CRYSTALLINE POLYMERS IN MULTILAYERED FILMS AND BLEND SYSTEMS

By

GUOJUN ZHANG

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Dissertation Advisor: Dr. Eric Baer

Department of Macromolecular Science and Engineering
CASE WESTERN RESERVE UNIVERSITY

August, 2014
We hereby approve the thesis/dissertation of

______________________________  Guojun Zhang

candidate for the Ph.D. degree *

(signed)  Prof. Eric Baer

(Chair of the committee)

Prof. David Schiraldi

Prof. LaShanda Korley

Dr. Andrew Olah

(date)  July 7, 2014

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

To my wife YaoYuan, To my son, Andy ChiShen Zhang and To my parents, Chenglian Zhang, Jiying Sun, Yujin Yuan and Jinfeng Wang
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Crystalline Polymers in Multilayered Films and Blend Systems

by

GUOJUN ZHANG

Abstract

CHAPTER 1: In this study, multilayer films of sPS-PPS (syndiotactic Polystyrene and Polyphenylene sulfide blend) against P4MP1 [Poly (4-Methylpentene-1)] with various compositions and layer thicknesses were prepared by a layer multiplying co-extrusion process. Incorporating the PPS into sPS layers before co-extrusion produced pores in the sPS layers upon a post-extrusion, uniaxial orientation. Confined crystallization of P4MP1 by sPS-PPS was examined before and after the uniaxial orientation. A melt and recrystallization method was employed to achieve the preferred in-plane orientation of P4MP1 crystals. This was characterized by the atomic force microscopy and x-ray spectroscopy. We found that with P4MP1 layer thickness smaller than 400 nm, a confinement effect will induce in-plane P4MP1 crystal orientation where the crystal c-axis is perpendicular to the film. This arrangement of crystals reduced oxygen’s tortuosity through the multilayer films. This conclusion was verified by increased oxygen permeability of the stretched-recrystallized multilayer films.

CHAPTER 2: High-density polyethylene (HDPE) was co-extruded against high glassy transition temperature (Tg) polycarbonate (PC) to fabricate multilayer films. Melt and recrystallization experiments were conducted on these extruded films to
study the effects of isothermal recrystallization temperature and layer thickness on HDPE lamellae orientation. WAXS and AFM were used to demonstrate lamellar morphology of HDPE layers. We report that HDPE lamellae show twisted morphology in 30 nm thin layers after confined crystallization at a high temperature (128 °C). It may be the first time that anyone has created such twisted lamellar morphology with HDPE in such a thin layer. Similar twisted morphology of HDPE was also observed when HDPE was co-extruded with another high Tg glassy polymer, polysulfone (PSF). Interestingly, the twisted HDPE lamellar morphology associated with an increased crystallinity improves both the oxygen and water vapor barrier properties of the multilayer films.

CHAPTER 3: Confined crystallization of high-density polyethylene (HDPE) in multiplayer films is studied in this paper. A new cyclic olefin copolymer (COC), HP030, is co-extruded with HDPE by a layer multiplying technique. The number of layers and layer compositions are changed to study the effect of layer thickness on the crystalline morphology of the HDPE layers under confinement. Atomic force microscopy (AFM) is used to investigate the crystalline morphology of the HDPE layers. MOCON ((Minneapolis, MN, commercial instrument) units are employed to measure both oxygen permeability and water vapor transport rate (WVTR) of these co-extruded HDPE/HP030 multilayer films. We report that when the HDPE layer nominal thickness is about 290 nm in the HDPE/HP030 multilayer films, the HDPE layer effective gas barrier property is improved approximately 2 times for oxygen and
5 times for water vapor. This is the result of confined spherulite morphology of HDPE, which increases the tortuosity for gas to diffuse through the films. Similar phenomenon is found for polypropylene (PP), when PP is co-extruded against polycarbonate (PC). The same experiments as for HDPE are conducted to confirm that PP spherulites have been confined by PC in PP/PC multilayer films. We discover that the confined spherulites of PP improve its gas barrier properties as well.

CHAPTER 4: Blends of linear low density polyethylene (LLDPE) and ethylene vinyl alcohol (EVOH) with different weight fractions are extruded to fabricate thin films. The extruded blend film morphology is investigated by atomic force microscopy (AFM). The extruded blend films have shown extended morphology along the extrusion direction (ED) and dispersed morphology along the transverse direction (TD). We report that due to this morphology, a two-dimensional (2-D) confined crystallization occurs. The EVOH has successfully confined the LLDPE from both film normal direction (ND) and transverse direction (TD) in this study. The confinement from ND results in an on-edge orientation of LLDPE, while the confinement from TD forces the on-edge oriented LLDPE crystals to further elongate along the extrusion direction (ED). This specific crystal orientation is different from one-dimensional (1-D) confined crystallization observed in multilayered films. Both wide angle X-ray scattering (WAXS) and small angle x-ray scattering (SAXS) are utilized to investigate the crystal orientations of LLDPE in the extruded blend films. Moreover, due to the morphology, the extruded blend films have
shown high oxygen barrier properties, which make this material valuable in packaging applications.

CHAPTER 5: The blend of linear low-density polyethylene (LLDPE) and ethylene vinyl alcohol (EVOH) with weight fraction of 50-50 is extruded by a multiplication extrusion system to fabricate thin films. Different numbers of multipliers are utilized to tailor the morphology of the extruded blend films. We found that as the number of multipliers increases, the blend film morphology transforms from an elongated and layer-like structure to the co-continuous structure and eventually becomes homogeneous. This is because during the multiplication process, the multipliers behave similar to static mixers that physically break the elongated and co-continuous like structure of LLDPE and EVOH into tiny domains. As the morphology evolves, the physical properties of the extruded blend films change dramatically. After the co-continuous and elongated morphology becomes homogenous, both the gas permeability and the transmission rate of these films increase. The tensile mechanical behaviors become isotropic at different deformation directions. Atomic force microscopy (AFM) and wide angle X-ray scattering (WAXS) are utilized to investigate the morphology and crystalline structure of the blend films. Oxygen gas permeability and water vapor transport rate (WVTR) of these blend films are measured by MOCON units. The transmission rate and mechanical properties are studied by the UV-vis and a mechanical tensile stretcher (MTS) respectively.
Part I

Crystalline Polymers in Multilayered Films
CHAPTER 1

Gas Permeability of Poly (4-Methylpentene-1) in a Confined Nanolayered Film System

1.1 Introduction

It is well known that gases usually cannot permeate through polymer’s crystalline region due to the tight packing of molecules [1]. However, poly (4-methylpentene-1) (P4MP1) is an exception that its crystalline region density is lower than its amorphous region, which suggests that the molecules are actually loosely packed in its crystalline region [1, 2]. This phenomenon is unusual, but is also reported in syndiotactic polystyrene (sPS) [3]. Many scientists have described this loose packing crystal polymorphism in P4MP1 as open channels [1, 2, 4-6]. These repeating, 4 Å diameter, open channels lie between methylene and methine groups that run along P4MP1’s c-axis, shown in Figure 1.1 [2]. The channel size implies that the crystalline region of P4MP1 should be permeable to certain gas molecules [1]. It was actually reported that the diffusion through the P4MP1 crystal region was about one third of its amorphous region [1, 2, 7].

Recently, layer multiplying co-extrusion has been recognized as an effective method of studying confinement of both semi-crystalline and amorphous polymers [8]. Polymer can be confined between hundreds of micro- or nanometer thick film layers [8]. Using this process, confined crystallization of a variety of semi-crystalline polymers, including polyethylene oxide (PEO), poly (ε-caprolactone) (PCL), and polypropylene (PP) have been studied and reported [9-12]. By co-extruding either
PEO or PCL between hard confining layers and reducing their individual layer thicknesses, high-aspect ratio, single-layer, in-plane lamellae crystals of PEO and PCL were formed [9-11]. These nanolayered crystal morphologies dramatically reduced their film’s permeability by 200-300 times compared to their bulk film controls [9-11]. Since P4MP1 has a distinct channel-containing crystalline morphology, an opposite result is expected for confined crystallized P4MP1 lamellae.

When P4MP1 in-plane oriented crystals are produced, P4MP1’s open channels should facilitate faster gas permeation, instead of creating impermeable, high-aspect ratio, single lamella crystals that reduce gas permeability. This expectation is due to the in-plane oriented P4MP1 crystals, which means the 4 Å diameter open channels along c-axis should be aligned perpendicular to the film surface. This result should reduce gas tortuosity within P4MP1’s crystal region and increase the film’s small gas flux rates. Furthermore, the channel size of 4 Å is larger than the molecules of hydrogen, oxygen and carbon dioxide, but is smaller than methane and propylene, etc. Therefore, this in-plane oriented P4MP1 crystal structure is potentially valuable for gas separation based on the size exclusion mechanism.

Confined crystallization in multilayer films requires a material whose melting temperature is higher than the confined material, so the to-be-confined polymer crystal can grow in a confined space. A hard polymer is usually required to sandwich the molten, soon-to-be confined crystalline polymer. Since syndiotactic Polystyrene’s (sPS’s) melting temperature is 274 °C, higher than P4MP1 whose melting temperature is 227 °C, confined crystallization should occur in this multilayer film system.
However, gas permeability calculations (equation 1.1) of this multilayer film system predict that sPS will mask P4MP1’s permeability change.

\[
\frac{1}{P_{\text{Film}}} = \frac{\phi_{\text{layerA}}}{P_{\text{layerA}}} + \frac{\phi_{\text{layerB}}}{P_{\text{layerB}}}
\]  

(1.1)

Where \(\Phi_A\) and \(\Phi_B\) are the volume fraction of each polymer in the multilayer film. \(P_A\) and \(P_B\) are the oxygen permeability of each polymer. In this particular case, polymer A is P4MP1 and polymer B is sPS. If we take P4MP1/sPS 50/50 film as an example, then \(\Phi_A\) can be rewritten as \(\Phi_{sPS}\); \(\Phi_B\) can be rewritten as \(\Phi_{P4MP1}\) (both are 0.5). \(P_{sPS}\) is the permeability of sPS and \(P_{P4MP1}\) is the permeability of P4MP1.

Since \(P_{sPS}\) is much smaller than \(P_{P4MP1}\) (Table 1.3), it means that \(\Phi_{sPS}/P_{sPS}\) is dominant in the equation. This also means confining P4MP1 with sPS alone will mask P4MP1’s permeability change.

To unmask this effect, small amounts of Polyphenylene Sulfide (PPS) were introduced into the sPS layers. Since sPS and PPS are immiscible, small beads of PPS should form in the sPS matrix. When these layers are stretched, their immiscible nature should produce pores at their interfaces without breaking the matrix; and the pores should be large enough to allow gas to diffuse through. Blending the two together before microlayer coextrusion could be accomplished by using a Haake twin-screw blender. The sPS-PPS blends could then be coextruded with P4MP1 during multilayer coextrusion. Moreover, through a post extrusion uniaxial stretching, holes in only the sPS layers should be preferentially produced while retaining sPS-PPS blends’ ability to confine P4MP1.
Following multilayer coextrusion, controlled stretching, and a melt and recrystallization procedure (will be discussed in details later) should produce in-plane oriented P4MP1 crystals between porous confining layers. Altogether, this procedure should allow gas to diffuse through large sPS-PPS pores, unmasking P4MP1’s oxygen permeability through its 4 Å channel. The increased oxygen permeability and Wide Angle X-ray Scattering (WAXS) patterns could then confirm that P4MP1’s c-axis open channels are aligned perpendicular to the film surface.

