlapping reflections from the (032), (\( \overline{1} \)32), (112), (2\( \overline{1} \)2), (1\( \overline{2} \)4), (204), and (004) planes. (120) and (032) reflections were observed as concentric rings in both
transverse (TD) and normal directions (ND), indicating no particular orientation of the PEO crystals. Very weak (224) and (024) reflections (2θ = 26.38) were also present. These reflections were not used for analysis since the full spectrum of these reflections could not be obtained due to the distance between sample and detector, limiting interpretation of crystal orientation. With the X-ray beam perpendicular to the plane of the film (ND), all reflection planes produced concentric rings, indicating isotropic orientation. No patterns were collected at 400% strain for PEO, as PEO is very brittle, and fractured at ~14%. As-extruded EAA control films showed similar patterns in both TD and ND. At 0% strain, EAA showed an isotropic ring of the orthorhombic (110) reflection from the PE comonomer. When stretched to 400%, EAA control displayed a concentrated, largely amorphous spot on the meridian, indicating alignment of the chains along the deformation axis, in both TD and ND.

Layered samples stretched to 0, 50, 100, 150, 250, and 400% strains were tested under the same conditions. Figure 2.3 displays simulated TD 2D WAXD patterns of the possible PEO crystal structures that can occur: in-plane, edge-on, and mixed in-plane and edge-on. In-plane orientation, where the chain orientation is perpendicular to the layer plane, is characterized by equatorial (120) arcs and (032) reflections at azimuthal = 67°, 113°, 237°, and 293° with respect to the meridian. (224), and (024) reflections (2θ = 26.38) will appear at azimuthal = 45° (Figure 2.3a). Edge-on lamellae with fiber orientation exhibits a similar pattern to the in-plane, only turned 90 degrees, with reflections aligned along the meridian (Figure 2.3b). A mixed in-plane and edge-on orientation results in superimposed patterns of the in-plane and edge-on orientation patterns (Figure 2.3c).
It was reported previously that the morphology of the EAA layers does not change with layer thickness. As EAA is stretched as a control, as well as within the layered films, the isotropic (110) reflection and amorphous ring gradually concentrate along the meridian, indicating alignment of the EAA chains along the deformation axis. All layered film patterns indicated EAA qualitatively behaves in the same manner in all samples, regardless of layer thickness. Therefore, EAA layers were disregarded in the layered films, and we will only discuss structural changes of the PEO layer.

**Thick Layers – Spherulitic Morphology**

Above 510 nm PEO layers, 2D WAXD showed similar results at each strain. Figures 2.4 and 2.5 show 2D WAXD patterns of layered EAA/PEO with 3600 and 510 nm PEO layers, respectively, in both transverse and normal directions (TD and ND) at 0%, 150%, and 400% strains, with corresponding sketches of the PEO morphology confined within the layered structure. Thick layers show concentric rings at 0% strain, in both TD and ND, of the (120) and (032) reflections, indicating isotropic orientation of the PEO crystals. At 510 nm, there is an expected spatial limitation in the layer thickness direction on the spherulite, and is therefore sketched as a truncated spherulite.

When these films are stretched to 50% strain (Figure 2.S1), TD broad meridional (120) and (032) arcs appear, indicating the presence of loosely edge-on PEO crystals in all samples. As they are stretched to 100% strain (Figure 2.S2), these edge-on reflections grow stronger, while maintaining much of the original orientation. Due to the initial spatial constraint of the 510 nm PEO layers, these samples began to display smaller, more concentrated arcs along the equator as well. Through the thickness of the film, corresponding meridional arcs appear, while maintaining a weak isotropic ring, indicating
a gradual alignment of the crystals in the direction of deformation. At 150% strain, the edge-on crystal reflections become stronger as broken crystals are turned or chains are pulled out and recrystallized along the deformation axis. The TD edge-on reflections continued to grow stronger from 250% (Figure 2.S3) to 400% strain. At this point, all chains have become aligned with the deformation axis within 510 nm and 3600 nm layers, and resulted in similar patterns in both the TD and ND, analogous to a typical PEO fiber pattern.30-31 Essentially, layers of 510 nm or thicker behave like bulk semi-crystalline polymers.

Thin Layers – Aligned PEO Lamellae Morphology

Figure 2.6 and Figure 2.7 show 2D WAXD patterns of the layered films with PEO layer thickness 125 nm and 25 nm, respectively, stretched to 0, 150, and 400% strain. Corresponding sketches of the PEO morphology confined within the layered structure are also shown. Unstretched 125 nm films showed TD (120) reflections as wide arcs along the equator, representing loosely aligned PEO crystals, where not all lamellae are parallel to the layer plane. ND patterns still exhibited isotropic orientation, resulting in a sketch of loose stacks of PEO lamellae. When the layer thickness approached the thickness of a single PEO lamella, ~25 nm, 2D WAXD patterns showed concentrated (120) equatorial arcs in the TD, while maintaining isotropic orientation in the ND. It must be noted that in-plane crystals do not give strong reflections when the X-ray beam is parallel to the (120) face, and therefore, were difficult to detect in the ND.

As these thinner PEO layer films were stretched to 50%, 100%, and then 150% strain, the (120) equatorial arcs became smaller and more concentrated, much like the 510 nm layer films, Figures 2.S1 and 2.S2. This behavior was most likely due to forced
alignment of the loosely in-plane crystals as the layers were thinned under strain. It is suggested that micro-necking (non-uniform deformation) was present within thinner 125 and 25 nm layers, as the initial PEO structures were such that uniform thinning of the PEO layers would be difficult. Many single crystal studies of various semi-crystalline polymers, such as PE and PP, have shown evidence of such non-uniform deformation at strains between 30-100% with fibrils connecting sections of undeformed crystal.\textsuperscript{13-14} ND patterns showed a continuation of the gradual alignment of the chains in the direction of deformation, with strengthened meridional reflections. At 400%, however, these thin layers still retained some in-plane crystals, which resulted in incongruent TD and ND X-ray patterns, as in-plane (120) crystal faces are parallel to the ND X-ray beam and cannot be detected.

In order to compare the different samples at each strain more quantitatively, the peak intensities of PEO (120) in-plane and edge-on crystals were obtained from 2D WAXD integrated intensity scans. An example using 90/10 25 nm at 400% strain patterns in the transverse and normal directions is shown in Figure 2.8a and 2.8b, respectively. The intensity of the (120) reflection in each direction was obtained by subtracting the baseline to give $I_{120, \text{on-edge}}$ (along the meridian) and $I_{120, \text{in-plane}}$ (along the equator). Percentages of crystals with in-plane orientation were compared for different strains, rather than absolute values, by dividing the equatorial (120) peak intensity by the total (Figure 2.8a-b). This was done so that comparisons could be made between the different layer thicknesses and strains, which varied in overall thickness and composition.

Figure 2.9 (a-b) shows the change in fraction of in-plane crystals with strain in the transverse and normal directions, respectively. As the layer thickness decreases, the
amount of initial in-plane orientation increases, reaching 100% at the 25 nm layer thickness. As the samples are stretched, the in-plane crystal fraction within thicker layers of 125 nm and greater, gradually decrease to 15% or less once at 400% strain. In contrast, the in-plane crystal fraction in 25 nm PEO layers decreased at a slower rate, and about 40% of the original in-plane orientation remains even at 400% strain. Normal direction intensities begin around 50%, which was expected, as all samples exhibited isotropic 2D WAXD patterns in this direction. All layer thicknesses showed similar decreases with strain, due to the inability to detect in-plane (120) reflections in this direction. The large amount of in-plane crystals retained in these samples could be due to simple spatial confinement and mechanical reinforcement of the crystals. Another possibility is that, like polyester and polyethylene single crystals, the direction of deformation along the crystal growth planes can result in different tilt processes that may leave crystals aligned towards one direction undeformed.12, 14 Since the PEO is randomly aligned in the plane of the film, it is highly likely that roughly half of the crystals were oriented at an angle that did not allow deformation, resulting in the retention of roughly half the original in-plane crystals.

2.3.3 Atomic Force Microscopy: Small Scale Structural Analysis

Atomic force microscopy (AFM) images were taken of EAA/PEO film cross-sections at 0%, 150%, and 400% strain to observe the small scale morphological changes that occurred under deformation. The images collected were then compared to the predicted PEO structures from WAXD patterns at each strain point sampled, Figure 2.10 (a-f) and Figure 2.11 (a-f). The EAA possesses low crystallinity and a lower modulus
than PEO, and appeared as a smooth, dark phase. PEO, with its high crystallinity, and higher modulus, appeared as the light phase, with apparent crystalline structures.

**Thick Layers – Spherulitic Morphology**

Un-stretched thicker PEO layers showed spherulitic features that deformed similar to bulk semi-crystalline polymers. 50/50 3600 nm PEO layers contained large spherulites, 1-2 of which spanned the width of the layer (Figure 2.10a). 50/50 510 nm PEO layers showed truncated spherulites that spanned the full width of the layer with no preferential orientation of the crystals (Figure 2.10d). These images are in good agreement with the AFM images obtained in an earlier study published by Wang et al.18

When stretched to 150% strain, both 3600 nm and 510 nm PEO layers displayed a mixture of stacked in-plane lamellae and broken edge-on crystals in layers of uniform thickness (Figure 2.10b and 2.10e). Stretching to 400% strain resulted in multiple edge-on crystallites spanning the layer thickness, most likely arising from re-crystallization (Figure 2.10c and 2.10f).

**Thin Layers – Aligned PEO Lamellae Morphology**

125 nm layers were composed of aligned lamellar stacks, 5-6 lamellae thick. These stacks were primarily aligned parallel to the layer plane, with some tilting (Figure 2.11a). 25 nm layers showed single PEO lamellae confined between the EAA layers (Figure 2.11d). These images are in good agreement with the AFM images obtained in an earlier study.18 Micro-necking was indeed present in 125 nm layers, as thinned areas made up of most likely re-crystallized edge-on PEO crystallites and non-deformed sections of aligned stacked lamellae were observed (Figure 2.11b). As the 25 nm PEO layers are stretched to 150%, small gaps are observed between the single lamellae, which
could either be cracks in broken crystals, or widening gaps between undeformed crystals. A bead-like structure was also observed (Figure 2.11e). This structure may arise from the non-uniform thinning of the lamellae, as they undergo chain tilting and chain slip with deformation. At 400% strain, 125 nm layers were composed of single edge-on crystallites spanning the layer thickness, as these layers have become very thin with strain (~25 nm) (Figure 2.11c). The thin, single lamella thickness layers were obscured by recovered EAA at high strain, and the PEO layers could not be visualized. (Figure 2.11f). In general, as the layer thickness decreases, thick PEO layers undergo axial alignment of the crystalline fraction, as seen in bulk materials, while thinner layers (<125 nm) deform non-uniformly through micro-necking, similar to findings of solution-grown single and multilayer crystals literature.

2.3.4 Thermal Behavior

Differential scanning calorimetry was performed on layered EAA/PEO films to give insight into the structure and stability of the crystals. The raw 1st heating endotherms for samples stretched to 0, 150, and 400% strains are shown in Figure 2.12 (a-c). PEO control films exhibit a sharp melting endotherm at 71 °C, consistent with aged PEO. EAA control films display a polyethylene (PE) melting endotherm at 98 °C and a smaller melting peak of secondary crystallites at 50 °C, related to unstable PE crystals due to hydrogen bonding of the carboxylic acid groups. Thicker unstretched films with 3600 nm, 510 nm, and 125 nm PEO layers showed EAA melting peaks at the same temperatures as the controls, but a lowered PEO melting peak at 68 °C. The 90/10 composition film exhibited the same behavior for EAA as the control, but PEO melting was depressed further than in the other layered films, 66 °C. This behavior may be due to
less perfect PEO crystals, as pure PEO single crystal fragments are often formed at different sites and connected by loosely packed crystals and tie chains, especially in the case of high molecular weight, resulting in lower packing energy, and a lower melting temperature. All PEO melting temperatures were elevated from the previously published value of 65 °C, however, due to aging of the PEO. Exposure to water in the atmosphere before drying plasticized the PEO, and allowed for better packing and further crystallization.