1.2 Materials and methods

The commercially-available P4MP1, “TPX MX004”, was obtained from Mitsui chemical corporation, Japan. Homopolymer of sPS was obtained from Dow Chemical Company, China. PPS (Fortron 0320) was generously provided by Ticona Company, USA. Melting temperatures and crystallization temperatures of these three materials were listed in Table 1.1.

sPS and PPS were melted and blended together with a Haake twin-screw extruder at 290 °C before multiplying coextrusion. Their respective weight ratios were 90/10. This 90/10 weight ratio was used for all sPS-PPS blend layers and all experimental conditions. Doping these small amounts of PPS into the sPS layer created immiscible interfaces between these two polymers. A forced-assembly, layer multiplication coextrusion process [8] then fabricated multilayer films of alternating layers of sPS-PPS blends and P4MP1. This process was diagrammed in Figure 1.2. The coextrusion temperature was selected on rheological compatibilities of sPS-PPS blends with P4MP1. Polymer melt rheological properties were measured as a function
of temperature by using a Kayeness Galaxy 1 melt flow indexer (MFI) at a shear rate of 10 s\(^{-1}\). This method simulated multilayer coextrusion flow conditions. Using this, an optimum multilayer coextrusion temperature of 290 °C was identified. Films with 129 alternating sPS-PPS layers and P4MP1 layers were then coextruded. Next, sPS-PPS blends were varied to P4MP1 by volume ratios of 90/10, 70/30 and 50/50 (listed in Table 1.2).

sPS-PPS/P4MP1 multilayer film thicknesses ranged from 50 to 150 μm, so the effect of individual P4MP1 layer thickness on the confined crystallization could be investigated. P4MP1 and sPS-PPS monolayer films were used as controls. The film take-off roll temperature was held constant at 160 °F for collecting all films.

Melt and recrystallization experiments were carried out on extruded multilayer films by varying temperatures. At this moment, there was no post extrusion treatment on the extruded multilayer films. Multilayer films with different P4MP1 layer thicknesses were heated to 250 °C in a Mechanical Testing System (MTS) temperature chamber from the MTS Solutions Company for 5 minutes to preferentially melt the P4MP1 layers but not the sPS-PPS layers. These films were then quenched to several different final temperatures using a cooling rate of about 200 °C min\(^{-1}\). Films were held at these temperatures for at least 20 minutes to finish the isothermal recrystallization experiments. Data from these experiments were used to determine the optimum isothermal recrystallization temperature to produce in-plane oriented P4MP1 crystals. The effects of layer thickness and isothermal crystallization temperature on the confined crystallization of P4MP1 were systematically studied in
this session. Films that were run through this procedure were designated “recrystallized multilayer films”.

Extruded sPS-PPS/P4MP1 multilayer films with volume ratios of 50/50, 70/30 and 90/10, whose total film thicknesses were 150 μm (individual P4MP1 layer thicknesses were 1200, 720, and 240 nm respectively) were uniaxially stretched (along the extrusion direction) at 105 °C in a MTS temperature chamber. This procedure should produce pores only in the sPS-PPS confining layer. These films were stretched with a 3×1 draw ratio at a rate of 600%/min. These uniaxially oriented films, therefore, had a final total film thickness of 50 μm and individual P4MP1 layer thicknesses of 400, 240 or 80 nm, depending on the starting layer thickness. These films were designated “stretched multilayer films”.

After uniaxial stretching, the melt and recrystallization experiment was applied to the stretched multilayer films in the same MTS temperature chamber using the same method mentioned above. These stretched multilayer films were heated to 250 °C in the temperature chamber for 5 minutes to preferentially melt the P4MP1 layers. Next, these films were quenched to 215 °C using a cooling rate of about 200 °C min⁻¹. These films were then held at 215 °C for at least 20 minutes, allowing P4MP1 layer isothermally recrystallize. After the melt and recrystallization procedure, the films were gradually cooled to room temperature. These films were designated “stretched-recrystallized multilayer films”.

sPS-PPS blend controls, P4MP1 controls, and sPS-PPS/P4MP1 multilayer films’ thermal properties were measured using a Perkin-Elmer (Boston, MA) Series 7
Differential Scanning Calorimeter (DSC) at a heating/cooling rate of 10 °C min\(^{-1}\). The crystallinity of P4MP1 in extruded multilayer films, recrystallized multilayer films, stretched multilayer films and stretched-recrystallized multilayer films were all checked by the same DSC using heating/cooling rate of 10 °C min\(^{-1}\).

The layered structure of extruded multilayer films, stretched multilayer films, and stretched-recrystallized multilayer films were all investigated by atomic force microscopy (AFM). AFM samples were embedded in epoxy (5 Minute Epoxy, Devcon, Rivera Beach, FL) and cured for 24 hours at room temperature. Cross sections were produced by cooling samples to -60 °C in liquid nitrogen and then microtomed. AFM images were obtained with a commercial scanning microscope probe (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA) whose spring constant was 50 Nm\(^{-1}\) and resonance frequency was in 284-362 kHz range. The tip radius was 10 nm. Phase and height images of the cross sections were recorded simultaneously.

Scanning Electronic Microscope (SEM) was used to characterize film surface and cross section morphologies of stretched multilayer films and stretched-recrystallized multilayer films at room temperature.

Two-dimensional WAXS patterns were obtained with a rotating anode X-ray generator (RU 300, 12 kW, Rigaku, Woodlands, TX), which produced a beam of monochromatic Cu K\(\alpha\) radiation (\(\lambda=0.154\) nm). The X-ray generator operated at 40 kV and 90 mA. The x-ray beam was aligned parallel to the film’s transverse direction (TD).
Oxygen flux \( J(t) \) rates for extruded controls, stretched controls, annealed controls, extruded multilayer films, recrystallized multilayer films, stretched multilayer films, and stretched-recrystallized multilayer films were all measured with a MOCON (Minneapolis, MN) OxTran 2/20 unit. The measurements were carried out in 1 atm pressure at 23 °C (+0.1) with a 0% relative humidity. The instrument was calibrated at 23 °C with a NIST-certified Mylar film with known oxygen transport characteristics. Oxygen permeabilities, \( P(O_2) \), were calculated from steady-state flux, \( J \), rates.

\[
P(O_2) = J \frac{l}{\Delta p}
\]

(1.2)

Where \( l \) is the overall film thickness and \( \Delta p \) is oxygen’s partial pressure drop across the film. The average reported \( P(O_2) \) values were taken from at least two samples. \( P \) values are reported in Barrer units. One Barrer equals to \( 10^{-10} \) (cm³ O₂) cm cm⁻² s⁻¹ cmHg⁻¹.

1.3 Results and Discussion

**Extruded sPS-PPS/P4MP1 multilayer films:**

DSC thermograms in Figure 3 showed melt and crystallization temperatures of P4MP1 and sPS in a sPS-PPS/P4MP1 50/50 multilayer film. These data were consistent with their bulk controls. This DSC showed a cold crystallization peak at 140 °C during the heating process. This implied that sPS did not fully crystallize during the fast cooling collecting process. In other words, quick multilayer film quenches did not allow sPS to fully crystallize. This point will be discussed later.
TD WAXS was used to check crystal orientation of extruded sPS-PPS/P4MP1 multilayer films with volume ratios of 50/50, 70/30, and 90/10. All sPS-PPS/P4MP1 multilayer films were with the same thickness of 50 micrometers. The TD WAXS images of all films exhibited isotropic reflection rings of P4MP1 (200), (212), (321) planes irrespective of P4MP1 layer thickness, seen in **Figure 1.4**. The same isotropic reflection ring was also observed in WAXS images of bulk P4MP1 controls (**Figure 1.4**). Neither in-plane nor on-edge biased P4MP1 crystal orientation was achieved. This observation was in contrast to previous confinement studies using PEO and PCL, where nanolayer confinement induced anisotropic lamellae orientation in extruded multilayer films with no post coextrusion treatment [9-11].

As we mentioned earlier, fast film quenching did not fully crystallize sPS in both control and multilayer films. This was confirmed by the DSC thermograph of the extruded sPS-PPS/P4MP1 50/50 composition multilayer film and the nearly amorphous WAXS patterns of the extruded bulk sPS controls (not shown). Therefore, while cooling, P4MP1 crystallized against soft sPS layers because P4MP1’s crystallization temperature ($T_{c,P4MP1}$) is 209 °C, which is greater than sPS’s glass transition temperature ($T_{g,sPS}$) of 105 °C. As mentioned above, hard layers are required for confined crystallization. Compared to on-edge orientation and isotropic orientation, in-plane oriented lamellae form relatively slowly. Based on this, melt and recrystallization process were considered necessary to the formation of P4MP1 in-plane oriented crystals.

AFM was also used to characterize the layer integrity of extruded
sPS-PPs/P4MP1 multilayer films, Figure 1.8 (a, b). Cross-sectional AFM images revealed continuous P4MP1 layers in all compositions. Only sPS-PPs/P4MP1 50/50 composition multilayer film was included as an example. The layer uniformity was not perfect, because sPS is a rare material to get. During the multiplying coextrusion process, only a limited amount of sPS was used. It was a challenge to achieve excellent layer distribution. However, the layers were all within the range as we expected.

Recrystallized sPS-PPs/P4MP1 multilayer films (This part is to study the effects of layer thickness and isothermal crystallization temperature on P4MP1 confined crystallization)

Melt and recrystallization experiments were carried out on extruded, unoriented multilayer films. These experiments allowed the effects of layer thickness and isothermal recrystallization temperatures on P4MP1 crystal orientation to be systematically studied. These studies also found an optimum condition for melt and recrystallization process. These studies were all performed using sPS-PPs/P4MP1 50/50 composition films. Based on the DSC thermograph in Figure 1.3, 250 °C was identified as the preferential P4MP1 layer melting temperature, since 250 °C is roughly 30°C higher than P4MP1’s melting temperature and a little more than 20 °C lower than sPS’s melting temperature. Heating the multilayer films also allowed sPS to fully crystallize during this process, thus becoming a harder confining surface at 250°C. Next, an isothermal crystallization temperature of 215 °C was chosen, because
it is moderately higher than P4MP1’s crystallization temperature. This step should produce in-plane orientation of P4MP1. After isothermal crystallization, these multilayer films were then slowly cooled to room temperature. DSC was used to check and compare the crystallinity of extruded multilayer films and recrystallized multilayer films. Similar $\Delta H$ values of P4MP1 were obtained (Table 1.6), which suggested that P4MP1 crystallinity kept unchanged after melt and recrystallization process.

50 and 150 micrometer films with P4MP1 layer thicknesses of 400 and 1200 nm, respectively, were separately heated to 250 °C in the MTS temperature chamber for 5 minutes to fully melt the P4MP1 layers. Next these films were quenched to 215 °C at a cooling rate of about 200 °C min$^{-1}$. The films were then held at 215 °C for at least 20 minutes for isothermal recrystallization. After the melt and recrystallization procedure, these films were slowly cooled to room temperature. Transverse direction (TD) WAXS images of the recrystallized multilayer films were shown in Figure 1.5. The reflection of P4MP1 (200) plane plays a key role in determining the crystal orientation of P4MP1.

50 micrometer recrystallized multilayer films, whose P4MP1 layer thicknesses were 400 nm, exhibited concentrated intensity arcs of P4MP1 (200) plane at their equator on the TD WAXS image. These arcs confirmed the presence of in-plane P4MP1 crystals whose c-axis was oriented perpendicular to the layer surface. However, 150 micrometer recrystallized multilayer film with thicker P4MP1 layers (1200 nm) showed little equatorial concentrated reflection of the (200) plane, which
implied that the preferred in-plane orientation was not achieved. Due to large layer thicknesses, other orientations were exhibited, which suggested in-plane orientation was a function of layer thickness. Based on these data, 400 nm layer thickness or below was considered suitable for formation of in-plane orientation of P4MP1.

The discussions above suggested that layer thickness was an important factor in this mechanism. Previous studies on confined crystallization in nanolayered or microlayered films [9-12] suggested that the isothermal crystallization temperature also played important roles. By tailoring the temperature, better crystal morphological orientation could be achieved. As such, 50 micrometer thick sPS-PPs/P4MP1 50/50 composition multilayer films were again selected to conduct melt and recrystallization experiments under different isothermal crystallization temperatures. The films were again heated to 250 °C in an MTS temperature chamber for 5 minutes to fully melt the P4MP1 layers, which were then quenched to several different temperatures (160, 180, 200, or 215 °C) at a cooling rate of about 200 °C min⁻¹. The films were then held at these temperatures for at least 20 minutes to finish the isothermal recrystallization. The WAXS images in Figure 1.6 showed similar reflections for all samples. The (200) plane of P4MP1 showed a sharp single pair of arcs at the equator in all images confirming the presence of P4MP1 in-plane oriented crystals.