Stretching to 150% strain resulted in the broadening of the PEO peaks as the PEO strain-recrystallized, producing crystallites that melt at higher temperature, ~71 °C for thicker layers and ~68 °C for 25 nm PEO layers. It should be noted here that the PEO control at 0% strain is plotted in each graph at each strain, as PEO fractured at 14% strain, to help emphasize the temperature shifts of the layered PEO melting peaks. At 400%, the strain-recrystallized PEO melting peak strengthened and the original PEO crystallites decreased, sharpening the broadened peak from 150% strain towards the higher melting temperatures. A shift of the melting peaks of EAA to 52 °C and 100 °C was also observed, indicating strain-induced recrystallization was present in the EAA layers as well. All thicker PEO layer films appeared almost identical, as was observed with TD WAXD. The 25 nm PEO layer film is visibly different, with slightly downshifted melting peaks (2 °C), and a slightly smaller peak shift with strain.

The weight percent crystallinity of the PEO and EAA fractions were calculated from \( \Delta H_m \) of each heating thermogram, using heat of fusion values of 197 J/g for PEO crystals and 290 J/g for PE crystals, correcting for weight composition of each sample. PEO control was determined to be 90% crystalline, significantly higher than
previously reported,\textsuperscript{17-19} due to water absorption and re-drying.\textsuperscript{32} (Figure 2.S4). PEO crystallinity within layers was lower, however, ranging between 66 and 80%, with thicker layers of 125 to 3600 nm possessing lower crystallinity values than the 25 nm single lamellae layers. EAA control was determined to be 37% crystalline, consistent with previously reported values.\textsuperscript{18} Films with 90/10 vol./vol. composition EAA/PEO possessed similar EAA crystallinity to the control, 35%, but those with a 50/50 vol./vol. composition possessed elevated EAA crystallinity, ranging from 45 to 52%. It is possible that the aging of the PEO nucleated further crystallization of the EAA within these films, and the effect is more apparent in the 50/50 compositions, as these EAA layers are thinner compared to the 90/10 composition and EAA control.

As these films were stretched, the PEO crystallinity was expected to decrease as crystals were broken up and chains pulled out from the lamellae, followed by an increase as the chains underwent strain-induced re-crystallization, with a possible subsequent decrease as a result of further orientation and fracture of the newly crystallized structures as it neared fracture of the sample.\textsuperscript{1-8,25} However, only the thicker PEO layers exhibited this progression, while the thinnest layers exhibited an initial increase in crystallinity before decreasing and increasing once again, Figure 2.13a. The crystallinity of the thickest PEO 3600 nm layers decreases gradually to 250% due to its isotropic orientation. The amount of interlamellar deformation before breakage and unfolding of crystals was greatest in these layers, since a large amount of PEO lamellae were aligned perpendicular to the deformation axis. Films with PEO layer thicknesses of 510 nm exhibited very similar behavior to the 3600 nm, as suggested by 2D WAXD. The crystallinity of the 125 nm PEO layer also gradually decreases, but at a slower rate than the thicker layers, most
likely due to the reinforcement resulting from the highly aligned PEO lamellar stack morphology.

Further reduction of the PEO layer thickness to 25 nm, with a single lamella aligned in the deformation direction, exhibited a small initial increase in the crystallinity before the expected decrease and subsequent increase, indicating initialization of chain pullout and strain re-crystallization at an earlier strain point than observed in thicker PEO layers, at 50% or earlier. It was previously discovered that these thinner layers were significantly mechanically reinforced due to the crystal orientation, which would require larger stresses to bring about lamellar tilting, breakage, and unfolding. Therefore, the small amount of strain re-crystallization initially found in these layers most likely originated from crystalline defects and lamellar edges. Enhanced reinforcement of the 25 nm layers caused a delay in the full onset of strain re-crystallization to between 150 and 250% strain.

Though strain-induced re-crystallization was observed in the EAA layers, the change in EAA crystallinity with stretching did not vary significantly with layer thickness, Figure 2.13b. Crystallinity values of films with 50/50 composition were comparable at each strain point, even possessing the same amount of EAA crystallinity, 52%, near the film fracture point. The 90/10 composition film and EAA control film behaved analogously, with lower crystallinity than the 50/50 composition films. These results support the earlier assumption that EAA deformation is not affected by the layer thickness.
2.4 Conclusions

The effect of confinement on the deformation behavior of poly(ethylene oxide) was studied using melt processed coextruded EAA and PEO multilayer films with varying PEO layer thicknesses from 3600 nm down to 20 nm. The deformation mechanism was found to shift as layer thickness was decreased between 510 nm and 125 nm. This change was evaluated with tensile testing, wide angle X-ray diffraction (WAXD), atomic force microscopy (AFM), and differential scanning calorimetry (DSC).

In general, layers of 510 nm or thicker behaved like bulk semi-crystalline polymers. The spherulitic structure within these layers underwent interlamellar and intralamellar deformation through the yield point, followed by subsequent chain pull-out and re-crystallization. These samples showed a gradual progression from isotropic orientation of the PEO crystals to almost full (> 85%) orientation of the chains along the deformation axis with concentrated meridional (120) arcs, like that of a typical PEO fiber.

Films with 125 nm and 25 nm exhibited similar features to those observed in the literature of single crystals and single crystal mats. As these films were stretched, the lamellae became increasingly aligned with the deformation direction, cracking, and micro-necking as strain increased. Single crystal thicknesses underwent strain-induced re-crystallization, while retaining ~40% of its original in-plane orientation, unlike any of the other layer thicknesses. The large amount of in-plane crystals retained in these samples could be due to simple spatial confinement and mechanical reinforcement of the crystals. Another possibility is that, like polyester and polyethylene single crystals, the direction of deformation along the crystal growth planes can result in different tilt processes; micro-
necking and uniform deformation takes place when stretched along one axis, with minimal deformation and cracking when stretched along the other axis.

In general, as the layer thickness decreases, thick PEO layers undergo axial alignment of the crystalline fraction, as seen in bulk materials, while thinner layers (≤125 nm) deform non-uniformly through micro-necking, as literature of solution-grown single and multilayer crystals has previously discussed. With the commercially-relevant method of melt coextrusion, we were able to overcome the limitations to the testing of solution-grown single crystals, and the artifacts that occur from their handling, and bridged the gap in knowledge between thick bulk materials and thin single crystals. The discovery of this shift in deformation mechanism that occurs between 510 nm and 125 nm due to crystal orientation can be very useful for future design of materials incorporating semi-crystalline polymers in confined spaces where mechanical properties are integral.
2.5 References


Table 2.1: Polymer material characteristics

<table>
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<tr>
<th>Material</th>
<th>Grade</th>
<th>$T_m$ (°C)</th>
<th>$X_c$ (wt%)</th>
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<td><strong>Confining Material</strong></td>
<td>Ethylene-co-acrylic acid (EAA) (AA 9.7wt%)</td>
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<tr>
<td><strong>Confined Material</strong></td>
<td>Poly(ethylene oxide) (PEO)</td>
<td>WSR-N80</td>
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Table 2.2: Layered sample characteristics

<table>
<thead>
<tr>
<th>EAA/PEO (v/v)</th>
<th>Number of layers</th>
<th>Nominal EAA Layer (nm)</th>
<th>Nominal PEO Layer (nm)</th>
<th>EAA $X_c$ (by wt%)</th>
<th>PEO $X_c$ (by wt%)</th>
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Table 2.3: Tensile properties of EAA/PEO (100%/min, T = 23°C)

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<tr>
<th>EAA/PEO (v/v)</th>
<th># Layers</th>
<th>Nominal Layer Thickness (nm)</th>
<th>1% Composite Modulus (MPa)</th>
<th>1% PEO Modulus (MPa)</th>
<th>Yield Strain (%)</th>
<th>Yield Stress (MPa)</th>
<th>Fracture Strain (%)</th>
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<td>33</td>
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<td>579 ± 43</td>
<td>10.6 ± 1.3</td>
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</table>
Figure 2.1: Stress-strain curves of EAA/PEO and controls (room temperature, 100%/min) showing: a) films retained ductility of EAA; b) increase in the modulus and yield stress, and decrease in the yield strain with decreasing layer thickness.
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PART II: Gradient Refractive Index Lenses
CHAPTER 3

Influence of Interdiffusion on Multilayered Gradient Refractive Index (GRIN) Lens Materials

3.1 Introduction

Polymeric gradient refractive index (GRIN) materials have the potential to vastly simplify the design of high-quality lens systems. These types of lenses have reduced weight and volumes compared to inorganic lenses, and possess enhanced focusing power and superior aberration correction as compared to traditional monolithic lenses with a single refractive index. GRIN lenses are commonly found in nature, with refractive index differences ranging from as low as 0.03, in the human eye, to 0.22, in a fish eye. Biological GRIN lenses consist of layered assemblies, and their index gradients are obtained through systematic variation in the protein and water concentration.\(^1\)-\(^8\) A bio-inspired class of synthetic lenses with controlled GRIN distributions was developed previously by assembling polymeric nanolayered films.\(^9\)-\(^10\) Transparent 4097-layer films of polymethylmethacrylate (PMMA) and poly(styrene-co-acrylonitrile) (SAN17), with individual layer thicknesses below the quarter wavelength (\(\lambda/4\)) were coextruded at 2% composition steps. Due to the miscibility of PMMA and SAN17,\(^11\)-\(^12\) mutual diffusion at the layer interfaces occurs during the melt co-extrusion of these films, the amount of interdiffusion dependent on the temperature and the contact time between the two polymers.

During the construction of these GRIN lenses, multiple 4097-layer films of different compositions are stacked and pressed together above the glass transition temperature, during which further interdiffusion between the films can take place. This can affect the final refractive index distribution, and subsequent performance of the lens. Therefore, the
understanding of the interdiffusion state of our starting lens materials, the coextruded films, is of utmost importance.

The interdiffusion of PMMA and SAN copolymers has previously been examined in simple bi-layer films using various techniques. Ellipsometry has been used to measure the refractive index profile through thin films of PMMA and SAN (5-40% AN content) annealed at 130 °C. The interfacial thickness determined from the refractive index profile was used to calculate a diffusion coefficient for each polymer pair. The mutual diffusion coefficient of SAN25 (160,000 g/mol) and PMMA (100,000-150,000 g/mol) was between $4 \times 10^{-15}$ and $7 \times 10^{-15}$ m²/sec.¹³ A different technique, rheometry, has also been utilized to examine PMMA and SAN29 at 120°C. The dynamic shear viscosity and dynamic complex shear modulus were measured over time, and the composition of the PMMA within the stacked assemblies was determined. The mutual diffusion coefficient was found to be $3.7 \times 10^{-16}$ m²/sec.¹⁴

Multilayer films have several advantages over other methods for the study of diffusion between polymers. Larger contact areas and a greater number of interfaces between the two materials amplify the effect of mutual diffusion. In conjunction with the size scale of these films (50 microns), the effect of interdiffusion can be detected using more common bulk characterization techniques, such as dynamic mechanical thermal analysis, differential scanning calorimetry, and oxygen permeability. Prior interdiffusion studies in multilayers have been carried out, using polymer pairs exhibiting varying degrees of miscibility.

Multilayered films of miscible polycarbonate (PC) and polyethylene terephthalate (PET), with hundreds to thousands of layers, were annealed at various temperatures and
times. The glass transitions of the two materials shifted closer together as contact time increased, approaching a single median value when annealed above 200 °C. A model based on Fick’s law of diffusion was developed to describe the mutual diffusion at the layer interface, and this model was utilized to determine a reasonable mutual diffusion coefficient that predicted the measured results.\textsuperscript{15}

Subsequent work examining the interdiffusion of HDPE and LLDPE of high polydispersity using DSC melting peaks required modification of the previous model to fit the experimental data.\textsuperscript{16-17} The broad molecular weight distribution caused a very different rate of change in the composition profile, with shorter chains diffusing at faster rates than longer chains. The diffusion coefficient was found to be highly dependent on molecular weight distribution, especially the high molecular weight tail, and less on the dimensions of the phases.

More recently, the previous model for PC/PET was modified to predict the permeability behavior, rather than thermal behavior, of multilayered films composed of nylon and EVOH with differing ethylene contents. The modified model was found to successfully predict the permeability behavior, using reasonable mutual diffusion coefficients consistent with their degree of miscibility.\textsuperscript{18}

In this work, we advance some results showing the effect of coextrusion contact time on the interdiffusion state, and the resulting optical properties, of PMMA and SAN multilayer films used to build GRIN lenses. The model relating permeability and the interdiffusion state within the layers is applied to predict permeability of the multilayer films, and to determine the mutual diffusion coefficient of PMMA and SAN.
Coextrusion contact time was varied by increasing the number of layers, as well as varying the pump rates of both polymers.
3.2 Experimental

Polymethylmethacrylate (PMMA), Plexiglas V920, of $M_w = 85,000$ g/mol,\textsuperscript{19} was obtained from Arkema. The poly(styrene-co-acrylonitrile) with 17 mol\% acrylonitrile (SAN17), Lustran Sparkle, had a molecular weight of $159,000$ g/mol.\textsuperscript{20} It was obtained from PolyOne Distribution. Table 3.1 summarizes the material properties.

For this study, films with 17, 129, 257, and 1025 alternating PMMA and SAN17 layers with 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, and 0/100 (vol./vol.) compositions were produced through a continuous coextrusion process using an ATBTA feedblock,\textsuperscript{21-22} where PMMA was extruded as the A material, and SAN17 as the B, with no third tie (T) material. The polymer melts were extruded through separate single screw extruders, and combined in the ATBTA feedblock. The ABA trilayer (with A layers half the thickness of B) was then sent through a series of multiplication dies, which cut, spread, and stack the melt, doubling the number of layers each time. PMMA was processed at 250 °C and SAN17 was processed at 260 °C. The multipliers were set at 255 °C. Low density polyethylene (LDPE) was used as a protective skin layer, and was peeled off before all testing. A total pump rate of 30 rpm was used to produce films of all layer numbers. Additional 129-layer films were collected at a slower total pump rate of 10 rpm. A single 50/50 composition of 33, 65, and 513 layers were extruded at 30 rpm to better visualize trends in the data. Table 3.2 lists the films produced, and reports their respective contact/diffusion times, $t$, calculated from the following equation:

$$t = \left( \frac{nV_{Multiplier} + V_{Surface} + V_{Exit}}{1.2cm^3/rev}(rev/min) \right) \times \left( \frac{\text{60 sec}}{\text{min}} \right)$$  \hspace{1cm} (3.1)
where $n$ is the number of multipliers, $V$ is the volume of each co-extrusion system component, and $rev$ is the pump rate. All overall film thicknesses were kept relatively constant, between 45 and 58 μm, with the target being 50 μm. This thickness variation arises from human error during manual film take-off. Films were stored at room temperature, and LDPE skin layers were removed before all testing.

Refractive index was measured in three different spots along the films with a Metricon Model 2010, which utilizes a prism coupling technique. A free-standing film was held to a prism of known refractive index under pressure, through which a laser light is shone. This setup is then rotated and the refractive index was determined as the drop in reflected laser light intensity detected due to the tunneling of laser light into the film at the critical angle. This critical angle is used by the Metricon to calculate the refractive index of the film, using Snell’s Law:\(^{23}\)

$$n_{\text{prism}} \sin \theta_{\text{prism}} = n_{\text{film}} \sin \theta_{\text{film}}$$

(3.2)

where $n$ is the refractive index and $\theta$ is the angle, where $n_{\text{prism}}$, $\theta_{\text{prism}}$, and $\theta_{\text{film}}$ are known.

Transmission measurements of free-standing films ($n = 3$) were collected on an Ocean Optics spectrometer, SD 2000 fiber optic spectrometer and OOI Base 32 software. Transmission within the visible range, at 633 nm to match the laser wavelength of the Metricon prism coupler, was recorded.

Oxygen flux, $J(t)$, at 0% relative humidity, 1 atm, and 23 °C was measured with a MOCON OXTRAN 2/20. The coextruded films were thick enough to obtain good non-steady state oxygen flux curves, from which permeability $P$ was determined according to\(^{24}\)

$$P = Jl / p$$

(3.3)
where $p$ is oxygen pressure and $l$ is the film thickness. Two films of each sample were tested to obtain the average permeability.

Films were prepared for atomic force microscopy (AFM) by embedding the films in a 5-minute epoxy resin, and cured overnight. Smooth cross-sections were obtained using a cryo-ultrarotome (MT6000-XL from RMC) at -40 °C, cutting perpendicular to the plane of the film with a glass knife. AFM was then performed in the tapping mode under ambient conditions, using a Nanoscope IIIa MultiMode atomic force microscope from Veeco Instruments with tips of 10 nm diameter. AFM phase images were analyzed using the NanoScope software to obtain a profile showing relative modulus differences across the image.
3.3 Results and Discussion

3.3.1 Optical Properties

The transparency and refractive index of these films can greatly affect the performance of the GRIN lens. High transparency and a single, compositionally dependent, refractive index are required for nanolayered polymer films suitable for the construction of optical quality GRIN lenses. The physical optics of multilayered films of two or more polymers of differing refractive index is quite well known. Wavelength-dependent optical reflections result from the sum of constructive interference of partial reflections at the layer interfaces as light penetrates these materials. The wavelength of the first-order reflection at normal incidence is expressed as: 25

\[ \lambda = 2(n_{\text{PMMA}}d_{\text{PMMA}} + n_{\text{SAN17}}d_{\text{SAN17}}) \]  

Films with layers larger than the wavelength of visible light (>800 nm) will exhibit reflections well away from the visible, and possess distinct separate refractive indices. Films with optical layer thickness (product of refractive index and layer thickness) of a wavelength to a quarter-wavelength thickness (100-800 nm), \( \lambda/4 \), will reflect in the near-infrared to visible, respectively, with maximum enhancement of reflectance at \( \lambda/4 \) thickness. 26 When layers are below the \( \lambda/4 \) thickness, the layers are too thin to give rise to constructive interference, and result in transparent films of a single refractive index.

Figures 3.1 (a-c) display representative transmission spectra for 50/50 composition films of different layer numbers. As expected, almost all visible and near-infrared light is transmitted by the thick 3125 nm layers, as these films reflect in the far infrared. As the layer thickness decreased to 1563 and 782 nm, transmission begins to dip in the near-infrared due to higher order reflections. The intermediate layer numbers, with layer
thicknesses of 195 and 395 nm, exhibited low intensity first order reflections in the near-infrared, with several higher order reflections in the visible. The films with thinnest layer thicknesses of 98 and 49 nm also transmit almost all visible and near-infrared light, with spectra very similar to the blend film. As a result, the transmission values in the visible range of the 129- and 257-layer films are slightly lower than those of the 17, 33, 65, and 513, and 1025 layers, Figure 3.1d. Even so, transmission remained greater than 85% throughout all compositions, regardless of layer number or pump rate (Figure 3.51).

Figure 3.2 shows the raw refractive index curves of 50/50 PMMA/SAN17 and control films obtained from a prism coupling technique. Thick 17-layer films exhibited multiple knees and two distinct mode patterns, indicated by arrows. This meant that these layers are still thick enough to exhibit multiple refractive indices. As the number of layers increase, the modes become more mixed, with no distinct patterns, and approach the median refractive index between PMMA and SAN17 controls. For simplicity, the first knee, the highest refractive index within the film, was plotted against composition at each number of layers in Figure 3.3 (a-d).

Films with 17 layers greatly deviated from the desired additive refractive index, favoring the higher composition material. As contact time increases in 129- and 257-layer films, from 105 seconds to 155 and 175 seconds, respectively, the refractive index approaches that of an additive index, but still does not agree at all compositions. The contact time at these layer numbers is still not long enough for the mutual diffusion of the polymers to reach equilibrium, and sections of pure polymer may still be present. This was more prominent in the middle composition region, since the thinner low composition layers of offset compositions will fully become mixtures at lower contact times than
those with more equal layer thicknesses. At 1025 layers, with 215 seconds of contact time, an additive refractive index is finally achieved at all compositions, behaving much like the melt blends.

Contact time between PMMA and SAN17 was also varied through changes of the pump rate during the coextrusion process. It can be seen in Figure 3.4 (a-c) that the refractive index at each composition of these films approaches that of the additive value with decreasing pump rate. Though the nominal layer thickness is much greater than the quarter-wavelength value, $\lambda/4$, interdiffusion has reduced the effective layer thickness to below the quarter-wavelength value, and can exhibit a single refractive index.

This reduction of the effective layer thickness through interdiffusion to give $\lambda/4$ behavior of the refractive index is illustrated in Figure 3.5. The change in refractive index of PMMA/SAN17 50/50 composition films as a function of nominal layer thickness is shown to converge nonlinearly from two separate refractive indices to a single refractive index as the layer thickness decreases. The shaded area indicates the calculated layer thicknesses below the quarter-wavelength thickness of visible light for a 50/50 composition, using equation 3.4.

Due to interdiffusion at the interfaces, the refractive indices of 50/50 composition films produced at 30 rpm, with layer thicknesses of 190 nm, are equal to the additive value of layers below the quarter-wavelength. As the pump rate is reduced, increasing contact time from 160 to 475 seconds, even films with nominal 375 nm layer thickness exhibit below quarter-wavelength behavior. To visualize the effect of interdiffusion on the layered structure, atomic force microscopy (AFM) was performed on cross-sections of the films.
3.3.2 Atomic Force Microscopy

Atomic force microscopy images supporting the effect of interdiffusion on the layer structure of 50/50 films is shown in Figure 3.6 (a-e). PMMA is the dark phase and possesses a lower tensile modulus of ~3.1 GPa, and the light phase is SAN17, with a higher tensile modulus of ~3.2 GPa.\(^{27-28}\) As expected at 17 layers, the interface between PMMA and SAN17 is sharp and distinct, with little mutual diffusion having occurred. As the layer number increases to 129, and then 257, layers can still be distinguished. However, the interface becomes progressively unclear, and the contrast between the light and dark phases decreases. Layers are no longer seen in the 1025L films, but rather a homogeneous blend of the two polymers, similar to the melt blend. Films with 513 layers also exhibited the appearance of a blend (Figure 3.S2a). The 129-layer films produced at reduced pump rates exhibited the same trend as those produced with varying layer numbers, Figure 3.7 (a-b). With increasing contact time, the layer interfaces were seen to become more and more diffuse, while the contrast between light and dark phases decreased.