Oxygen permeability of the 50 micrometer sPS-PPs/P4MP1 50/50 extruded film and recrystallized multilayer film (at 215°C) as well as the extruded controls were then tested. However, as it was predicted earlier in the introduction, recrystallized multilayer films did not show different permeability compared to the
extruded multilayer films, because the low permeability of sPS-PPS layer masked the change of P4MP1 layer. These data were listed in Table 1.3. Based on the experiments above, it is clear that P4MP1 in-plane orientation can be achieved in 50 micrometer films with P4MP1 layer thickness less than 400 nm after the isothermal recrystallization process. However, in order to detect the permeability change of P4MP1 layer after recrystallization, a highly permeable confining layer is needed. As such, a post extrusion uniaxial orientation was used to increase sPS-PPS layer porosity. Therefore, the final total film thickness targets of 50 micrometers for stretched multilayer films and a 250 °C melting along with isothermal recrystallization at 215 °C will be the standard for achieving in-plane P4MP1 crystals for later study.

**Stretched sPS-PPS/P4MP1 multilayer films:**

In blends of sPS-PPS, a 10 to 90 weight ratio of PPS to sPS was dispersed into sPS’s matrix. The immiscible qualities of the two materials exhibited bead-like particles of PPS within sPS. Since the interface compatibility of these polymers is poor, uniaxial stretching was expected to generate pores at the interface of sPS and PPS in their layers. The stretching temperature of 105 °C was selected because it is higher than both their glass transition temperatures ($T_{g,sPS}=100°C$ and $T_{g,P4MP1}=50 °C$). Even though sPS is a sem-crystalline polymer, it requires heating to 140 °C to fully crystallize. Therefore, both sPS and P4MP1 should stretch at 105 °C. Different stretching conditions were applied to extruded multilayer films. It was determined that the draw ratio of 3×1 with a strain rate of 600% min$^{-1}$ produced the best sPS-PPS
layer porosity (stretching is along the extrusion direction).

It is widely known that uniaxial or biaxial stretching dramatically impacts the structure of sPS and P4MP1 polymers. When sPS and P4MP1 polymers were stretched, their crystal’s c-axis oriented from the stretch, which will be discussed in details later. All three samples with different volume ratios (sPS-PPS/P4MP1 of 50/50, 70/30, 90/10 ratios) were uniaxially oriented under the same conditions. 150 micrometer thick films were used for every composition, so the final film thickness, after orientation, would be 50 micrometers (P4MP1 layer thickness would be 400, 240, 80 nm respectively), which was consistent with previous recrystallized multilayer film thicknesses.

After sPS-PPS layers were uniaxially stretched, holes were generated around PPS particles, which was shown by SEM surface images and cross section images in Figure 1.9 (a, b). These holes were measured and averaged 5 μm vertically and 1 μm horizontally, which is large enough for most gas molecules to pass. Shown in the SEM cross sections, these data suggested that the holes spanned the layers where they dwelled, producing sPS-PPS porous layers. These images also showed that the P4MP1 and sPS-PPS layer’s sPS matrix remained unbroken, but only stretched. This was also confirmed by AFM cross section images in Figure 1.8(c). All three compositions of sPS-PPS/P4MP1 “stretched multilayered films” showed similar porous morphology. The 50/50 composition was shown as a representative example. P4MP1 controls and sPS-PPS controls were also uniaxially stretched using the same method. Oxygen permeability tests were conducted on 50/50 and 70/30 stretched
multilayer samples and stretched controls. Increased oxygen permeability was observed due to the increased porosity of sPS-PPS layer, which will be discussed in details later.

**Stretched-recrystallized sPS-PPS/P4MP1 multilayer films**

The previously discussed melt and recrystallization method was applied to the stretched sPS-PPS/P4MP1 multilayer films to produce in-plane P4MP1 lamellae crystals between porous confining layers. These stretched films were again heated to 250 °C to melt P4MP1 layer. Since the sPS-PPS layers remained solid at this temperature, the porosity of sPS layer was not expected to change. After holding the stretched multilayer films at 250 °C in an MTS temperature chamber for 5 minutes, these films were quenched to 215 °C at a cooling rate of about 200 °C min⁻¹. These films were then held at 215 °C for at least 20 minutes to finish isothermal recrystallization. Both SEM and AFM images (Figure 1.9 (c, d) and Figure 1.8d) showed porosity in the sPS-PPS layers and continuous layer morphology of these stretched-recrystallized multilayer films. These holes in the stretched-recrystallized multilayer films seemed to be a bit larger than those in the stretched multilayer films as shown in SEM cross section images (Figure 1.9b, Figure 1.9d). However, the size was still around 5X1 µm as we claimed earlier. Instead, when looked at the SEM surface images, these holes seemed to be slightly smaller than those in stretched films (Figure 1.9a, Figure 1.9c). This discrepancy was due to 1) the distribution of slightly different sized holes throughout each sample, and 2) the result of scanning only a
small portion of the samples. Furthermore, the stretched sPS-PPS controls were heated to 250°C, quenched to 215 °C and held at 215 °C for 20 minutes. The same heat history as “melt and recrystallization process” was applied to the stretched sPS-PPS controls so that we could confirm that the “melt and recrystallization process” had no effect on oxygen’s permeability of the sPS-PPS layers. If the hole size changed (for example, aggregate into larger holes) during the melt and recrystallization process, we should have seen a change of sPS-PPS control’s permeability. However, the permeability of sPS-PPS controls kept nearly unchanged (Table 1.5), which suggested that the hole size in sPS-PPS layers did not change during the “melt and recrystallization process”.

All stretched-recrystallized multilayered samples were checked by WAXS to confirm the P4MP1 in-plane crystal orientation.

sPS-PPS/P4MP1 50/50 and 70/30 composition films were tested by a Mocon oxygen unit to study the effect of P4MP1 crystal orientation on its oxygen’s permeability. sPS-PPS/P4MP1 90/10 film was not studied for oxygen permeability due to its relatively poor film quality. The increased oxygen permeability was observed for both stretched-recrystallized sPS-PPS/P4MP1 50/50 and 70/30 multilayer films, which will be further discussed later.

The P4MP1 monolayer control and stretched P4MP1 control were also heated to 215°C and then were annealed at 215°C for 20 minutes. If the high temperature could relax the amorphous region of P4MP1, the permeability of P4MP1 controls would have increased. However, the annealed P4MP1 controls showed slightly lower
permeability than that of the extruded P4MP1 control (Table 1.5). This means the high temperature did not relax the amorphous region of P4MP1. Furthermore, the crystallinity of P4MP1 layers remained constant in extruded multilayer films, recrystallized multilayer films, stretched multilayer films and stretched-recrystallized multilayer films. This was supported by the similar delta H values determined from the DSC curves. (Table 1.6) The P4MP1 delta H values listed in Table 1.6 were directly determined from the DSC curves without normalizing for the weight fractions. Multilayer films of sPS-PPS/P4MP1 50/50 (v/v) were used in this study. Due to a consistent composition, the relative amounts of each component is constant, therefore, similar crystallinity will yield similar delta H.

WAXS of stretched and stretched-recrystallized sPS-PPS/P4MP1 multilayer films

P4MP1 crystal orientation was investigated by WAXS characterization. Transverse direction (TD) WAXS patterns from extruded multilayered films exhibited isotropic diffraction rings similar to the P4MP1 control, which has been previously discussed. The innermost ring (scattering angle $2\theta = 9.8^\circ$) consisted of the reflections from the P4MP1 (200) planes [4, 6, 7]. The second ring ($2\theta = 17.5^\circ$) contained the (212) reflection [4, 6, 7]. However, an additional amorphous halo from the sPS layer at $2\theta = 21.2^\circ$ was also seen in Figure 1.7 a, 1.7d, 1.7g.

TD WAXS patterns of uniaxially stretched multilayer films (Figure 1.7b, 1.7e, 1.7h) and stretched-recrystallized (Figure 1.7c, 1.7f, 1.7i) multilayer films showed
highly orientated P4MP1 lamellae, which resulted from stretching and confined recrystallization respectively. WAXS patterns of stretched sPS-PPS/P4MP1 multilayer films (P4MP1 layers are of 400, 240, or 80 nm) exhibited a sharp, 2-position reflections at the upper-most and lower-most of (200) plane. This implied P4MP1 crystals were highly oriented against the direction of film stretch. Uniaxial stretching also produced, at $2\theta = 21.2^\circ$, two pairs of arcs in sPS. These pairs were present after “melt and recrystallization process”, suggesting sPS was oriented and remained similar orientation after recrystallization. However, sPS orientation was not characterized here, because the focus of this paper is on the orientation of P4MP1 layer.

For stretched-recrystallized multilayer films, P4MP1 (200) plane [4, 6, 7] exhibited a sharp single pair of arcs at the equator, thus confirming the presence of in-plane oriented crystals of P4MP1 [9-11] whose c-axis was oriented perpendicular to the film layer (Figure 1.7c, 1.7f, 1.7i). Uniaxial orientation appeared to effect P4MP1 crystal orientation, but in-plane orientation was only achieved after the melt and recrystallization process.

Effect of P4MP1 crystal orientation on its oxygen permeability

The effect of crystal orientation on the stretched-recrystallized multilayer film’s gas permeability was investigated by measuring its oxygen permeability. The data were listed in Table 1.4 & Table 1.5. A two-component series model was used to calculate the effective permeability of P4MP1 layer. The example below used a
sPS-PPS/P4MP1 50/50 composition multilayer film to show the calculation process.

\[
P_{Film} = \left( \frac{\Phi_{P4MP1}}{P_{P4MP1}} + \frac{1 - \Phi_{P4MP1}}{P_{sPS-PPS}} \right)^{-1}
\]  
(1.3)

Where \(\Phi_{P4MP1}\) is the volume fraction of P4MP1, which is 50% here. \(P_{P4MP1}\) and \(P_{sPS-PPS}\) are the oxygen’s permeability of P4MP1 and sPS-PPS controls, respectively.

Uniaxial stretching of extruded sPS-PPS/P4MP1 multilayered films at 105 °C generated holes in sPS-PPS layers, which increased gas permeability of sPS-PPS layer. Equation (1.3) was, therefore modified to account the drastically increased permeability of the sPS-PPS blend layers, shown below as Equation (1.4).

\[
P_{Film} = \left( \frac{\Phi_{P4MP1}}{P'_{P4MP1}} + \frac{1 - \Phi_{P4MP1}}{P'_{sPS-PPS}} \right)^{-1}
\]  
(1.4)

Where \(\Phi_{P4MP1}\) is the volume fraction of P4MP1, which is 50%. \(P'_{P4MP1}\) and \(P'_{sPS-PPS}\) are the oxygen permeability of stretched P4MP1 control and stretched sPS-PPS control, respectively.

Uniaxial stretching by MTS at 105 °C had no effect on oxygen permeability of P4MP1 in its control but had dramatic impact on the permeability of sPS-PPS control (Table 1.4). Therefore, the increase of multilayer film oxygen permeability was only due to the increased porosity of sPS-PPS layers. By bringing the values of \(P'_{P4MP1}\) and \(P'_{sPS-PPS}\) into equation (1.4), the calculated oxygen permeability values for multilayer films were consistent with measured values (Table 1.4).

Oxygen permeability of stretched sPS-PPS control kept nearly unchanged after the “melt and recrystallization process”, which has been discussed before (Table
Thus any changes to the sPS-PPS/P4MP1 stretched-recrystallized multilayer film’s permeability should have resulted only from P4MP1’s crystal orientation. As shown in Figure 1.7c, 1.7g, 1.7i, the WAXS pattern suggested an in-plane orientation of P4MP1 crystals. This crystal orientation is hypothesized to align the open channels in P4MP1 crystals perpendicular to the film surface. Since oxygen’s diameter is ~3.5Å, smaller than P4MP1’s 4 Å open channel diameters, oxygen molecules should have diffused through the channels within P4MP1’s crystals. These channels, thus, reduced gas tortuosity across these films. As we predicted, the stretched-recrystallized sPS-PPS/P4MP1 multilayer films showed increased oxygen permeability compared to the stretched multilayer films. (Table 5). By rearranging Equation 1.4, an expression for determining the effective oxygen permeability of P4MP1 layer (P_{P4MP1,eff}) in sPS-PPS/ P4MP1 stretched-recrystallized multilayer film systems was produced as Equation (1.5).

\[
P_{P4MP1,eff} = \Phi_{P4MP1} \left( \frac{1}{P_{\text{Film}}^n} - \frac{1 - \Phi_{P4MP1}}{P_{sPS-PPS}^n} \right)^{-1}
\]

(1.5)

Where \( P_{\text{film}}^n \) is the measured stretched-recrystallized film permeability, \( \Phi_{P4MP1} \) is the volume fraction of P4MP1, \( P_{sPS-PPS}^n \) is the tested permeability of sPS-PPS control after melt and recrystallization process. The effective oxygen permeability of P4MP1 was then calculated as 73.1 barrer (Table 5).

\[
P_{P4MP1,eff} = 0.5 \left( \frac{1}{77.6} - \frac{1 - 0.5}{82.5} \right)^{-1} = 73.1 \text{Barrer}
\]

This value was much higher than P4MP1’s extruded control oxygen permeability.
which was measured at 29.0 barrer. This result suggested P4MP1’s permeability is a function of its crystal orientation. Consistent with these data, the sPS-PPS/P4MP1 70/30 composition system yielded similar results, shown in Table 1.4 and Table 1.5.