In order to better understand why the refractive index changes in such a way with increasing contact time, the amount of interdiffusion between the layers must be determined more quantitatively. This was done using oxygen permeability to probe for the interdiffusion between PMMA and SAN17, as PMMA and SAN17 possess dissimilar oxygen permeability values. A model previously developed\(^ {18}\) to relate the permeability of layered nylon and EVOH films and the amount of diffusion at the interfaces was applied to the current system. Composition profiles from the model were then used to give insight into the layer structure.
3.3.3 Oxygen Permeability

Figure 3.8 presents the effect of layer number (30 rpm) on oxygen permeability data of the coextruded PMMA/SAN17 films, plotted against a series model and a miscible blend model. SAN17 control films possess a P(O₂) of 0.90 barrer, and PMMA control films have a P(O₂) of 0.07 barrer. These values are reasonable according to literature values for PMMA and SAN polymers. If the layers are discrete, the permeability of the films can be predicted by a series model, described by the following:

\[
P_{film} = \left[ \frac{\phi_{PMMA}}{P_{PMMA}} + \frac{\phi_{SAN17}}{P_{SAN17}} \right]^{-1}
\]  

(3.5)

\(P\) is oxygen permeability and \(\phi\) is the volume composition. If the layers have fully diffused into one another, the permeability of the films can be predicted by a miscible blend model, expressed as:

\[
\ln P_{film} = \phi_{PMMA} \ln P_{PMMA} + \phi_{SAN17} \ln P_{SAN17}
\]  

(3.6)

At 17 layers, oxygen permeability follows that of a series model, possibly indicating that there is either little interdiffusion between the 2 materials, or the amount of interphase is so small in relation to the layer thickness that it cannot be detected. At the highest number of layers, 1025 layers, the layers are completely diffused together, and the permeability of these films follows the miscible blend model. Films with an intermediate number of layers, 129 and 257, fall between the two models, indicating an intermediate state of interdiffusion between the two polymers.

With low contact time during extrusion, the layers remain discrete. As the contact time during extrusion increases, the interdiffusion between the two miscible polymers,
PMMA and SAN17, increases. Eventually, the two polymers become fully diffused into one another, like a blend. A model based on the contact time during the multilayer process and the oxygen permeability can be used to predict the observed permeability trend, and to determine the mutual diffusion coefficient of these two polymers.

### 3.3.4 Modeling the Oxygen Permeability of the PMMA/SAN17 Layered Films

A model developed to successfully describe the interdiffusion of nylon and poly(ethylene-co-vinyl alcohol) multilayer film was applied to the present system. To analyze the interdiffusion process, an interdiffusion element was defined as one-half of a PMMA layer together with one-half of the adjacent SAN17 layer and the interface. Only one-half of each layer was required due to the symmetry of the multilayered structure. Uniformity of the layers ensured that the interdiffusion element was representative of the entire multilayered structure, and the large number of layers allowed end effects to be neglected. The mutual diffusion coefficient, \( D \), was assumed to be constant and independent of composition, and the position of the interface between the diffusing species was assumed to be fixed.

The composition of the layers as a result of interdiffusion can be obtained from Fick’s equation for a non-steady state diffusion, accounting for the initial condition of a sharp interface with complete separation of the components, and zero composition gradients at both the boundaries of the interdiffusion element:

\[
W_{\text{SAN17}}(x,t) = \frac{L_{\text{SAN17}}}{L_{\text{PMMA}} + L_{\text{SAN17}}} + \sum_{m=1}^{\infty} \frac{2}{m\pi} \sin \left( \frac{m\pi x}{L_{\text{PMMA}} + L_{\text{SAN17}}} \right) \cos \left( \frac{2m\pi x}{L_{\text{PMMA}} + L_{\text{SAN17}}} \right) \exp \left( -\frac{4\pi^2 m^2 D t}{(L_{\text{PMMA}} + L_{\text{SAN17}})^2} \right) \tag{3.7}
\]

\( W(x,t) \) is the weight percent composition at position \( x \) and diffusion time \( t \), \( L \) is the layer thickness.
Figure 3.9 shows a weight composition profile of films with nominal 50/50 composition films with varying contact times due to multiplier number. As diffusion will take place within the multiplier dies during the coextrusion process, layer thicknesses for the model were calculated based on the multiplier dimensions, and not on the final film thickness. Diffusion time, \( t \), was calculated from equation 3.1, using the number of multipliers, \( n \), the volume of each co-extrusion system component, \( V \), and the pump rate - an arbitrary value at this point. An accuracy of 0.001\% was achieved with \( m = 15 \).

With increasing contact time, the two materials diffuse together at the interface, creating a gradient in the actual composition of the layers. As expected, the composition profile shows the layers progress from almost discrete layers at 17 layers, to a smooth gradient at intermediate layer numbers, and a homogeneous 50/50 blend at 1025 layers. This weight composition profile was then converted to a permeability profile, using the permeability equation for miscible blends:

\[
\ln P(x,t) = \phi_{PMMA}(x,t)\ln P_{PMMA} + (1 - \phi_{PMMA}(x,t))\ln P_{SAN17} \tag{3.8}
\]

where \( \phi_{PMMA} \) is the volume fraction of PMMA and \( P_{PMMA} \) and \( P_{SAN17} \) is the permeability of pure PMMA and SAN17, respectively. Figure 3.10 shows permeability profiles that were calculated from the corresponding composition profiles in Figure 3.9.

Subsequently, the permeability profile was sliced into \( q \) equal parts, and the total permeability of the interdiffusion element was calculated from the series model,

\[
\frac{1}{P_{\text{calculated}}} = \sum_{1}^{q} \frac{1}{P(x,t)} \tag{3.9}
\]

An error less than 2\% was achieved with \( q = 41 \). \( D \) was varied to match the calculated permeability of the interdiffusion element and the measured film permeability. Given
that the measured and calculated permeability from the interdiffusion model for PMMA/SAN17 match well, an accurate determination of the mutual diffusion coefficient, $D$, can be determined. The best fit data was determined such that the deviation in the model permeability calculation was within the experimental error of the measurement in intermediate layer numbers, 129 and 257. Comparison of the measured film permeability with the calculated permeability obtained using the best fit of $D$ for all the number of layers is shown in Figure 3.11. The best fit $D$ found was $7.0 \times 10^{-13}$ m$^2$/sec, and this value was applied to the 129-layer films produced at lower pump rates.

When contact time was increased through pump rate variation, the permeability increases with decreasing pump rate, which increases the contact time, Figure 3.12 displays the oxygen permeability of 129L PMMA/SAN17 films produced at different pump rates as a function of PMMA composition. The permeability is not as high using this method as films with varying layer number at similar contact times, however. This is because increasing the number of layers also increases the number of interfaces where mutual diffusion can occur. The model was again applied, using the previous $D$ value, $7.0 \times 10^{-13}$ m$^2$/sec, for various layer number films produced at 30 rpm. The model, shown as dotted lines, is also compared to the measured O$_2$ permeability as a function of PMMA composition in Figure 3.12, with very good agreement.

The magnitude of $D$ is reasonable when compared to values of the mutual diffusion coefficient reported for similar miscible polymer pairs. For example, $D$ for PMMA and SAN29 at 120°C is on the order of $10^{-16}$ m$^2$/sec.$^{14}$ Polymer molecular weights can affect the mutual diffusion coefficient between two materials; interdiffusion increasing with lower molecular weight. In this model, molecular weight was not
considered. However, effects of molecular weight on the interdiffusion can be detected through the measured film permeability.

**3.3.5 Relating Atomic Force Microscopy to the Model**

Figure 3.13 shows the calculated composition profiles, using $D$ of $7.0 \times 10^{-13}$ m$^2$/sec, compared to the AFM phase profiles that represent the difference in moduli across the layers. As PMMA has a lower modulus than SAN17, the phase profile minima represent PMMA-rich material, and maxima represent SAN17-rich material. The composition profiles were very similar in shape to the AFM profiles scanned from AFM images collected. The number of maxima and minima may differ in some samples due to the angle of the AFM images. At 17 layers, the profile shows a very sharp transition between the PMMA and the SAN layers, with plateaus at the minima and maxima equal to each layer thickness. As the number of layers increases to 129 and 257, the transition slope becomes less steep, and the amplitudes decrease. At these layer numbers, there are no plateaus in modulus like before. The layers are thinner in these films, and more mutual diffusion has occurred to create a gradient within the layers. Finally, with 1025 layers, all that is detected is noise, very similar to the profile of the melt blend. A comparison for the 50/50 513L film is shown in Figure 3.52 (b-c). Though the AFM phase image appears to be a homogeneous blend, and the signal is noisy, the modulus profile shows that there are still larger amplitude differences than the 1025L films, which was expected.

Variable pump rate 50/50 129L film AFM phase profiles are compared to their calculated composition profiles in Figure 3.14 (a-b), showing the same trend. The AFM phase profiles showed a gradual change from higher amplitude differences to smaller amplitudes as contact time increased, and the transition between minima and maxima
became less and less steep, which match well with the calculated composition profiles. These composition profiles were then used to better understand why layers thicker than the $\lambda/4$ thickness are behaving as layers with thicknesses below the $\lambda/4$, with a single additive refractive index.

### 3.3.6 Relating Structure to Optical Properties

As the refractive index is measured using only the outer 3 layers of each film (the outermost being only half that of the others), the outer three layers of the 50/50 calculated composition profiles were then plotted against bars the width of the maximum layer thickness to exhibit a single additive refractive index, Figures 3.15 and 3.16. For 50/50, the maximum layer thickness is 65 nm to give transparent, additive refractive index films. The shaded areas of 65 nm are shown in each composition profile. Layers with greater than 65 nm thick sections of greater than or equal to 99% pure PMMA or SAN17, such as those of 17 and 129 layers produced at 30 rpm, resulted in refractive indices that deviate from the additive value. Layers with less than 65 nm thick sections of greater than or equal to 99% pure PMMA or SAN17, however, result in refractive indices that followed the additive line. These films were the ones with 257 or greater number of layers, and those with 129 layers produced at lower pump rates.
3.4 Conclusions

The interdiffusion of two materials used to fabricate polymeric GRIN lenses was followed by studying multilayer films of coextruded alternating PMMA and SAN17, with increasing number of layers and decreasing pump rate. The model applied successfully described the interdiffusion of PMMA and SAN17 produced with these various contact times, and a reasonable mutual diffusion coefficient was determined. AFM confirmed the modeled profiles were in good agreement with actual composition at each number of layers, and optical properties were investigated. Though the optical clarity of these films was not affected by the interdiffusion state due to the miscibility of PMMA and SAN17, the refractive index was greatly influenced. Multiple refractive indices were detected by the prism coupler in films of 17 and 129 layers. 257L, 1025L, and melt blends showed single refractive indices that followed the additive line. Comparison of 50/50 composition films at all layer numbers and pump rates showed that though the maximum layer thickness to produce a single additive refractive index is 65 nm for PMMA and SAN17, nominal layers of 190 nm at 30 rpm pump rate and nominal layers of 375 nm at 20 and 10 rpm rates show an additive refractive index. These samples display such behavior because they have ≤ 65 nm thick sections of ≥ 99% pure material. Interdiffusion essentially decreases the effective layer thickness, and allows for optical behavior equal to layer thicknesses below the quarter-wavelength, although layers are much thicker nominally.

The finding that it only requires a reduction of a material to 99% purity within the calculated maximum quarter-wavelength value to achieve single additive refractive indices within polymer layers is very useful for optics. This effect of interdiffusion can
help to optimize the fabrication process of polymeric gradient refractive index lenses. It can also be exploited in future designs of gradient refractive index optics to create novel structures and distributions.

The determined mutual diffusion coefficient of these polymers at temperatures during the lens-making process may be extrapolated from $D$ at the coextrusion temperature. This will allow for future studies of the interdiffusion at the interfaces between sections of differing compositions in the lens, and give a better understanding of its effect on the resulting lens refractive index distribution and lens performance.
3.5 References


Table 3.1: Polymer material characteristics

<table>
<thead>
<tr>
<th>Material</th>
<th>Grade</th>
<th>Refractive Index (633 nm)</th>
<th>Processing Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(methylmethacrylate)</td>
<td>Plexiglas V920</td>
<td>1.489</td>
<td>255</td>
</tr>
<tr>
<td>Poly(styrene-co-acrylonitrile)</td>
<td>Lustran Sparkle</td>
<td>1.573</td>
<td>255</td>
</tr>
</tbody>
</table>
Table 3.2: Layered sample characteristics

<table>
<thead>
<tr>
<th>Number of layers</th>
<th>Total Pump Rate (rpm)</th>
<th>PMMA/SAN17 Composition (v/v)</th>
<th>Contact Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>30</td>
<td>90/10, 80/20…20/80, 10/90</td>
<td>105</td>
</tr>
<tr>
<td>33</td>
<td>30</td>
<td>50/50</td>
<td>120</td>
</tr>
<tr>
<td>65</td>
<td>30</td>
<td>50/50</td>
<td>140</td>
</tr>
<tr>
<td>129</td>
<td>10</td>
<td>90/10, 80/20…20/80, 10/90</td>
<td>475</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>90/10, 80/20…20/80, 10/90</td>
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<td>257</td>
<td>30</td>
<td>90/10, 80/20…20/80, 10/90</td>
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<tr>
<td>513</td>
<td>30</td>
<td>50/50</td>
<td>195</td>
</tr>
<tr>
<td>1025</td>
<td>30</td>
<td>100/0, 90/10, 80/20…20/80, 10/90, 0/100</td>
<td>215</td>
</tr>
<tr>
<td>Melt Blends</td>
<td>30</td>
<td>90/10, 80/20…20/80, 10/90</td>
<td>-</td>
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Figure 3.1 (a-d): Transmission of 50/50 PMMA/SAN17 films: a) Representative transmission spectra of 17L, 33L, and 65L films, b) Representative spectra of 129L and 257L films, c) Representative spectra of 513L, 1025L, and blend films, d) Transmission at 633 nm as a function of layer thickness.
Figure 3.2: Raw refractive index curves of 50/50 PMMA/SAN17 and control films produced with a 30 rpm total pump rate.
Figure 3.3 (a-d): Change in refractive index of PMMA/SAN17 films produced with a 30 rpm total pump rate with composition at a) 17L, b) 129L, c) 257L, and d) 1025L and melt blends.
Figure 3.4 (a-b): Change in refractive index of 129L films with composition produced at a) 30 rpm, b) 10 rpm.
Figure 3.5: Change in refractive index of PMMA/SAN17 50/50 composition films as a function of nominal layer thickness. Shaded area indicates layer thickness below the quarter-wavelength of visible light.
Figure 3.6: 50/50 PMMA/SAN17 atomic force microscopy images, 30 rpm: a) 17L, b) 129L, c) 257L, d) 1025L, e) melt blend.
Figure 3.7: 50/50 129L PMMA/SAN17 atomic force microscopy images: a) 30 rpm, b) 10 rpm.
Figure 3.8: Oxygen permeability of PMMA/SAN17 films with different layer numbers as a function of PMMA composition, 30 rpm.
Figure 3.9: Weight composition profile of nominal 50/50 composition PMMA/SAN17 films with different contact times.
Figure 3.10: Permeability composition profile of nominal 50/50 composition PMMA/SAN17 films with different contact times.
Figure 3.11: Model $O_2$ permeability compared to measured $O_2$ permeability of PMMA/SAN17 films with different layer numbers, 30 rpm, as a function of PMMA composition, $D = 7.0 \times 10^{-13}$ m$^2$/s.
Figure 3.12: Oxygen permeability of 129L PMMA/SAN17 films with different pump rates as a function of PMMA composition, compared to the model $O_2$ permeability, $D = 7.0 \times 10^{-13}$ m$^2$/s.
Figure 3.13: 50/50 PMMA/SAN17 (30 rpm) AFM phase profiles compared to calculated composition profiles, $D = 7.0 \times 10^{-13}$ m$^2$/s: a) 17L, b) 129L, c) 257L, d) 1025L, e) melt blend.
Figure 3.14: 50/50 129L PMMA/SAN17 atomic force microscopy phase profiles compared to calculated composition profiles, $D = 7.0 \times 10^{-13} \text{ m}^2/\text{s}$: a) 30 rpm, b) 10 rpm.
Figure 3.15: Composition profiles of 50/50 PMMA/SAN17 film outer 3 layers used to measure refractive index (30 rpm): a) 17L, b) 129L, c) 257L, d) 1025L. Shaded areas are 65 nm wide, equal to the maximum layer thickness below the quarter-wavelength of a 50/50 composition film.
Figure 3.16: Composition profiles of 129L 50/50 PMMA/SAN17 outer 3 layers used to measure refractive index: a) 30 rpm, b) 10 rpm.
Figure 3.S1. Transmission of 50/50 PMMA/SAN17 films, 30 rpm: a) Representative transmission spectra, b) Transmission at 633 nm as a function of layer thickness.
Figure 3.82 (a-c). 50/50 513 PMMA/SAN17, 30 rpm: a) atomic force microscopy images and b) phase profile, compared to c) calculated composition profile, $D = 7.0 \times 10^{-13}$ m$^2$/s.
APPENDIX
APPENDIX A

Soft, Mechanically Deformable GRIN Lenses

A.1 Introduction

There is a need for lighter, simpler, and more compact optical devices. Polymeric gradient refractive index (GRIN) materials have reduced weight and volumes compared to inorganic lenses, and possess enhanced focusing power and superior aberration correction as compared to traditional monolithic lenses with a single refractive index. Zoom capability, however, is a desirable feature of optical devices that often requires extra weight and volume and added complexity to optical devices. Typical zoom lens systems need complex lens groups to move back and forth to adjust the image size. Polymeric variable GRIN lenses which alter their shape or index distribution to produce focal length changes without translational movement can be very beneficial.

Composite, variable focal length lenses composed of a combination of hard polymeric GRIN lens and a silicon shell were developed previously. Composite, variable focal length lenses were constructed using a combination of deformable and rigid polymeric materials. These all-polymer tunable lenses, in which pressure applied to a membrane containing a compliant cross-linked polymer gel caused symmetric shape changes to the outer surface, were able to change the focal length of the lens by a factor of 1.9 by compressing the reservoir only 1.3 mm.¹

The purpose of this study was to expand the nanolayered polymeric GRIN materials to include soft deformable materials for future use in variable focus systems. These materials would have several advantages over the previous system. A single lens would
reduce volume and weight, and a gradient refractive index distribution would improve focusing power and correct for spherical aberration.

A.2 Experimental

For this study, films with 129 to 4097 alternating layers with 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, and 0/100 (vol./vol.) compositions were produced through a continuous coextrusion process using an ATBTA feedblock, with no third tie (T) material. The polymer melts were extruded through separate single screw extruders, and combined in the ATBTA feedblock. The ABA trilayer (with A layers half the thickness of B) was then sent through a series of multiplication dies, which cut, spread, and stack the melt, doubling the number of layers each time. Table A.1 summarizes the optical and mechanical properties of the polymer pairs used in these coextrusion trials. Tensile values were either obtained from technical data sheets or obtained experimentally.

Table A.1

The stress–strain behavior in uniaxial tension was measured with ASTM D1708 microtensile specimens cut from compression molded control sheets. Specimens were stretched in an MTS (Eden Prairie, MN) Alliance RT30 mechanical testing machine at a strain rate of 100% min\(^{-1}\) at room temperature. Engineering stress and strain were defined conventionally.

The polymer pairs were processed where a viscosity match was found at temperatures within 10 °C of one another. The multipliers were set at an average temperature between the two temperatures when an offset was needed. Polypropylene, polyoxymethylene, or low density polyethylene (LDPE) were used as a protective skin layer, and were peeled off before all testing and post-processing for lens fabrication. A
total pump rate of 30 rpm was used to produce films of all layer numbers. The target overall film thickness for these films was 20-50 μm, to maintain layer thicknesses below the quarter-wavelength of visible light. Actual overall film thicknesses ranged from 10-70 μm. Films were stored at room temperature, and skin layers were removed before all testing or post-processing. Table A.2 summarizes the films produced, and reports the success of each system attempted. Systems 1-4 and 6 were unsuccessful at producing either good films or sheets for lens fabrication, and this work will only discuss the trials of system 4, and the successful systems 5 and 7.

Refractive index was measured in three different spots along the films with a Metricon Model 2010, which utilizes a prism coupling technique. A free-standing film was held to a prism of known refractive index under pressure, through which a laser light is shone. This setup is then rotated and the refractive index was determined as the drop in reflected laser light intensity detected due to the tunneling of laser light into the film at the critical angle. This critical angle is used by the Metricon to calculate the refractive index of the film, using Snell’s Law:

$$n_{\text{prism}} \sin \theta_{\text{prism}} = n_{\text{film}} \sin \theta_{\text{film}} \quad (A.1)$$

where $n$ is the refractive index and $\theta$ is the angle, where $n_{\text{prism}}$, $\theta_{\text{prism}}$, and $\theta_{\text{film}}$ are known.

Transmission measurements of free-standing films ($n = 3$) were collected on an Ocean Optics spectrometer, SD 2000 fiber optic spectrometer and OOI Base 32 software. Transmission within the visible range, at 633 nm to match the laser wavelength of the Metricon prism coupler, was recorded.

Films were stacked with a linear refractive index distribution from 100/0 to 50/50 or 0/100 samples into a 6 mm stack. A Carver hydraulic compression molder was used to
compression mold these stacks into 4 mm sheets, using temperatures at which the materials possessed a similar viscoelastic strength for uniform flow/deformation. These temperatures were determined through dynamic mechanical analysis of the extruded films, using a TA Instruments DMA Q800. Samples were cut along the film extrusion direction, into 30 mm x 8.5 mm rectangles, loading only 13 mm of the length between the clamps. Temperature was ramped at 3 °C/min, at a frequency of 1 Hz, and a displacement of 10 μm (~0.08% strain).

Stacks were placed in the press with minimal pressure (contact between platens and press platens) and preheated for 1 min. Pressure was slowly increased at 2,500 psi intervals to a maximum of 20,000 psi, waiting for pressure to hold steady at each pressure step. The stack was then held at maximum pressure for 1 min before cooling with water. The average total time for this procedure was 4.5 minutes.