These results supported our hypothesis that in-plane oriented P4MP1 crystals could improve the gas flux of extruded films. Due to the interesting channel-contained crystalline structure of P4MP1, this multilayered film could be very useful as gas separation membranes. Especially, P4MP1 is already widely used in industry for its transparency, thermal stability, and chemical-resistant properties.

1.4 Conclusions

Multilayer films of sPS-PPS/P4MP1 were produced and exhibited in-plane oriented crystals as a result of P4MP1 melt recrystallization in confined nanolayered films. These films were uniaxially stretched to produce pores only in the sPS-PPS layers by exploiting the two polymers’ immiscible nature. This step was done to increase the permeability of the sPS layer to a value higher than P4MP1 so any effect of P4MP1’s channel orientation on gas permeability would be unmasked in these multilayer films. The P4MP1 layers of these multilayer films exhibited much higher (~3X) oxygen permeability than its control due to aligning P4MP1’s open channels perpendicular to the film surface. The reported channel diameter of P4MP1 is about 4 Å, bigger than oxygen molecule, which is around 3.5 Å. This size difference, P4MP1 channel orientation perpendicular to the film, porous sPS-PPS layers, allowed higher oxygen fluxes across these multilayered films.
1.5 References


Table 1.1
Thermal properties of polymer controls

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<th>Material</th>
<th>Melting temperature °C</th>
<th>Crystallization temperature °C</th>
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<td>P4MP1</td>
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<td>209</td>
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<tr>
<td>sPS</td>
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<td>PPS</td>
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Table 1.2
Multilayer film systems produced in the paper

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<th>Systems (sPS-PPS)/P4MP1</th>
<th>Number of Layers</th>
<th>Film Thickness (µm)</th>
<th>P4MP1 Thickness (nm)</th>
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</thead>
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<td>50, 150</td>
<td>400, 1200</td>
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</tr>
<tr>
<td>90/10</td>
<td>129</td>
<td>50, 150</td>
<td>80, 240</td>
</tr>
<tr>
<td>Material</td>
<td>Oxygen Permeability (Barrer)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------------------------</td>
<td>-----------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extruded P4MP1 control</td>
<td>29.0±0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extruded sPS control</td>
<td>3.0±0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extruded PPS control</td>
<td>1.2±0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extruded sPS-PPS control</td>
<td>2.3±0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extruded 50 µm 129-layer P4MP1/sPS-PPS</td>
<td>5.4±1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recrystallized 50 µm 129-layer P4MP1/sPS-PPS</td>
<td>5.6±1.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 1.4
Oxygen permeability for stretched samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>P4MP1 layer thickness (nm)</th>
<th>Oxygen Permeability (Barrer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretched P4MP1 control</td>
<td>/</td>
<td>29.0±0.6</td>
</tr>
<tr>
<td>Stretched sPS-PPS control</td>
<td>/</td>
<td>81.2±1.9</td>
</tr>
<tr>
<td>Stretched 129-layer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sPS-PPS/P4MP1 50/50 film</td>
<td>400</td>
<td>44.0±9.6</td>
</tr>
<tr>
<td>tested Final film 50 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stretched 129-layer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sPS-PPS/P4MP1 50/50 film</td>
<td>400</td>
<td>42.8</td>
</tr>
<tr>
<td>calculated Final film 50 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stretched 129-layer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sPS-PPS/P4MP1 70/30 film</td>
<td>240</td>
<td>49.0±5.3</td>
</tr>
<tr>
<td>tested Final film 50 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stretched 129-layer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sPS-PPS/P4MP1 70/30 film</td>
<td>240</td>
<td>53.8</td>
</tr>
<tr>
<td>calculated Final film 50 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Samples</td>
<td>Oxygen permeability of P4MP1 layer calculated (Barrer)</td>
<td>Oxygen permeability of total film tested (Barrer)</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>-------------------------------------------------------</td>
<td>---------------------------------------------------</td>
</tr>
<tr>
<td>Stretched-recrystallized sPS-PPS/P4MP1 50/50 composition</td>
<td>73.1</td>
<td>77.6±11.6</td>
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<tr>
<td>Stretched-recrystallized sPS-PPS/P4MP1 70/30 composition</td>
<td>80.5</td>
<td>81.0±9.6</td>
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<tr>
<td>Stretched-recrystallized sPS-PPS blend control</td>
<td>/</td>
<td>82.5±1.7</td>
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<td>Extruded P4MP1 control after annealing</td>
<td>/</td>
<td>27.2±0.5</td>
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<tr>
<td>Stretched P4MP1 control after annealing</td>
<td>/</td>
<td>27.6±0.3</td>
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Table 1.6
ΔH values of P4MP1 in sPS-PPS/P4MP1 50/50 (v/v) extruded multilayer films, recrystallized multilayer films, stretched multilayer films and stretched-recrystallized multilayer films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>ΔH values of the P4MP1’s melting j/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruded film</td>
<td>4.11</td>
</tr>
<tr>
<td>Recrystallized film</td>
<td>4.08</td>
</tr>
<tr>
<td>Stretched film</td>
<td>4.13</td>
</tr>
<tr>
<td>Stretched-recrystallized film</td>
<td>4.09</td>
</tr>
</tbody>
</table>

Note: After normalizing by the weight fraction, every delta H value should be at least twice of the figure listed above.
Fig. 1.1 Schematic drawing of the channels between P4MP1 molecular chains
**Figure 1.2.** Layer-multiplying coextrusion process. The polymer melts are combined in the ABA feedblock. The figure illustrates how two elements multiply the number of layers from 3 to 9.
Figure 1.3. DSC thermograms of extruded 129-layer sPS-PPS/P4MP1 50/50 film.
Fig. 1.4 2-D WAXS patterns of
a) extruded 129 layer 50 µm (sPS-PPS)/P4MP1 50/50 composition film,
b) extruded 129 layer 50 µm (sPS-PPS)/P4MP1 70/30 composition film,
c) extruded 129 layer 50 µm (sPS-PPS)/P4MP1 90/10 composition film,
d) extruded 50 µm P4MP1 control.
Fig. 1.5 2-D WAXS patterns of recrystallized (sPS-PPS)/P4MP1 50/50 multilayer samples with different P4MP1 thickness.

a) extruded 129 layer 150 µm film,
b) extruded 129 layer 50 µm film,
c) recrystallized 129 layer 150 µm film,
d) recrystallized 129 layer 50 µm film.
Fig. 1.6 2-D WAXS patterns of recrystallized (sPS-PPS)/P4MP1 50/50 multilayer samples at different temperature.

a) recrystallized 129 layer film at 215 °C,
b) recrystallized 129 layer film at 200 °C,
c) recrystallized 129 layer film at 180 °C,
d) recrystallized 129 layer film at 160 °C.
Fig. 1.7 2-D WAXS patterns of 50µm samples

- a-c) extruded, stretched, stretched-recrystallized 129 layer
  (sPS-PPS)/P4MP1 50/50 film,
- d-f) extruded, stretched, stretched-recrystallized 129 layer
  (sPS-PPS)/P4MP1 70/30 film,
- g-i) extruded, stretched, stretched-recrystallized 129 layer
  (sPS-PPS)/P4MP1 90/10 film.
Fig. 1. AFM phase images of partial cross-sections of
(a) extruded (50/50) sPS-PPS/P4MP1 150 µm multilayered film,
(b) extruded (50/50) sPS-PPS/P4MP1 50 µm multilayered film,
(c) stretched (50/50) sPS-PPS/P4MP1 50 µm multilayered film and
(d) stretched-recrystallized (50/50) sPS-PPS/P4MP1 50 µm multilayered film.
Fig. 1.9 SEM phase images of
(a) stretched sPS-PPS/P4MP1 50/50 multilayered film surface image,
(b) stretched sPS-PPS/P4MP1 50/50 multilayered film cross section image,
(c) stretched-recrystallized sPS-PPS/P4MP1 50/50 multilayered film surface image and
(d) stretched-recrystallized sPS-PPS/P4MP1 50/50 multilayered film cross section image.
CHAPTER 2

The Effect of Confined Crystallization on High-density Poly(ethylene) Lamellar Morphology

2.1 Introduction

Intensive research activities have been applied to polyethylene (PE) in the past several decades [1-14]. Crystallization behaviors and crystalline morphology of polyethylene have been extensively investigated in various systems by different methods [1-5, 7-17]. Confined crystallization of polyethylene block copolymers has been reported repeatedly [16, 17]. However, long range one-dimensional (1-D) confined crystallization of polyethylene by a hard polymer in co-extruded thin multilayer film systems has not been systematically studied.

Layer multiplying co-extrusion as a complementary way to study polymer crystallization confinement has been reported recently [18]. A variety of polymers were co-extruded to fabricate multilayer films with hundreds or thousands of alternating layers. This technique offers the flexibility of choosing confining polymers and confined polymers. It also enables people to easily tailor the polymer layer thickness. Confined crystallizations of different semi-crystalline polymers in the multilayer film systems were systematically studied [19-24]. Large aspect ratio, in-plane oriented, single lamellae of poly (ethylene oxide) (PEO) and poly(ε-caprolactone) (PCL) were achieved in extruded multilayer films [19-21]. This
structure dramatically reduces gas permeability through the overall multilayer films [19-21].

It would be extremely interesting if in-plane oriented polyethylene single lamellae can be achieved, especially for high-density polyethylene (HDPE). It is well known that HDPE has good oxygen gas barrier and water vapor barrier properties and is widely used as an inexpensive packaging material. In-plane oriented lamellae of HDPE should improve its gas barrier properties significantly. In order to achieve this goal, a systematic study of HDPE crystallization behavior under confinement in multilayer systems is required. Polystyrene (PS) against HDPE multilayer films has previously been studied [12-14]. However, PS with a Tg of 105 °C cannot really confine HDPE layers during the extrusion process.

HDPE with high crystallinity (~65%) was therefore coextruded with polycarbonate (PC) and polysulfone (PSF) separately. The high Tg of PC and PSF permit melt and recrystallization experiments to be conducted. This gives us the best chance to investigate the lamellae orientation of HDPE in extremely thin layers.

The effects of isothermal crystallization temperature and HDPE layer thickness on HDPE lamellae orientation are carefully studied in this paper. Instead of in-plane oriented lamellae a highly oriented and twisted HDPE lamellar morphology was observed when HDPE layers recrystallized at high temperature (128 °C) against high Tg confining polymers. In other words, the stem of HDPE lamellae rotate [4] in confined layers. It has been widely reported that polyethylene can have twisted lamellar or banded spherulites morphology [4, 9-11, 25]. However, it was also
recognized that reducing layer thickness of HDPE (from micro-scale to nan-scale) could inhibit the twisting of HDPE lamellae in multilayer films [14]. This may be the first time that anyone has created highly twisted HDPE lamellae in 30 nm thick layers. The causes of the lamellar twisting are still controversial, which has been nicely and carefully discussed in a review paper written by Bernard Lotz and Stephen Z.D. Cheng in 2005 [26]. Isothermal recrystallization at such a high temperature is possibly responsible for the twisted morphology of HDPE lamellae in our extremely thin layers and will be discussed in this study. Our observation and discussion should contribute to the cause of lamellar twisting in a general way.

The relationship between the twisted HDPE lamellar morphology and its gas permeability is also studied in this paper. Water vapor transport rate and oxygen permeability were used to check the structure–property relationships of the HDPE nano-layers.