Lenses were shaped using 2 different spherical mold designs. Mold #1 had equal male and female molds with radius of 13.6 mm and Mold #2 had a male radius of 18.1 mm and female radius of 20.7 mm. Circles slightly smaller than the largest radius of the molds were cut from defect-free sections of the GRIN sheets. These circles were then placed between the molds with the high refractive index side against the male mold, inside a spacer to form lenses of final thickness 2.7 mm. The setup was placed inside the press set at temperatures used to form sheets and preheated for 20 min before slow application of low pressure, ~500 psi, over a 5 min period. The shaped lens was then water cooled under pressure to room temperature. The lens was then fixed to a holder and polished.
Figure A.1 shows how deformation was achieved through a compressive stress applied by surface contact with rigid rings, used previously on silicone shells.\(^1\) Controlled squeezing of the rings together was achieved through 2 threaded metal holders. This displaces the soft lens and results in a shape change of the outer surface, leading to a reduction of its average radius of curvature and its focal length. Two generations of this lens tuning device were used in this work. The 2\(^{nd}\) generation tuning device included markings to determine quantitative distances of tuning, and a window for future installation of a stress sensor. A placido-cone topographer was used to measure the radius of curvature using the top 0.35 - 0.7 mm of the lens, and the data was extracted and plotted.

A two-pin-hole measurement, illustrated in Figure A.2, was constructed to measure the dynamic back focal length of the deformable lenses. A collimated HeNe laser beam with wavelength of 633 nm, is separated via a two pin-hole aperture card at a known separation, \(d_1\). These two parallel beams pass through the plano side of the tunable lens, bending at the lens focal length, and ultimately terminate on a screen at a distance, \(L\), from the back surface of the optic. The focal length of the optic can be determined by a geometric interpretation of the spacing of the two HeNe pinhole lasers as viewed on the imaging screen \(d_2\), the initial distance between the two pinhole laser beams \(d_1\), and the length between the back of the lens and the screen \(L\), according to:

\[
F = \frac{d_1 \cdot L}{(d_1+d_2)} \tag{A.2}
\]
A.3 Results and Discussion

A.3.1 Part A: Lens Fabrication

Deformable nanolayered materials have previously been coextruded with variable visible spectrum reflections based on reversible tensile deformation. The goal of this work is to, for the first time, reduce the soft, deformable material individual layer thicknesses below 50 nm resulting in transparent materials which can potentially be utilized to create GRIN optics. When the layers are this thin, the material behaves as an effective medium. The films will be transparent and the refractive index can be varied smoothly between those of the constituent materials by controlling the relative thickness of the layers.

System #4: PU/Bynel

An ethylene-vinyl acetate copolymer, Bynel 3860, and polyurethane, Pellethane 2355-95AE showed promise as a soft, deformable nanolayered system for variable focal length GRIN lenses. These materials possessed high clarity, a $\Delta n$ of 0.062, and low moduli, Table A.1. PU/Bynel films with 1025 layers were successfully coextruded in several different compositions. Films extruded without protective skin layers possessed low transparency, ~40%, which was greatly improved to 50-75% when a sacrificial polypropylene (PP) skin layer was added, Figure A.3a.

“Sheets” of each composition were made by stacking four films and compression molding at 70°C for 3 minutes under pressure as a simulation of the subsequent steps to forming lenses. This process improved film transparency even further by another 5-30%, Figure A.3b. As-extruded 1025-layer PU/Bynel films also showed promising
composition-dependent refractive indices (Figure A.4a) that followed the additive equation:\(^8\)

\[ n_{\text{film}} = n_1 \Phi_1 + n_2 \Phi_2 \quad (A.3) \]

When these films were pressed down to improve their transparency, however, it was found that layers did not deform uniformly, and caused the refractive index to change, Figure A.4b. Therefore, no further materials development was continued with this system.

System #5: Carbothane/Pellethane

Pellethane 2363-55DE (polytetramethylene ether-glycol based polyurethane) and Carbothane PC-3595A (polycarbonate-based polyurethane) were the next system selected to build soft, deformable GRIN lenses. These two materials had a similar \( \Delta n \), 0.063, to the previous system, possessed high transparency, low moduli, and were very well matched in viscosity for co-extrusion. As previous successful systems used miscible polymers, the miscibility of Pellethane 55DE and Carbothane 95A were scouted first through melt blends. Melt blends of Carbothane/Pellethane compositions 25/75, 50/50, and 75/25 were produced using a mini twin screw extruder (\( T = 210 \degree C \), screw speed of 25 rpm, 4 min cycle time). These blends maintained high transmission and their refractive indices were composition-dependent, Figure A.5 (a-b).

A coextrusion run to produce 4097L Carbothane/Pellethane films in 10% composition steps successfully produced good quality 50-micron films with polyethylene (PE) skin layers. All films produced were highly transparent and had composition-dependent refractive indices, Figure A.6 (a-b). Linear distribution GRIN stacks of 6 mm
thick were made using the 11 compositions produced, and compression molded into 4 mm sheets.

Temperatures for pressing were determined using dynamic mechanical analysis, choosing temperatures where the two polymers possessed similar storage and loss moduli, Figure A.7 (a-b). The best conditions for Carbothane/Pellethane sheets were pressing at 90°C on the Carbothane side and 170°C on the Pellethane side for 4 minutes under pressure in a hydraulic press. The resulting 4 mm sheets were soft, deformable, and were ~60% transparent, Figure A.8 (a-b). Figure A.8c shows the GRIN lens shaped from these GRIN sheets, with thickness of 2.7 mm, and a radius of curvature of 13.6 mm. The lens was then polished and characterized.

Image quality of the Carbothane/Pellethane lens showed low contrast, ~23%, but the images were discernable. This was the first time an image was taken from a soft deformable lens, Figure A.9. The lens curvature change was then investigated with compressive stress, discussed in the following section. Due to the harder nature of Pellethane, and its UV sensitivity that causes yellowing, System #7: Carbothane/Texin was investigated.

System #7: Carbothane/Texin

Polyether-based polyurethane Texin RXT90A has higher transparency and a lower modulus than the Pellethane 2355-95AE polymer, Table A.1. Preliminary melt blend experiments were again conducted, blending at 210 °C, a screw speed of 25 rpm, and 4 min cycling time. The blends were pressed into films and additive refractive index and high transmission were confirmed before coextrusion (not shown).
Eleven compositions of Carbothane and Texin were successfully coextruded into 4097-layered films with a protective skin layer of LDPE. Figure A.10 shows the high transmission and composition-dependent refractive indices of the extruded films. As before, 6 mm stacks with a linear refractive index distribution were produced using the 11 compositions, and compression molded into a 4 mm sheet, using temperatures where the two polymers possessed similar storage and loss moduli, Figure A.11.

Carbothane/Texin sheets were pressed at 100°C on the Carbothane side and 140°C on the Texin side for 4 minutes under pressure in a hydraulic press. The resulting 4 mm sheets were considerably softer and more easily deformed than the previous system, and had transmission values of ~70-75% for Carbothane/Texin, significantly higher than that of the previous system, Figure A.12 (a-b). These sheets were subsequently formed into lenses with a thickness of 2.7 mm and a radius of curvature of 20.9 mm, Figure A.12c. This lens mold allowed for more uniform flow of the layers than Mold #2. The curvature change with compressive stress was then studied, as with the Carbothane/Pellethane system. Due to the water sensitivity of Texin, this lens could not be polished with current polishing techniques for image quality evaluation.

A.3.2 Part B: Deformation Behavior/Equipment-Test Set-up (courtesy of Kezhen Yin)

Carbothane/Pellethane and Carbothane/Texin both exhibited encouraging characteristics as soft lens materials. They both made excellent quality elastomeric films and were able to be post-processed into lenses that were more transparent than any other polymer combinations attempted up to this point. In order to determine the feasibility of using these materials as variable focus lenses, these lenses were deformed and the resultant shape changes and optical properties were evaluated.
System #5: Carbothane/Pellethane

The curvatures of the Carbothane control and Carbothane/Pellethane GRIN lenses were tuned using the 1st generation tuning device. The radius of curvature of the Carbothane control and Carbothane/Pellethane GRIN lenses decreased 17% and 23% with compressive stress, respectively. The shape profiles extracted from the placido-cone images of the lenses with applied stress are shown in Figure A.13 (a-b). These showed that the lenses initially possessed a circular shape and squeezing caused the lens outer surface to form a parabola. Unfortunately, the focal length measurement setup was not available at this time to test this GRIN lens.

System #5: Carbothane/Texin

Tuning device #2 was used to adjust the radius of curvature of Carbothane/Texin GRIN lenses. The curvature of this lens was found to decrease 19% with the new lens design of wider radius. The parabolic shape profiles of the Carbothane/Texin GRIN lens with compressive stress are shown in Figure A.14. The focal length change vs. squeezing distance was then measured using a two pin-hole process, Figure A.15. Focal length was found to decrease from 36.3 to 33.0 mm when compressed 0.5 mm in the thickness direction.

A.4 Conclusions

Several different polymer pairs were investigated for the fabrication of soft, deformable lenses with variable focus ability. Carbothane/Pellethane and Carbothane/Texin both exhibited encouraging characteristics as soft lens materials. They both made excellent quality elastomeric films and were able to be post-processed into lenses that were more transparent than any other polymer combinations attempted up to
this point. In order to determine the feasibility of using these materials as variable focus lenses, these lenses were deformed and the resultant shape changes and optical properties were evaluated.

Image quality of the Carbothane/Pellethane lens showed low contrast, ~23%, but the images were discernable. This was the first time an image was taken from a soft, deformable lens. The lens curvature was found to decrease 23% with compressive stress. Due to the harder nature of Pellethane, the lower transparency of 60%, and its UV sensitivity that causes yellowing, however, no further work was conducted on this system.

Higher transparency, 75%, and softer GRIN sheets were able to be formed from Carbothane/Texin. The GRIN lenses fabricated from these materials were able to deform and change their radius of curvature by 19%. A compression of 0.5 mm in the thickness direction resulted in a focal length decrease from 36.3 to 33.0 mm. The image quality of these GRIN lenses could not be evaluated, however, as Texin is a water-sensitive polymer that could not be polished using the current polishing techniques.

Although these are important breakthroughs, transmission of 75% is still not high enough for optical devices. In order to increase the transparency of the lenses, the polymers have been coextruded as blends, as this has been successful in eliminating certain processes that cause scattering in the hard GRIN materials systems (unpublished). The blends also have high transmission, 90%, and composition-dependent refractive indices, Figure A.16. The small deviation of the refractive indices towards the lower index most likely arises from uneven feeding of the Carbothane and Texin pellets during extrusion, as Carbothane pellets are much smaller. This can easily be avoided by re-
pelletizing the pellets to similar sizes. Future efforts will include fabrication of lenses from these materials and characterization of their optical and mechanical properties.

Other future considerations include installation of a force sensor to quantify the force applied on the lenses. As these lenses are tuned through a compressive stress only on the outer edges of the lens, the stress is uneven through the material. This stress distribution could be studied and modeled in the future for better understanding of the materials used to improve the lens design or deformation method.

A.5 References


Table A.1: Soft materials for nanolayer coextrusion.

<table>
<thead>
<tr>
<th>System</th>
<th>System</th>
<th>Polymer</th>
<th>Refractive Index (@ 633 nm)</th>
<th>Transparency (@ 633 nm)</th>
<th>Tensile Stress (MPa)</th>
</tr>
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<tr>
<td>System #1</td>
<td>Polyester</td>
<td>Pellethane 2355-95AE</td>
<td>1.552</td>
<td>N/A</td>
<td>8.27 MPa at 50%</td>
</tr>
<tr>
<td>Δn = 0.062</td>
<td>polyadipate-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>based PU</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>System #2</td>
<td>EO</td>
<td>Engage 8200</td>
<td>1.510</td>
<td>N/A</td>
<td>6.90 MPa at 1030%*</td>
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<td>Δn = 0.120</td>
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<tr>
<td></td>
<td>THV</td>
<td>Dyneon THV 221GZ</td>
<td>1.390</td>
<td>(90 ± 2)</td>
<td>20 MPa at 600%*</td>
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<td>System #3</td>
<td>EMAC</td>
<td>Westlake EMAC SP2205</td>
<td>1.508</td>
<td>N/A</td>
<td>12 MPa at 800%*</td>
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<td>Δn = 0.118</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>THV</td>
<td>Dyneon THV 221GZ</td>
<td>1.390</td>
<td>(90 ± 2)</td>
<td>20 MPa at 600%*</td>
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<td>System #4</td>
<td>Polyester</td>
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<td>(78 ± 2)</td>
<td>8.27 MPa at 50%</td>
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<tr>
<td>Δn = 0.062</td>
<td>polyadipate-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>based PU</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>System #5</td>
<td>polycarbonate</td>
<td>Carbothane PC-3595A</td>
<td>1.496</td>
<td>(90 ± 3)</td>
<td>6.89 MPa at 100%</td>
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<tr>
<td>Δn = 0.063</td>
<td>-based PU</td>
<td></td>
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<tr>
<td></td>
<td>ether-based PU</td>
<td>Pellethane 2363-55DE</td>
<td>1.557</td>
<td>(86 ± 5)</td>
<td>15.9 MPa at 100%</td>
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<td>System #6</td>
<td>polycarbonate</td>
<td>Carbothane PC-3595A</td>
<td>1.496</td>
<td>(90 ± 3)</td>
<td>6.89 MPa at 100%</td>
</tr>
<tr>
<td>Δn = 0.020</td>
<td>-based PU</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polyester-based</td>
<td>Elastollan 70A</td>
<td>1.516</td>
<td>(90 ± 2)</td>
<td>4.37 MPa at 100%</td>
</tr>
<tr>
<td>System #7</td>
<td>polycarbonate</td>
<td>Carbothane PC-3595A</td>
<td>1.496</td>
<td>(90 ± 3)</td>
<td>6.89 MPa at 100%</td>
</tr>
<tr>
<td>Δn = 0.045</td>
<td>-based PU</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Polyester-based</td>
<td>Texin RXT 90A</td>
<td>1.541</td>
<td>(91 ± 1)</td>
<td>11.4 MPa at 100%</td>
</tr>
</tbody>
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* Values taken from technical data sheets
### Table A.2: Soft nanolayered samples summary

<table>
<thead>
<tr>
<th>System</th>
<th>Polymer</th>
<th>Processing Temperature (°C)</th>
<th>Number of Layers</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>System #1&lt;br&gt;Δn = 0.062</td>
<td>Pellethane 2355-95AE&lt;br&gt;Pebax 2533</td>
<td>205&lt;br&gt;205</td>
<td>129, 257</td>
<td>129L were reflective, 257L layers broke up</td>
</tr>
<tr>
<td>System #2&lt;br&gt;Δn = 0.120</td>
<td>Engage 8200&lt;br&gt;Dyneon THV 221GZ</td>
<td>225&lt;br&gt;225</td>
<td>513</td>
<td>Layers delaminated with post-processing</td>
</tr>
<tr>
<td>System #3&lt;br&gt;Δn = 0.118</td>
<td>Westlake EMAC SP2205&lt;br&gt;Dyneon THV 221GZ</td>
<td>230&lt;br&gt;230</td>
<td>1025</td>
<td>Reflective films, T = 20-40%</td>
</tr>
<tr>
<td>System #4&lt;br&gt;Δn = 0.062</td>
<td>Pellethane 2355-95AE&lt;br&gt;Dupont Bynel 3860</td>
<td>195&lt;br&gt;195</td>
<td>1025</td>
<td>T = 75-85% films; Layers did not deform uniformly; Opaque sheets</td>
</tr>
<tr>
<td>System #5&lt;br&gt;Δn = 0.063</td>
<td>Carbothane PC-3595A&lt;br&gt;Pellethane 2363-55DE</td>
<td>210&lt;br&gt;210</td>
<td>4097</td>
<td>Successful T = 90% films; T = 65-70% sheets</td>
</tr>
<tr>
<td>System #6&lt;br&gt;Δn = 0.020</td>
<td>Carbothane PC-3595A&lt;br&gt;Elastollan 70A</td>
<td>210&lt;br&gt;210</td>
<td>4097</td>
<td>T = 90% films; Iridescent sheets</td>
</tr>
<tr>
<td>System #7&lt;br&gt;Δn = 0.045</td>
<td>Carbothane PC-3595A&lt;br&gt;Txin RXT 90A</td>
<td>205&lt;br&gt;205-210</td>
<td>4097</td>
<td>Successful T = 90% films; T = 70-75% sheets</td>
</tr>
</tbody>
</table>
Figure A.1. Procedure for tuning of lens curvature and tuning apparatus.
Figure A.2. Illustration of 2-pinhole HeNe back focal length measurement testing set-up at CWRU to measure the shift in focal length as a function of compression for tunable homogenous and/or GRIN lenses.
Figure A.3. Improved transmission of extruded 1025L PU/Bynel films by a) extrusion with a removable polypropylene (PP) skin and b) thinning layers through compression molding of 4 film stacks.
Figure A.4. Change in PU/Bynel film refractive index with compression molding: a) as extruded and b) compression-molded.
Figure A.5 (a-b): Optical properties of Carbothane/Pellethane blend films as a function of Carbothane composition a) transmission at 633 nm and b) refractive index.
Figure A.6. Optical properties of 4097L Carbothane/Pellethane films: a) transmission; b) refractive index.
Figure A.7. Dynamic mechanical curves of Carbothane/Pellethane films: a) Storage and b) Loss.
Figure A.8. Deformable GRIN sheets and lenses produced with Carbothane/Pellethane compositions 100/0 to 50/50, $\Delta n = 0.03$: a) Pressed 3.8 mm GRIN sheet, 60% transmission; b) deformability of GRIN sheet; and c) shaped soft GRIN lens (image not to scale).
Figure A.9. Image quality of deformable GRIN lens produced with Carbothane/Pellethane compositions 100/0 to 50/50, $\Delta n = 0.03$, only 6 compositions with large 10% composition steps: a) 3-bar pattern and b) US Air Force pattern.
Figure A.10. Optical properties of 4097L Carbothane/Texin films: a) transmission; b) refractive index.
Figure A.11. Dynamic mechanical curves of Carbothane/Texin films: a) Storage and b) Loss.
Figure A.12. Deformable GRIN sheets and lenses produced with Carbothane/Texin compositions 100/0 to 0/100, $\Delta n = 0.045$: a) Pressed 4.1 mm GRIN sheet, $T = 70$-$75\%$; b) deformability of GRIN sheet; and c) lens pre-form (before polishing).
Figure A.13. Shape profiles of a) Carbothane control lens and b) Carbothane/Pellethane GRIN lens
Figure A.14. Shape change vs. squeezing of Carbothane/Texin GRIN lens
Figure A.15. Focal length change vs. squeezing of Carbothane/Texin GRIN lens
Figure A.16. Optical properties of compatibilized Carbothane/Texin films: a) transmission; b) refractive index.
APPENDIX B

Photopatternable Multilayer Films for Optical Data Storage

B.1 Introduction

A 1D polymeric photonic crystal can be produced by forced assembly of microlayered films using two optically transparent materials with different refractive indices.\textsuperscript{1-3} With the addition of a photo-reactive material within the layers, we can produce a 1D photonic crystal that can be modified after the coextrusion process. The selectively altered additive must produce a change in refractive index by undergoing a photochemical reaction or a relaxation as the material is exposed to high-energy ultraviolet light. Using photolithography techniques, a pattern with areas of differing reflectivity or color can be made (Figure B.1).

An initial study was done using cinnamic acid (CA), a well known chemical that undergoes a $2\pi + 2\pi$ cycloaddition photodimerization upon exposure to UV light, with a maximum decrease in refractive index of 0.01.\textsuperscript{4} In this study, a blend of 12 wt% cinnamic acid in poly(methylmethacrylate) (PMMA) was layered with a different grade of PMMA to produce a 1024 layer film. When exposed to UV light, the active layer of 12 wt% cinnamic acid gave a 0.006 decrease in refractive index. Monolithic PMMA/CA film, PMMA/PMMA multilayer film, and the multilayer film containing cinnamic acid were masked with a checkerboard photomask and exposed to UV light. The pattern could only be observed in the films that had both a multilayer structure and a photoreactive additive.

The purpose of this work was to fabricate an improved pattern-able 1D photonic crystal capable of a larger refractive index change within one of the layers. The larger refractive index change will allow for easier reading of the pattern; a less sensitive
method will be required to detect the differences within the film/medium. Two different approaches were used: 1) layers of a polymer negative photoresist, poly(vinyl cinnamate); and 2) orientation and selective relaxation of polyester layers.

**B.2 Experimental**

Poly(vinyl cinnamate) (PVCi), MW = 45,000-55,000 g/mol, was obtained from Sigma-Aldrich and polystyrene (PS) CX5238 was obtained from Entec Polymers. These materials were melt blended in PVCi/PS compositions of 50/50 and 25/75. PS Styron 685D was purchased from Dow Chemical, Plexiglas V826 polymethylmethacrylate (PMMA) was obtained from Arkema, and TEONEX TN8756C poly(naphthalate-co-terephthalate) (PEN-co-PET) was obtained from Teijin Kasei. These polymers were all used as received.

Multilayer films with 128 alternating layers and a 50/50 (vol./vol.) composition were produced through a continuous coextrusion process using an AB feedblock\footnote{ENREF_2 ENREF_21}. The polymer melts were extruded through separate single screw extruders, and combined in the AB feedblock. The AB bilayer was then sent through a series of multiplication dies, which cut, spread, and stack the melt, doubling the number of layers each time. Table 1 and Table 2 summarize the material properties of the polymer pairs used in each approach.

Poly(vinyl cinnamate) (PVCi) and polystyrene (PS) blends of 50/50 or 25/75 were coextruded with poly(methyl methacrylate) (PMMA) with polyethylene (LDPE) skin layers. Overall core film thickness varied for each approach. Films of 7 to 13 microns were produced for the poly(vinyl cinnamate) approach to give layer thicknesses of 50-100 nanometers. Poly(naphthalate-co-terephthalate) (PEN-co-PET) was coextruded
against either PS or PMMA with protective LDPE skin layers. Films of 11 to 172 microns were produced for the polyester approach to enable different draw ratios of the polyester down to 50-100 layer thicknesses, Table B.3.

Refractive index was measured in three different spots along the films with a Metricon Model 2010, which utilizes a prism coupling technique. A free-standing film was held to a prism of known refractive index under pressure, through which a laser light is shone. This setup is then rotated and the refractive index was determined as the drop in reflected laser light intensity detected due to the tunneling of laser light into the film at the critical angle. This critical angle is used by the Metricon to calculate the refractive index of the film, using Snell’s Law:

\[
\sin \theta_{\text{prism}} \sin \theta_{\text{film}} = n_{\text{film}} \sin \theta_{\text{film}} \tag{B.1}
\]

where \( n \) is the refractive index and \( \theta \) is the angle, where \( n_{\text{prism}}, \theta_{\text{prism}}, \text{ and } \theta_{\text{film}} \) are known. Measurements were taken in both the TE and the TM mode (in plane and through thickness of the film) for the polyester approach since these films were stretched and could cause birefringence.