2.2 Materials and experiments

High-density polyethylene (grade Surpass 167) with density of 0.967 g/cm³ (HDPE) was produced by Nova Chemical USA. Polycarbonate (PC) (grade number Apec 1745) was obtained from Bayer Material Science. Polysulfone (PSF) (grade Udel 3700) was obtained from Solvay Company, USA. The thermal properties of these resins are listed in Table 2.1.

A forced-assembly, layer multiplication coextrusion process describe somewhere else [18] was used to fabricate multilayer films of 257 alternating layers
of PC and HDPE and also used to fabricate the 257 alternating layers of PSF and HDPE films. The process is demonstrated in diagram in Figure 2.1. The coextrusion condition was selected on viscosity compatibilities of each pair of polymers. A Kayeness Galaxy 1 melt flow indexer (MFI) was used to check the polymer viscosity as a function of temperature at a shear rate of 10 s⁻¹. These measurements determined that the optimum multilayer coextrusion temperature for PC/HDPE systems is 285 °C and the optimum temperature for PSF/HDPE systems is 290 °C.

All multilayer films were collected by the film take-off roll to control the final film thickness. The film take-off roll temperature was held constant at 80 °C while collecting all films. The film thickness and corresponding HDPE layer thickness are listed in Table 2.1.

Melt and recrystallization experiments were carried out on extruded multilayer films under different temperatures. The multilayer films were heated to the specified temperatures in order to melt the HDPE layers and then were quenched to specified temperatures for isothermal recrystallization for different lengths of time. The details of these experiments will be discussed later in the result and discussion section.

Atomic force microscopy (AFM) was employed to investigate the layered structures of extruded multilayer films and recrystallized multilayer films. Multilayered samples were embedded in epoxy (5 Minute Epoxy, Devcon, Rivera Beach, FL) and cured for 24 hours at room temperature. Cross sections were microtomed after cooling the samples to -120 °C in liquid nitrogen. AFM images were obtained with a commercial scanning microscope probe (Nanoscope IIIa, Digital
Instruments, Santa Barbara, CA) with normal tapping mode. The spring constant was 50 N/m and resonance frequency was in the 284-362 kHz. Both phase and height images of the cross sections were recorded simultaneously.

The thermal properties of selected samples were characterized using a Perkine Elmer (Boston, MA) Pyris differential scanning calorimeter (DSC) unit at a heating/cooling rate of 10 °C/min.

Two-dimensional (2-D) Wide Angel X-ray (WAXS) patterns were obtained with a rotating anode X-ray generator (Rigaku, Woodlands, TX), which produced a beam of monochromatic Cu Kα radiation (λ=0.154 nm). The X-ray generator operated at 45 kV and 0.88 mA. Small ribbon like specimens were cut from the multilayered and then aligned parallel to the x-ray beam by tightly attaching to the x-ray sample holder.

Oxygen flux J(t) rates for selected samples were characterized with a MOCON (Minneapolis, MN) OxTran 2/20 unit. The experiments were conducted in 1 atmosphere pressure at 23 °C (+0.1) with a 0% relative humidity. The instrument was calibrated at 23 °C with a NIST-certified Mylar film with known oxygen transport characteristics. Oxygen permeability, $P(O_2)$, were calculated from steady-state flux, J, rates.

$$ P(O_2) = J \frac{l}{\Delta p} $$

Where $l$ is the overall film thickness and $\Delta p$ is oxygen’s partial pressure drop across the film. The average reported $P(O_2)$ values were taken from at least two samples. $P$ values are reported in Barrer units. One Barrer equals to $10^{-10}$ (cm$^3$ O$2$ ) cm cm$^{-2}$.
Water Vapor Transport Rates (WVTR) for selected samples were measured with a MOCON (Minneapolis, MN) PERMATRAN W 3/33 unit. The experiments were conducted in 1 atmosphere pressure at 37.8 °C (+0.1) with a 100% relative humidity. The instrument was calibrated at 37.8 °C with a NIST-certified Mylar film with known water vapor transport characteristics.

2.3 RESULTS AND DISCUSSION

2.3.1 Morphology of HDPE after extrusion:

WAXS was used to check crystal orientation of HDPE layers in coextruded PC/HDPE multilayer films. The X-ray beam was aligned at the transverse direction (TD) of the extruded film. HDPE layer thickness is ~30 nm in this study.

The TD WAXS images of extruded HDPE control and extruded 40 µm PC/HDPE multilayer film exhibited clear reflection rings of HDPE (110) and (200) planes, seen in Figure 2.2a and Figure 2.2b. The extruded PC control showed halos with no distinctive reflection rings as PC is an amorphous polymer.

The innermost ring (2θ≈21.79°) represents the (110) plane of HDPE crystal. The outer ring (2θ≈24.20°) represents the (200) plane of HDPE crystal [4, 12, 14, 27]. Isotropic orientation was achieved for bulk HDPE control. However, for the coextruded PC/HDPE multilayered film, on-edge orientation of HDPE crystals was observed [13, 14]. This was confirmed by a pair of vertical reflection arcs of HDPE (200) crystal plane in the WAXS pattern. This implies that the a-axis of HDPE crystal
is perpendicular to the film surface (or at the film normal direction ND), while the c-axis should be parallel to the film surface. In this paper, we defined the long axis (HDPE lamellae growing direction) as the b-axis [12], the chain folding direction as the c-axis. The schematic drawing is listed in Figure 2.2.

HDPE crystallized quickly during the cooling of extrusion process. Because of the hard glassy confining layers, confined crystallization of HDPE occurred. However, in-plane orientation was not achieved immediately after the extrusion process. Instead, on-edge orientation was obtained. This is different from many other polymers in multilayer systems reported before [19-24]. As mentioned earlier, it will be interesting, if in-plane orientation of HDPE crystal can be achieved. Therefore, the melt and recrystallization process was utilized. According to previous research, crystallizing at relatively high temperature can usually lead to in-plane orientation of polymer crystals [19-24]. By using the melt and recrystallization process, isothermal crystallization temperature and recrystallization time can be easily controlled.

2.3.2 Morphology of confined HDPE in PC/HDPE system:

The effect of crystallization condition on HDPE lamellar morphology

Melt and recrystallization experiments were carried out on extruded PC/HDPE multilayer films, which allowed the effects of HDPE layer thickness and isothermal recrystallization temperature on HDPE crystal orientation to be systematically studied.

Based on the DSC thermograph shown in Figure 2.3, 155 °C was identified as
the preferential HDPE layer melting temperature. Since 155 °C is roughly 25 °C higher than HDPE’s melting temperature and about 20 °C lower than PC’s glass transition temperature, HDPE will be fully melted when the confining layers of PC remain solid and hard.

Coextruded 40 μm 257 layer PC/HDPE (90v %/10v %) film was used in this experiment. The HDPE layer thickness of ~30 nm is close to the size scale of the HDPE lamellar thickness [12]. Small pieces of PC/HDPE films were heated at a rate of 10 °C/min to 155 °C to fully melt the HDPE layers. Next, the films were separately quenched to 128 °C and 110 °C by a cooling rate of 200°C/min after they had been kept at 155 °C for 20 minutes. Then, the melted HDPE layers recrystallized against hard confining layers of PC at 128 °C and 110 °C separately. Because 128 °C is very close to the melting peak of HDPE, the crystallization rate of HDPE could be extremely slow at such a high temperature. The film recrystallized at 128 °C was then held at 128 °C for 60 hours to make sure HDPE crystallization was complete. The film recrystallized at 110 °C was held at 110 °C for 2 hours to finish the recrystallization process. These experiments were performed in a Perkin DSC Pyris unit.

After melt and recrystallization procedure, these films were slowly cooled to room temperature at a cooling rate of 10 °C/min. Both Transverse Direction (TD) and Extrusion Direction (ED) WAXS patterns of these recrystallized samples were obtained, which are shown in Figure 2.4. After melt and recrystallization there is no difference between TD and ED for the HDPE layers because the heat history from
extrusion was completely removed. The TD and ED WAXS patterns therefore are identical for every sample.

The reflection of the HDPE (200) plane plays a key role in determining the crystal orientation of HDPE here. As we mentioned above, the reflection of the HDPE (200) plane is correlated to the $a$-axis of the HDPE crystal [12].

We observed that the PC/HDPE multilayer film recrystallized at 128 °C showed a different X-ray pattern from the extruded PC/HDPE film, while the PC/HDPE film recrystallized at 110 °C showed the same X-ray pattern as the extruded PC/HDPE film. The major difference between the film recrystallized at 128 °C and the extruded film, lies in the (200) reflection plane of the HDPE lamellae ($2\theta \approx 24.20$). The extruded PC/HDPE film (Figure 2.4a) and PC/HDPE multilayer film recrystallized at 110 °C (Figure 2.4b) showed ordinary on-edge orientation, which was confirmed by the vertical scattering arcs from the HDPE (200) plane. However, for PC/HDPE multilayer film recrystallized at 128 °C, each scattering concentration of the (200) plane, split into three arcs (Figure 2.4c). More interestingly, the $\pm 40^\circ$ reflection showed much stronger intensity than the reflection at film normal direction (ND). These three orientations of the $a$-axis directly indicated that a few $a$-axes are still at ND but most are at $\pm 40^\circ$ away to the ND. In other words, most part of the lamellae stem tilted and, as a result, it is quite possible that the lamellae rotate [11]. The splits of (200) plane or the tilted chains suggested a possible rotation (twist) of HDPE lamellae, which was also observed by A. Keller etc. in a different experiment [4].
In order to confirm the different HDPE lamellae orientations between the coextruded PC/HDPE film and PC/HDPE film recrystallized at 128 °C, 1-D profile of WAXS and azimuthal scans of the HDPE (200) plane and the HDPE (110) plane are plotted and compared in Figure 2.5. By doing this, we can accurately confirm the degree of chain titling.

The 1-D X-ray profile (Figure 2.5a) shows the same reflection planes of coextruded PC/HDPE film and PC/HDPE film recrystallized at 128 °C. The (200) plane and (110) plane yielded the same 2θ values for both samples. The azimuthal scan of HDPE (110) (Figure 2.5c) also showed similar intensity peaks as observed from the 2-D WAXS pattern. However, as mentioned above, the (200) plane (Figure 2.5b) showed very different peaks for extruded PC/HDPE film from PC/HDPE film recrystallized at 128 °C. Based on the (200) azimuthal scan, it is clear that the PC/HDPE multilayer film recrystallized at 128 °C showed two maxima intensity at ± 40° to the ND (φ=140° or φ=220°). It also showed some intensity at ND but weaker than the intensity of the peaks at ± 40°, which is consistent with our previous arguments that most of the a-axis shifted.

After comparing our results with existing literatures [4, 9-12], we speculate that the shift of HDPE crystal a-axis may be a result of lamellar twisting. We defined the lamellae growing direction as its crystal b-axis [12]. The b-axis is in a plane parallel to the film surface and the a-axis is supposed to be perpendicular to the film surface [12]. If HDPE lamellae partially helically twist along the b-axis at a certain angle, such as 40°, as a result, HDPE lamellae stem will tilt for about 40°. This should
let the \( a \)-axis to shift \( \pm 40° \) to the film normal direction (ND). If this is the case, the twisted lamellar morphology is fully responsible for 3 maxima scattering concentrations of the (200) plane. Besides, when most of the HDPE lamellae twist (or most part of each lamella twist), the \( a \)-axis intensity at \( \pm 40° \) will be greater than the intensity at ND. In other words, the number of twisting per HDPE lamella determines the intensity of the 3 scattering concentrations of HDPE (200) crystal plane.

The schematic drawings are listed in Figure 2.6. Figure 2.6.1a shows the morphology of our sample. HDPE lamellae are highly oriented (on-edge) but \( 40° \) twisted when recrystallized at 128 °C. Figure 2.6.1b shows a possible model of partially twisted HDPE lamellae reported in the literature [12] as a comparison, in which less HDPE lamellae were reportedly twisted (the twisting angle is still 40 °); therefore the intensity at ND is greater than that of the \( \pm 40° \) to the ND. This is different from our sample. In Figure 2.6.1c, it shows the ordinary on-edge orientation of extruded PC/HDPE multilayer film.

However, only WAXS pattern is not enough to confirm the HDPE twisted lamellar morphology. The twisted lamellar is one of the possible explanations for the shift of HDPE crystal \( a \)-axis. AFM was utilized to investigate the HDPE lamellar morphology.

AFM cross section images obtained by normal tapping mode were used to check the HDPE lamellar morphology in PC/HDPE multilayer films.

Figure 2.7a shows the partial cross section of a 40\( \mu \)m thick extruded
PC/HDPE film. Continuous layers of HDPE and PC are observed. On-edge oriented HDPE lamellae are seen too. Figure 2.7b-2.7f are the partial cross section of the recrystallized (at 128 °C) PC/HDPE film with different scan sizes. Continuous layers of HDPE and PC are observed. More importantly, the twisted morphology of HDPE lamellae is clearly seen in all images, which are indicated by the white arrows. For example, in Figure 2.7c, in a 2 μm scale, the HDPE single lamellae twist several times. The twisted lamellae are helical. This morphology hence confirms that the tilting of HDPE a-axis is the result of lamellar twisting. In order to more clearly observe the twisted morphology, figure 2.7f is presented. It is the same image as Figure 2.7e, just with different view angle. Basically, Figure 2.7f is a rotated version of Figure 2.7e so that the 3-D topography can be seen. The twisted lamellae are clearly indicated by the arrows.

Similar twisted HDPE lamellar morphology was also reported for UHMWPE in a solution by Kunez et al. [26]. Based on both WAXS patterns and AFM images, we confirm that when HDPE isothermally crystallizes at high temperature (128 °C) in a confined system, its lamellae on-edge orient and twist.

The question that emerges from this study is why do HDPE lamellae exhibit a twisted morphology only when recrystallized under high temperature (128 °C) when samples that are extruded and recrystallized at low temperature (110 °C) do not show the same twisting of the lamellae. We believe that this is related to the cause of the lamellar twisting in confined spaces. Keith and Padden suggested that uneven surface stress caused the chain tilting [11]. Although this proposal is disputable, in our case,
crystallization of HDPE between rigid glassy substrates apparently is related to the surface stress.

When HDPE isothermally crystallized at high temperature (128 °C), HDPE lamellar thickening occurred [9, 11, 29, 30]. This can be confirmed by the increased melting temperature of HDPE listed in Table 2.3. When thickening happens under high temperature, it increases the HDPE lamellae surface stress [29, 30]. When thickened HDPE lamellae grows against the hard confining material, PC, accumulated surface stress arising from the confinement effect (there is not enough space in layer direction to accommodate HDPE lamellae, surface stress therefore increases due to congestion.) cannot be released unless the lamellae twist. In other words, the HDPE lamellae are forced to rotate to release the surface stress in the confined space. This did not happen when HDPE isothermally crystallized at a lower temperature such as 110 °C or with extruded films, because the relatively faster crystallization rate in these instances resulted in a less orderly molecular packing and thinner lamellae [9, 11, 29, 30]. The increased randomness represented as broad reflections in WAXS patterns (Figure 2.4a & 2.4b) and the thinner lamellae exhibited no basis of twisting when there was enough space.

Our observation that HDPE lamellae do not twist in 30 nm layers with extruded sample is consistent with earlier findings [14], which suggested that the twisting lamellae of HDPE were reduced in nano-layered films after co-extrusion (the process of taking films off the extruder is similar to quenching). Therefore, the twisted lamellar morphology was observed only under high crystallization temperature.
The effect of HDPE layer thickness on its lamellar morphology

We observed that after PC/HDPE film recrystallized at 128 °C, HDPE lamellae showed highly oriented and 40° twisted morphology. This is due to the confinement effect of PC layers on HDPE layers (the confined crystallization increases and accumulates the surface stress). All films used above are 40 μm thick with HDPE layer thickness of ~30 nm, which is very close to its scale of lamellae thickness [12]. The effect of confinement is obvious. We wonder if HDPE layer thickness increases whether the HDPE lamellae can still show the oriented and twisted morphology.

Different PC/HDPE films with different compositions and thicknesses were used to study the effect of HDPE layer thickness on its confined crystallization. All samples used in this study are listed in Table 2.2. HDPE layer thickness varies from 30 nm to 375 nm. All three samples were heated to 155 °C and held there for 20 minutes to fully melt the HDPE layers. Next, these films were quenched to 128 °C and held there for 60 hours to make sure HDPE crystallization was complete. After the recrystallization process was complete, all films were slowly cooled to room temperature. These experiments were performed in a DSC Pyris unit.

TD WAXS was then used to check the lamellar orientation of these three recrystallized PC/HDPE films. In Figure 2.8a, it shows again, the WAXS pattern of PC/HDPE films with HDPE layer thickness of ~30 nm. As discussed before, highly oriented and twisted HDPE lamellar morphology was obtained. This is confirmed by two maxima scattering intensity of the (200) plane at ± 40° to the film normal
direction. When HDPE layer thickness increases, the (200) reflection intensity gradually becomes one wide arc, which implies that the twisted HDPE lamellar morphology disappears. When HDPE layer thickness is 75 nm (Figure 2.8b), the split scattering intensity of HDPE (200) plane can be barely seen. When the HDPE layer thickness is 375 nm, split scattering concentrations of the HDPE (200) plane completely disappears, which suggests an ordinary on-edge orientation. Layer thickness of 375 nm is about 10 times larger than HDPE lamellae thickness, which means the confinement effect is dramatically reduced and the reflection arc is therefore broadened.

Based on experiments above, we believe that when HDPE layer thickness is ~30 nm, HDPE lamellae thickened and were forced to twist to release the accumulated surface stress under high crystallization temperature. However, as HDPE layer thickness increases there is enough space for HDPE lamellae to release the surface stress during the slow crystallization process. No surface stress will be accumulated. In other words, slow crystallization in an open space permits HDPE lamella to freely packing orderly so that the surface stress can be released. Similar observation was made for LLDPE by D.C. Bassett et al [29, 30]. The authors claimed that slower growth allowed lamellae pack orderly so twisting has no origin [29]. But the situation is different when HDPE crystallized in extremely thin layers. Our observation suggests that the combination of slow lamellar growth, lamellae thickening and confinement by hard polymers will result in an increase of surface stress. As a response, HDPE lamellae have to twist to release the surface stress caused
by confinement effect.

2.3.3 Morphology of confined HDPE in PSF/HDPE system:

It is clear that HDPE layers can be confined by high Tg PC layers. We wonder whether the glassy substrate plays a role in confining HDPE lamellae. Therefore, high Tg PSF was used to coextrude with the same HDPE.

Polysulfone (PSF) has a glassy transition temperature of 184 °C, which is quite similar to high Tg PC. The 40 μm thick 257 layer PSF/HDPE 90/10 film was used in this study. HDPE layer thickness is ~30 nm in this PSF/HDPE film, which is the same as used in the PC/HDPE film. The same melt and recrystallization experiment was carried out on the PSF/HDPE film. PSF/HDPE film was first heated to 155 °C and held for 20 minutes (165 °C was also tried, but no difference was observed). Next, the film was quenched to 128 °C and isothermally crystallized at 128 °C for 60 hours in the Perkin DSC Pyris unit.

WAXS was again used to check the HDPE lamellae orientation. For PSF/HDPE 90/10 film, the result was similar to the PC/HDPE experiment above. See (Figure 2.9a). After recrystallization at 128 °C, 30 nm thick HDPE layers show the highly oriented and twisted lamellar morphology in the PSF/HDPE system as it did in the PC/HDPE system. It is clear that 1) Hard confining layers are necessary to produce twisted HDPE lamellae. 2) High recrystallization temperature and thin layer are both responsible for the HDPE twisted lamellar morphology.
2.3.4 Effect of twisted HDPE lamellar morphology on its gas barrier properties:

Based on previous research results, we know that when in-plane oriented lamellar morphology was achieved in multilayer films, gas permeability of these multilayer films will be reduced dramatically [19-21]. We wonder whether the twisted lamellar morphology has any effects on the film gas permeability properties.

The 40 um 257 layer PC/HDPE (90/10 composition) film was selected in this permeability study. The film was heated to 155 °C and recrystallized at 128 °C in an oil bath so that we have a large enough sample to perform the permeability tests. The recrystallized PC/HDPE film was masked by alumina masks purchased from Mocon Inc. The test area of masked film is 5 cm².

Oxygen gas permeability and water vapor transport rate were separately measured by a Mocon Oxtran 2/22 unit and a Mocon PERMATRAN W 3/33 unit. The results are listed in Table 2.3.

The WVTR of PC/HDPE film recrystallized at 128 °C was reduced ~3 times compared to extruded PC/HDPE film. The oxygen permeability of PC/HDPE film recrystallized at 128 °C was reduced ~2 times compared to extruded PC/HDPE film. The crystallinity of the HDPE layer also increased from 39% to 47%. The ΔH₀ for calculating HDPE crystallinity from DSC in this paper is 293 J/g [31]. It is difficult to have an extruded control that has exactly 40% crystallinity. Therefore, we have to conclude that the decrease in gas permeability of PC/HDPE film recrystallized at 128 °C is due to both the twisted HDPE lamellar morphology and the increased crystallinity of HDPE.
2.4 Conclusions

Highly (on-edge) oriented and 40° twisted HDPE lamellae were achieved in an HDPE/PC nanolayered film system. This twisted HDPE lamellar morphology is a result of confined crystallization when HDPE layers are extremely thin (~30nm) and recrystallize under high temperature (128 °C). This may be the first time that HDPE lamellae were seen to be highly twisted in such a confined space under high isothermal crystallization temperature. Similar twisted lamellar morphology of the same HDPE was also observed in a HDPE/PSF system.

The reason for twisting is because thickened HDPE lamellae must find a way to release the surface stress accumulated from the confinement by confining layers. Confined in thin layers, HDPE lamellae are forced to twist. High isothermal crystallization temperature and small enough layer thickness are required to achieve this morphology. These results support the concept that, at least, for HDPE, surface stress plays an important role in lamellar twisting.

It was also found that the twisted lamellar morphology and the increased crystallinity of HDPE layers, improves the gas and water vapor barrier properties of the multilayer films by ~3 times for water vapor transport and ~2 times for oxygen permeability.
2. 5 References


<table>
<thead>
<tr>
<th>Material</th>
<th>Melting/Glassy transition temperature °C</th>
<th>Crystallization temperature °C</th>
</tr>
</thead>
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<tr>
<td>HDPE</td>
<td>131</td>
<td>120</td>
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<tr>
<td>PSF</td>
<td>184</td>
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<tr>
<td>PC</td>
<td>172</td>
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Table 2.2
PC/HDPE multilayer films used to study the effect of HDPE layer thickness on the confinement effect.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Composition v/v</th>
<th>Number of Layers</th>
<th>Film Thickness (µm)</th>
<th>HDPE Thickness (nm)</th>
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<tbody>
<tr>
<td>PC/HDPE</td>
<td>90/10</td>
<td>257</td>
<td>40</td>
<td>~30</td>
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<tr>
<td>PC/HDPE</td>
<td>90/10</td>
<td>257</td>
<td>100</td>
<td>~75</td>
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<tr>
<td>PC/HDPE</td>
<td>50/50</td>
<td>257</td>
<td>100</td>
<td>~375</td>
</tr>
<tr>
<td>Sample</td>
<td>( P_{\text{H}_2\text{O}} ) g.mil/100in(^2) day</td>
<td>( P_{\text{O}_2} ) Barrer</td>
<td>HDPE layer crystallinity %</td>
<td>HDPE melting peak from DSC °C</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-----------------------------------------</td>
<td>----------------------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>HDPE control</td>
<td>0.13±0.04</td>
<td>0.23±0.01</td>
<td>65</td>
<td>131</td>
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<tr>
<td>PC control</td>
<td>16.5±0.5</td>
<td>1.3 ± 0.1</td>
<td>/</td>
<td>/</td>
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<tr>
<td>Extruded film (40 µm)</td>
<td>5.3±0.2</td>
<td>2.9±0.2</td>
<td>39</td>
<td>131</td>
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<tr>
<td>Recrystallized at 128 °C (40 µm)</td>
<td>1.8±0.2</td>
<td>1.2±0.1</td>
<td>47</td>
<td>133</td>
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Fig. 2.1 Schematic of multilayer extrusion process showing how 3 layers become 9 layers [16].
Fig. 2.2 2-D WAXS patterns for extruded multilayer samples.

a) extruded HDPE control,
b) extruded 257 layer PC/HDPE multilayer film with 30 nm HDPE layers,
c) extruded PC control.
Fig. 2.3 Melt recrystallization of HDPE layers based on DSC thermograms for PC/HDPE system. The recrystallization temperatures were chosen as 128 and 110 °C.
Fig. 2.4 2-D WAXS patterns for PC/HDPE samples recrystallized at different temperature.
   a) TD pattern of extruded PC/HDPE samples
   b) TD pattern of recrystallized PC/HDPE at 110 C
   c) TD pattern of recrystallized PC/HDPE at 128 C.
   d) ED pattern of extruded PC/HDPE samples
   e) ED pattern of recrystallized PC/HDPE at 110 C
   f) ED pattern of recrystallized PC/HDPE at 128 C.
   The bottom row shows the schematic drawings of the X-ray patterns.
**Fig. 2.5** Analysis of 2-D WAXS pattern for chosen samples. (red curves are for film recrystallized at 128 °C; blue curves are for extruded film)

a) 1-D profile for PC/HDPE film recrystallized at 128 °C and extruded film.

b) Azimuthal scan for HDPE 200 plane of film recrystallized 128 °C and extruded film,

c) Azimuthal scan for HDPE 110 plane of film recrystallized 128 °C and extruded film.
Fig. 2.6.1 Comparison of different HDPE lamella morphology based on X-ray patterns

a) PC/HDPE film recrystallized at 128 °C,
b) PS/HDPE extruded film from ref.12.
c) PC/HDPE extruded film.