An Oriel Hg Research Arc Lamp Model 66907, equipped with a 100W Hg lamp and manual shutter, supplied the photo-stimulation for the photo-patternable films. Samples were placed directly in front of the beam, the diameter of which was adjusted depending on the sample and method of patterning. A diameter of 3 cm was used for masking of both types and the smallest diameter possible, ~1.5 mm, was used for direct writing on PEN-co-PET-containing samples. Time varied from several minutes to hours for masked samples, while direct writing only required a maximum of 2 seconds.
Masking was achieved using a mesh grid with 25 μm diameter wire, and 500 μm x 500 μm squares.

**Approach #1: Poly(vinyl cinnamate)**

Due to the cost of the photoresist material, the viscosity was measured using a Thermo HAAKE miniLab twin screw extruder, which only required 5 grams. The materials were ramped through a series of shear rates at a minimum of 3 temperatures. Viscosity of the PMMA and PS were also measured using a conventional melt flow indexer (MFI) at the same temperatures, which allowed for determination of a conversion factor between the two methods. The PVCi viscosity values obtained through the HAAKE miniLab at similar shear rates were then converted to an expected value from the melt flow indexer for determination of coextrusion conditions.

The photocrosslinking reaction of PVCi was monitored by examining the change in refractive index and the change in the Fourier transform infrared (FTIR) spectrum. FTIR spectra were obtained from a Nicolet 870 Nexus FT-IR system using the transmission mode. Two peaks at 1637 and 1710 cm⁻¹ were of interest; the double bond that participates in the photodimerization reaction, and the unsaturated ester carbonyl adjacent to the double bond, respectively. As the cinnamate chromophores dimerize, the two peaks decrease as the double bond is converted into single, saturated bonds.⁵

**Approach #2: Polyester**

Thermal analysis was performed on the sheets with a Perkin-Elmer (Boston, MA) DSC-7 calorimeter under a nitrogen atmosphere. Samples weighing 5–10 mg were cut from the films, and thermograms were obtained at a heating rate of 10°C min⁻¹. 1st heating thermograms were used to determine appropriate stretching temperatures for the
films: above the glass transitions of the glassy materials and below the cold crystallization temperature of PEN-co-PET.

Square specimens measuring 85 mm x 85 mm were cut from the extruded films, marked and marked with a grid pattern. These were stretched uniaxially in an MTS (Eden Prairie, MN) Alliance RT30 mechanical testing machine at a strain rate of 100% min\(^{-1}\) at 140 °C. These were also stretched biaxially in a Bruckner (Greenville, SC) Karo IV Biaxial Stretcher. The sheets were simultaneously drawn at 140 °C at an engineering strain rate of 20% s\(^{-1}\) for PEN-co-PET/PS and 2% s\(^{-1}\) for PEN-co-PET/PMMA based on the original specimen dimensions. The uniformity of the drawn specimen was determined from the even deformation of the grid pattern. The preheat time before drawing was fixed at 60 s.

**B.3 Results and Discussion**

*Approach #1: Poly(vinyl cinnamate) Approach*

Poly(vinyl cinnamate) (PVCi), a well-known negative photoresist, is a polymer made of poly(vinyl alcohol) esterified with cinnamic acid was found to undergo the same photodimerization reaction as cinnamic acid, resulting in a maximum change in refractive index of ~ 0.037, almost 4x that of the small molecule. Figure B.2 (a-b). Being a large molecule, it also solved diffusion/sublimation issues of cinnamic acid during melt processing.\(^5\)

The photocrosslinking reaction of PVCi was monitored by examining the change in refractive index and the change in the Fourier transform infrared (FTIR) spectrum, Figure B.3. The two peaks at 1637 and 1710 cm\(^{-1}\) were of interest; the double bond that participates in the photodimerization reaction, and the unsaturated ester carbonyl adjacent
to the double bond, respectively. As the cinnamate chromophores dimerize, the two peaks decrease as the double bond is converted into single, saturated bonds.\textsuperscript{5}

Poly(vinyl cinnamate) degrades at temperatures above 200°C and was found to be a brittle film. PVC\textsubscript{i} was blended with other glassy polymers, and found to be the most thermally and UV stable in blends with styrene-acrylonitrile copolymer, SAN17, or PS. However, SAN17 requires a significantly higher processing temperature than PS, and was eliminated as a possibility. Blending with PMMA resulted in an opaque, immiscible blend. Blends with polycarbonate (PC) and glycol-modified poly(ethylene terephthalate) (PETG) had very poor thermal stability, degrading the PVC\textsubscript{i} within 20 min at 200°C.

A low viscosity polystyrene (PS) resin blended with the PVC\textsubscript{i} in compositions of 50/50 and 25/75 PS/PVC\textsubscript{i} showed high refractive index changes of 0.010 – 0.026, about 4x that of the original cinnamic acid system. Thermogravimetric analysis of these blends was promising for the anticipated coextrusion step. A viscosity match within our processing window was found between the blends and PMMA VS 100 below 200°C, and a microlayer run using the plug feed method was carried out with only 50-100 grams of these materials, Figure B.4 (a-b).

The films produced contained reactive PVC\textsubscript{i}, confirmed by FTIR before and after UV treatment of the films, Figure B.5. However, they were not photonic, for two possible reasons. The PVC\textsubscript{i} may have thermally crosslinked, changing the refractive index, or it may have phase separated from the PS during the process, scattering light within the layers. Experiments with monoliths were subjected to processing temperatures at coextrusion residence times, 10-30 minutes, to test these theories. The heat-treated films showed a large drop in refractive index from the thermal treatment, showing little
change in refractive index after UV exposure, caused by the loss of cinnamate groups on
the PVCi polymer chain. Therefore, no further work was conducted on this system.

Approach #2: Polyester Approach

Polyesters such as poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN), when oriented, result in large changes in refractive index.\(^8\text{--}^{10}\) PEN-co-PET obtained from Teijin Kasei was layered against an amorphous polymer, such as PS or PMMA, which does not change refractive index with orientation. Thick films with thick layers were stretched down to layer thicknesses on the nanometer scale, from which photonic reflections can be produced.

The temperatures for stretching were determined using differential scanning calorimetry (DSC). The glass transition of PS and PMMA (not shown) was detected at \(~110\ °C\). Cold crystallization of the PEN-co-PET was initialized around 190 °C. Therefore, the films were stretched between the temperatures of 120 and 180 °C. The best results were obtained at 140 °C.

The orientation of these films through stretching either uniaxially or biaxially resulted in large positive changes in refractive index of the polyester layers, increasing the difference in refractive index between the layers, Figure B.7 (a-b). This, in turn, increased the reflectivity of the photonic crystal, as well as affecting the color that was reflected. Also, orientation-induced refractive index changes in each plane of the polymer material were not equal, resulting in birefringence. Depending on the amount of birefringence, the 128L photonic films were sometimes not only reflective but could also polarize light.
Due to strong absorption of UV by PEN-co-PET, heating these films with a strong UV beam caused a relaxation of the oriented PEN-co-PET. This stimulated a decrease in the refractive index, as well as a change in the layer thickness of this layer, resulting in a change in the reflected color. Selective localized heating of the film could create a pattern in the photonic crystal film, shown schematically in Figure B.8.

Figure B.9 (a-b) shows that these films can either be directly written into using a focused UV beam, or masked to form a pattern in the film. The color change of these films was very obvious, changing from blue/violet to yellow or red. The volume change brought about by this relaxation process, however, was very large. In order to make these materials more commercially viable, this volume change must be reduced. Some preliminary experiments using UV absorbers to reduce the UV exposure time were conducted, with small success. Further improvements could be made through the use of a smaller UV beam and reducing the draw ratio of the films to give smaller, but still significant, refractive index changes (example: from blue/violet to green).

B.4 Conclusions

Fabrication of photo-patternable polymeric 1D photonic crystals was attempted in this work, using two different approaches. The PVCi approach was not successful. Coextrusion of 25/75 PS/PVCi blend against PMMA produced nonreflective films using the plug feed method. FTIR confirmed PVCi remained reactive within the layers after the process. However, the films did not undergo a large enough refractive index change to create a distinct pattern.

The alternative approach to produce patternable multilayer films by orientation and selective relaxation was more successful. These films gave distinct patterns and
could be written in either directly or masked, but were also accompanied by significant volume changes in the films through the relaxation process. This volume change may be controlled by either increasing the speed of the relaxation process using a UV absorber or a focused UV beam with a smaller spot size. The draw ratio of the films could also be tailored to give smaller, but still significant, refractive index changes and volume changes.

**B.5 References**

Table B.1: Materials for the photoresist approach.

<table>
<thead>
<tr>
<th>Material</th>
<th>Grade</th>
<th>Neat Refractive Index (633 nm)</th>
<th>Irradiated Refractive Index (633 nm)</th>
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<tr>
<td>Poly(methylmethacrylate)</td>
<td>Plexiglas VS 100</td>
<td>1.489</td>
<td>1.489</td>
</tr>
<tr>
<td>Poly(vinyl cinnamate)</td>
<td>Sigma-Aldrich</td>
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<td>1.584</td>
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<td>Polystyrene</td>
<td>PS CX5238</td>
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Table B.2: Materials for the polyester approach.

<table>
<thead>
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<th>Layer</th>
<th>Material</th>
<th>Grade</th>
<th>Processing Temperature (°C)</th>
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<td>Non-reactive</td>
<td>Poly(methyl methacrylate)</td>
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<td>Layer</td>
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<tr>
<td>Reactive</td>
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<td>TEONEX TN8756C</td>
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Table B.3: 50/50 128L PEN-co-PET/PS and PEN-co-PET/PMMA layered sample characteristics

<table>
<thead>
<tr>
<th>System</th>
<th>Film Thickness (μm)</th>
<th>Layer Thickness (nm)</th>
<th>Draw Ratio</th>
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<tr>
<td></td>
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<td>85</td>
<td>1x1</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>180</td>
<td>2x1, 2x2, 3x3, 4x4</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>270</td>
<td>3x1, 2x2, 3x3, 4x4</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>360</td>
<td>4x1, 2x2</td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>760</td>
<td>3x3</td>
</tr>
<tr>
<td></td>
<td>172</td>
<td>1340</td>
<td>4x4</td>
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<tr>
<td>PEN-co-PET/PMMA</td>
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<td>1340</td>
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Figure B.1. Principles of photopatterns

\[ \lambda = 2(n_1 d_1 + n_2 d_2) \]
Figure B.2 (a-b). Poly(vinyl cinnamate): a) The structure and photodimerization reaction; b) The refractive index change with photocrosslinking.
Figure B.3. FTIR spectrum of PVCi and the change in the spectrum with UV exposure.
**Figure B.4 (a-b).** Coextrusion of PVCi-containing films: a) Viscosity match of 25/75 and 50/50 PS/PVCi to PMMA b) Plug feed method microlayer run setup.
Figure B.5. FTIR spectra of multilayer films before and after UV treatment show the presence of reactive PVCi within the films after the microlayer process.
Figure B.6. Process to produce patternable photonic crystals by orientation and relaxation of PEN-co-PET.
Figure B.7 (a-b). Change in refractive index of PEN-co-PET with a) uniaxial and b) biaxial orientation.
**Figure B.8.** Process to produce patternable photonic crystals by orientation and relaxation of PEN-co-PET.
Figure B.9 (a-b). Polyester patternable 1D photonic crystals: a) Direct writing on film; b) grid-masked film.
CHAPTER 1


**CHAPTER 2**


CHAPTER 3


APPENDIX A


APPENDIX B