Fig. 2.6.2 Schematic drawing of a normal HDPE lamella and a twisted HDPE lamella.
Fig. 2.7 Normal tapping mode AFM phase images for cross section of
a) PC/HDPE extruded film, image size 5µm x5µm,
b) PC/HDPE film recrystallized at 128°C, image size 5µm x5µm,
c) PC/HDPE film recrystallized at 128°C, image size 2µm x2µm,
d) PC/HDPE film recrystallized at 128°C, image size 1.2µm x1.2µm,
e) PC/HDPE film recrystallized at 128°C, image size 1.02 µm x1.02µm,
f) PC/HDPE film recrystallized at 128°C, image size 1.02µm x 1.02µm
with view angle of 46°.
**Fig. 2.8** 2-D WAXS patterns for samples recrystallized at 128 C.

a) 40 um PC/HDPE 90/10 with HDPE layer thickness of 30 nm
b) 100 um PC/HDPE 90/10 with HDPE layer thickness of 70 nm
c) 100 um PC/HDPE 50/50 with HDPE layer thickness of 375 nm
Fig. 2.9 Comparison of 2-D WAXS patterns for recrystallized HDPE confining by different glassy polymers.

a) recrystallized PSF/HDPE at 128 °C,
b) recrystallized PC/HDPE at 128 °C.
CHAPTER 3

The Effect of Confined Spherulite Morphology of High-density Polyethylene and Polypropylene on Their Gas Barrier Properties in Multilayered Film Systems

3.1. Introduction

In recent years, confined crystallization of polymers in multilayer thin film systems has been extensively investigated and reported [1]. The multiplication co-extrusion process [2] has been recognized as an effective way to study one-dimensional (1-D) confined crystallization of polymers in a variety of polymer systems [1, 3-15]. Films with hundreds or thousands of alternating layers of different polymers can be easily prepared by this technique [2-16]. The individual layer thickness within these multilayer films can vary from ~10 nanometers (nm) to several micrometers (μm) [1, 2]. The flexibility of this multiplication co-extrusion technique enables us to study the crystallization behaviors of polymers at different scales. It is well known that when layer thickness decreases, the crystalline morphology of polymers gradually transforms from three-dimensional (3-D) spherulite phases into one-dimensional (1-D) lamellae phases [1]. The 1-D single lamellae of poly (ethylene oxide) (PEO) and poly (ε-caprolactone) (PCL) have already been reported in previous studies [1, 3-5].

The in-plane oriented 1-D single lamellae of PEO and PCL have demonstrated considerably reduced oxygen permeability with layer thickness of ~20 nm [1, 3-5]. In these studies, it is also found that when layer thickness of PEO and PCL is several
hundred nanometers, gas permeability has already been reduced [1, 3-5]. At this scale, in-plane oriented, large aspect ratio, single crystals should have not formed yet. Instead, confined spherulites or crystalline discoids exist [1]. This phenomenon implies that the polymer’s crystalline morphology starts to greatly affect the gas barrier property before the single lamellae appear.

This specific area (confined spherulite) has not been emphasized enough compared to the investigations for single lamellae. Therefore, it would be extraordinarily beneficial to study the relationship between the confined spherulite morphology of polymers and their gas permeability.

As commonly used plastic materials, polyethylene (PE) and polypropylene (PP) have been studied by many scientists for different applications [10-19]. High density polyethylene (HDPE) and PP’s mechanical properties and low production cost would be even more valuable if their gas barrier properties can be further improved due to the confined spherulite morphology within multilayer films. With enhanced gas barrier properties, the multilayer films of HDPE or PP will be excellent for packaging applications. Especially, multilayer structure has already been pervasively used in the packaging industry and extensively reported in patents [20-24], because multilayer structures can reduce the deleterious effects of defects in a single polymer layer.

In this study, multilayer films of HDPE/HP030 (a cyclic olefin copolymer (COC) with nearly no crystallinity) and PP/PC with different layer thickness were fabricated. Confined spherulite morphology of both HDPE and PP were discovered. AFM and wide angle X-ray scattering (WAXS) were used to verify the confined
spherulite morphology of HDPE and PP layers. MOCON units were employed to measure oxygen permeability and water vapor transport rate (WVTR) of these multilayer films. Improvements of gas barrier properties were observed. These results support our hypothesis that the confined spherulite morphology of HDPE and PP increases the tortuosity of the pathway for gas to diffuse.

Moreover, we also observed that HDPE and PP layers showed best barrier properties for both water vapor and oxygen when their layer thicknesses are ~290 nm under confinement. When HDPE or PP layer thickness became thinner or thicker, barrier properties were worsened. It is believed that this a result of compromising from two competing effects. Confined spherulite morphology improves the gas barrier property of HDPE/HP030 and PP/PC multilayered films. However, when layer thickness of HDPE and PP decrease too much, on-edge orientation of crystals becomes dominant, which then starts to deteriorate the barrier property.

### 3.2. Materials and experiments

High density polyethylene (HDPE) with a claimed density of 0.963 g/cm³ was offered by the Dow Chemical Company, USA. HP030, a cyclic olefin copolymer (COC) from Taiwan Synthetic Rubber Corporation, was generously offered by the Dow Chemical Company, USA. HP030 is a transparent and nearly 100% amorphous glassy polymer with good mechanical and good gas barrier properties. Its glassy transition temperature is claimed as ~137 °C, which makes it a suitable confining layer for HDPE. Polypropylene (PP), grade number 1572, was purchased from
ExxonMobil Chemical Company, USA. Polycarbonate (PC), grade number Apec 1702, was purchased from Bayer Chemical Company, USA. The characteristics of these resins are listed in Table 1.

The thermal properties of HDPE resin, HP030 resin, PP resin, PC resin, and extruded multilayer films were all investigated by using a PerkinElmer (Boston, MA) Pyris differential scanning calorimeter (DSC) unit with a heating/cooling rate of 10 °C/min.

Multilayer films of HDPE/HP030 with 33, 65, 129 and 257 alternating layers were fabricated using a forced-assembly, layer multiplication co-extrusion process [2]. Multilayer films of PP/PC with 33, 65, 129 and 257 alternating layers were also prepared by the same layer multiplication co-extrusion technique [2]. A surface layer extruder was used to add skin layers at the end of extrusion process for both HDPE and PP. The same HDPE and PP were used as the skin layer materials for HDPE/HP030 and PP/PC systems, respectively. The additional skin layers were utilized to protect the layered-core structure and could not be removed due to excellent adhesion.

The extrusion process is shown in Figure 1a. The temperature for the coextrusion was selected based on viscosity compatibilities of each pair of polymers. The melt viscosity properties of HDPE, HP030, PP and PC were characterized as a function of temperature by using a Kayeness Galaxy 1 melt flow indexer (MFI) at a shear rate of 10 s⁻¹. An optimum multilayer co-extrusion temperature of 255 °C and
270 °C were identified for the HDPE/HP030 system and PP/PC system respectively. All multilayer film thicknesses were controlled by tuning the speed of the film take-off roll. The film take-off roll temperature was held constant at 80 °C for collecting all films. Figure 1b shows a schematic drawing of the ‘257-layer 1/3 skin HDPE/HP030 (75/25) film’ as an example. This film consists of a layered-core and 2 thick skin layers outside. Skin layers are 1/3 by volume of the overall film, so 2/3 of the film is the layered-core. Layered-core has 257 alternating layers of HDPE and HP030 with the volume fraction of 75% and 25% respectively.

Totally nine different multilayer films of HDPE/HP030 with different number of layers were fabricated. The information is listed in Table 2. The same information for seven PP/PC multilayer films is listed in Table 3.

Oxygen flux J(t) rates for the extruded HDPE control, extruded HP030 control, extruded PP control, extruded PC control and extruded multilayer films, were measured with a MOCON (Minneapolis, MN) OxTran 2/20 unit. The measurements were carried out at 1 atmosphere pressure at 23 °C (+0.1) with a 0% relative humidity for all samples. The instrument was calibrated at 23 °C with a NIST-certified Mylar film with known oxygen transport characteristics. Oxygen permeability, P(O₂), were calculated from steady-state flux, J, rates.

\[
P(O_2) = J \frac{l}{Δp}
\]  

(3.1)

Where \( l \) is the overall film thickness, (in units of ‘mil’, 1 mil=25.4 µm) and \( Δp \)
is oxygen’s partial pressure drop across the film, which is 1 here. The average reported $P(O_2)$ values were taken from at least two samples. $P(O_2)$ values are reported in Barrer units. One Barrer equals to $10^{-10} \text{ cm}^3 \text{ O}_2 \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$.

The WVTR for the extruded HDPE control, extruded HP030 control, extruded PP control, extruded PC control and extruded multilayered films, were all measured with a MOCON (Minneapolis, MN) PERMATRAN-W® Model 3/33 unit. The measurements were carried out at 1 atmosphere pressure at 37.8 °C (+0.1) with a 100% relative humidity for all samples. The instrument was calibrated at 37.8 °C with a NIST-certified Mylar film with known water vapor transport characteristics.

$$P(H_2O) = WVTR \frac{l}{\Delta p}$$

Again, $l$ is the overall film thickness (in units of ‘mil’, 1 mil=25.4 µm) and $\Delta p$ is water vapor’s partial pressure drop across the film, which is 1 here. The average reported water vapor permeability, $P(H_2O)$ values were taken from at least two samples. $P(H_2O)$ values are normalized by the actual measured thickness and reported in the unit of g.mil/100in².day.

The crystalline morphology of HDPE and PP layers was investigated by atomic force microscopy (AFM). For cross section images, the AFM samples were embedded in epoxy (5 Minute Epoxy, Devcon, Rivera Beach, FL) and cured for 24 hours at room temperature. The cross sections were then produced by cooling samples to -120 °C in liquid nitrogen, after which they were microtomed. For HDPE layer surface images, the AFM samples were stuck to a pin like metal holder with the same!
epoxy and cured at room temperature for 24 hours. The samples were then cooled to -120 °C in liquid nitrogen and microtomed from the film normal direction (ND). All AFM images were recorded with a commercial scanning microscope probe (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA) whose spring constant was 50 Nm⁻¹ and resonance frequency was in the 284-362 kHz range. Both phase and height images of the cross sections/layer surface were recorded simultaneously.

Wide angle X-ray scattering (WAXS) was utilized to study the HDPE and PP crystal orientations. All 2-D WAXS patterns were obtained with a rotating anode X-ray generator (Rigaku, Woodlands, TX) with a beam of monochromatic Cu Kα radiation (λ=0.154 nm). The X-ray generator was operated at 45 kV and 0.88 mA.

All the experimental results will be discussed in two separate parts as the first part for HDPE/HP030 system and the second part for PP/PC system.

3.3. RESULTS AND DISCUSSION

3.3.1 Confinement of HDPE in HDPE/HP030 systems.

The effect of HDPE layer thickness on its gas barrier property.

Nine different HDPE/HP030 multilayer films were studied in this paper. All samples used in the permeability study had an overall film thickness of about 1mil (~25.4 μm). The number of layers, layer compositions, HDPE layer nominal thickness and overall crystallinity of these films are all listed in Table 2. The nominal HDPE layer thickness (calculated from the composition and overall film thickness) varied from ~99 nm to ~792 nm. Based on our previous studies, we know that the actual
layer thickness usually has some deviations [2] but it is not regarded as an important factor here. Every multilayer film has thick HDPE skin layers that could not be removed without breaking the layer structure. The thick skins are necessary for protecting the layered-core.

A schematic drawing of the 257-layer 1/3 skin HDPE/HP030 (75/25) multilayer film is shown in Figure 1b as an example. As we can see, a total of 1/3 (each side is 1/6) volume fraction of the multilayer film is HDPE skin. The skin consists of the same HDPE that is used in the layered-core. The layered core is constructed of 257 alternating layers of HDPE and HP030 with a volume fraction of 75 over 25 (HDPE over HP030).

Water transport rates (WVTR) measurement was first conducted on these extruded HDPE/HP030 multilayer films using a MOCON PERMATRAN-W® Model 3/33 unit. The test condition was 37.8 °C (+0.1) with a 100% relative humidity. The 100% relative humidity was achieved by using a wet sponge. The measurements were repeated at least twice for every sample. The direct results from the MOCON unit were the WVTR in the unit of g/100in².day. The WVTR was then normalized by the actual measured film thickness (mil) to get the water vapor permeability value, $P_{(H2O)}$, which is in the unit of g.mil/100in².day. The film thickness used to normalize the $P_{(H2O)}$ was recorded by a Mitutoyo digital micrometer with accuracy of ±0.001mm.

The overall film permeability, $P_{(H2O, \text{ overall})}$ usually follows the series model calculation for layered assemblies. This gives the equation:
\[
\frac{1}{P_{\text{overall}}(\text{H}_2\text{O})} = \frac{\varphi_{\text{HDPE,skin}}}{P_{\text{HDPE,skin}}(\text{H}_2\text{O})} + \frac{\varphi_{\text{HDPE,layers}}}{P_{\text{HDPE,layers}}(\text{H}_2\text{O})} + \frac{\varphi_{\text{HP030,layers}}}{P_{\text{HP030,layers}}(\text{H}_2\text{O})}
\]  

(3.3)

Where \( \varphi_{\text{HDPE,skin}} \), \( \varphi_{\text{HDPE,layers}} \) and \( \varphi_{\text{HP030,layers}} \) are the volume fractions of HDPE skins, HDPE layers and HP030 layers respectively. The sum of these three parameters is 1.0. \( P_{\text{HDPE,skin}}(\text{H}_2\text{O}) \), \( P_{\text{HDPE,layers}}(\text{H}_2\text{O}) \) and \( P_{\text{HP030,skin}}(\text{H}_2\text{O}) \) are the water vapor permeability of the overall film, HDPE skin, HDPE layers and HP030 layers respectively.

It is interesting that all multiplayer films have showed different permeability values (Table 2). These measured results suggest that something has changed morphologically within the multilayer films. Otherwise the water vapor permeability values should remain identical. HDPE layers are expected to be confined by HP030 layers. Therefore the effective HDPE layer water vapor permeability, \( P_{\text{HDPE,layer}}(\text{H}_2\text{O}) \) is possibly the origin of this change. In order to obtain the \( P_{\text{HDPE,layer}}(\text{H}_2\text{O}) \) values, we need make some assumptions: 1) Since HDPE skins are very thick, and are similar to bulk controls, HDPE skin’s permeability should remain the same as the bulk HDPE control. 2) HP030 is a nearly amorphous polymer. It is reasonable to predict that HP030’s permeability should not change observably in layered films.

Based on these assumptions, equation (3.3) can be rewritten as:

\[
P_{\text{HDPE,layer}}(\text{H}_2\text{O}) = \varphi_{\text{HDPE,layer}} \left( \frac{1}{P_{\text{overall}}(\text{H}_2\text{O})} - \frac{\varphi_{\text{HDPE,skin}}}{P_{\text{HDPE,skin}}(\text{H}_2\text{O})} + \frac{\varphi_{\text{HP030,layers}}}{P_{\text{HP030,layers}}(\text{H}_2\text{O})} \right)
\]  

(3.4)

Here, we are going to use 257-layer 1/3 skin HDPE/HP030 (75/25) film as an example to perform the calculation. Water vapor permeability for HDPE control and
HP030 control are 0.20 g.mil/100in$^2$.day and 1.10 g.mil/100in$^2$.day respectively as listed in Table 2. So, $P_{(H_2O, HDPE, skin)}=0.20$ g.mil/100in$^2$.day and $P_{(H_2O, HP030, layers)}=1.10$ g.mil/100in$^2$.day. The HDPE skin accounts for 0.33 (1/3) of total film volume, so $\phi_{HDPE, skin}$ equals to 0.33. The layered-core is therefore 1-0.33=0.67 (2/3), 75% of which is HDPE layer, so $\phi_{HDPE, layers}$ is $0.67 \times 0.75 \approx 0.50$ and $\phi_{HP030, layers}$ is $0.67 \times 0.25 \approx 0.17$. The measured $P_{(H_2O, overall)}$ value for 257-layer HDPE/HP030 with 1/3 skin film is 0.16 g.mil/100in$^2$. Then based on equation (4), we get the $P_{(H_2O, HDPE, layer)}=0.11$ g.mil/100in$^2$.day. This is nearly 2x lower compared with the HDPE bulk control of 0.20 g.mil/100in$^2$.day. It is obvious that effective HDPE layer showed improvements for water vapor barrier properties compared to the HDPE control within this film.

By using equation (3.4), the $P_{(H_2O, HDPE, layer)}$ of all multilayer films were calculated. The results are listed in Table 2, 5th column. As we expected, $P_{(H_2O, HDPE, layer)}$ for all samples were lower than the HDPE bulk control (lower gas permeability means better barrier property), and these calculated values were different from each other. This confirmed that HDPE layers were confined, and the confined HDPE layers resulted in improved water vapor barrier property.

The calculated effective HDPE layers water vapor permeability values, $P_{(H_2O, HDPE, layer)}$, are also plotted as a function of HDPE nominal layer thickness shown in Figure 2. From the curve, it is clearer to see that there is a concave up trend. As the layer thickness decreased, the water vapor permeability of HDPE layer decreased at beginning and reached the minimum value when the layer thickness was ~290 nm.
But, when layer thickness continued decreasing, the water vapor permeability turned around and increased. The minimum water vapor permeability from ‘65-layer 1/2 skin HDPE/HP030 (75/25) film’ actually decreased ~5x compared to the HDPE bulk control.

In order to confirm this phenomenon, oxygen permeability measurements were also conducted on the same multilayer films. The results are shown in Table 2. Based on the same assumptions, by replacing \( P_{\text{H2O}} \) with \( P_{\text{O2}} \) (permeability of oxygen, in the unit of Barrer), equation (3.4) can be rewritten as:

\[
P_{\text{O2,HDPE,layer}} = \frac{1}{P_{\text{O2,overall}}} - \frac{\varphi_{\text{HDPE,skin}}}{P_{\text{O2,HDPE,skin}}} + \frac{\varphi_{\text{HP030,layers}}}{P_{\text{O2,HP030,layers}}} \quad (3.5)
\]

The effective HDPE layer’s oxygen permeability values, \( P_{\text{O2,HDPE,layer}} \) were calculated by equation (3.5). The calculated values are listed in Table 2, 7th column. Similar results to water vapor permeability were obtained. When HDPE layer thickness was at ~290 nm, it showed the minimum oxygen permeability. The effective HDPE layer’s oxygen permeability values, \( P_{\text{O2,HDPE,layer}} \) are also plotted as a function of HDPE layer thickness in Figure 3. The trend is similar to what we have seen in Figure 2.

This is interesting because in previous PEO/PS system [3, 4], the oxygen permeability continues dropping when PEO layer thickness decreases from micro-scale to nano-scale. No such a concave up trend was observed in other semi-crystalline polymeric multilayer film systems. This point will be discussed in details later.
As we assume, HDPE layers have shown improved permeability after being confined in the layers. We know that the HDPE spherulites size are in the micro-scale, and when the layer thickness decreases into a range of 100 nm-800 nm, no spherulites should exist. Instead, the spherulites are squeezed into discords or lamellae bundles. These squeezed spherulites usually increase the tortuosity for gas diffusion. Hence, the crystalline morphology under confinement is most likely to be the reason for the barrier property improvements.

The relationship between HDPE layer morphology and its barrier properties.

A differential scanning calorimeter (DSC) was first used to investigate the HDPE crystallinity in every multilayer film sample, because crystallinity can also affect the gas barrier properties. Since the HDPE skins could not be removed, the $\Delta H$ values from the DSC’s HDPE melting peaks were the sums of layered-core and skin layers. In other words, the HDPE crystallinity calculated based on DSC was the crystallinity for the overall multilayer film, not solely for the layered-core. The $\Delta H$ values were normalized by weight fraction based on the volume fraction and the density of each material. The $\Delta H_0$ (100% crystallinity $\Delta H$ value) used to calculate HDPE crystallinity is 293 J/g in this study [25]. The crystallinity values are listed in Table 2.

We have assumed that the thick HDPE skin layers are similar to the HDPE bulk control. Hence, any change of crystallinity for the multilayer films should arise from the HDPE layered-core. However, no specific trend or significant difference was
observed for the crystallinity. All samples have shown similar crystallinity to HDPE bulk control, which suggest that HDPE crystallinity has nothing to do with the barrier improvements in our system. Therefore, as we mentioned earlier, most likely it is the HDPE confined crystalline morphology that should contribute to the permeability improvements [1].

The sample showing the best barrier properties was hence selected to investigate the crystalline morphology of HDPE layers by atomic force microscopy (AFM). Both cross section and HDPE layer surface images were taken here.

**Figure 4** shows the partial cross section of 65-layer 1/2 skin HDPE/HP030 (75/25) film with HDPE layer thickness of 290 nm. The white line indicates the possible border of HDPE skin and the layered-core. As shown in the image, the border is not distinctive, which suggests that the adhesion between HDPE skin and layered-core is excellent. This is the reason why HDPE skin layers could not be removed. Continuous layers of HDPE and HP030 were observed in the image. Different crystalline morphologies from HDPE skins and HDPE layers were noticed in **Figure 4a**. In the HDPE skin, spherulites spreading out in the layer thickness direction can be seen, which was indicated by a red circle. However, in the HDPE layers, the spherulites were confined and squeezed by the HP030 layers. Therefore, there were only lamellae bundles, or confined spherulites, which were produced by squeezing the spherulites in the layer direction. In other words, HDPE lamellae were forced to tilt down due to the confinement effect of the HP030 layers. The lamellae bundles are more clearly seen in a zoom-in image (**Figure 4b**). By comparing the
diameter of HDPE spherulites in the skin layer and the squeezed spherulites (lamellae bundles) in the HDPE/HP030 layers, it is clear that in the layers, the squeezed spherulites are flattened.

The same sample (different piece of specimen from the same film) was prepared to be microtomed from the film normal direction (ND) in order for the surface morphology of HDPE layers being discovered. The specimen was attached to a specific pin-like metal holder by epoxy and then the film surface was aligned parallel to the microtome knife and cooled down to -120 °C. HDPE skin was cut off by microtome so that the HDPE layers can be exposed. Several trials were conducted in order to make sure the exposed surface is the HDPE layer and not the HP030 layer. The morphology of HDPE and HP030 are different enough that it is easy to tell from the AFM image, which layer is which.

Spherulites are seen from the AFM surface image (Figure 5), which verifies that the HDPE spherulites have transformed from 3-D form into 2-D form (or disks) due to the confinement effect. The lamellae within the confined spherulites were tilted down. The squeezed spherulites behaved like impermeable thin disks dispersed in the HDPE layers, which increased the tortuosity for gas to diffuse through the whole multilayer film. Therefore, the improved gas barrier property of HDPE/HP030 multilayer films is a result of confined and fattened spherulites.

The confined spherulite morphology explains perfectly why the HDPE layer shows lower permeability compared to HDPE bulk control. However, it is still unclear why the maxima improvement for barrier property is shown when the HDPE layer
thickness is around 290 nm. In other words, why doesn’t the permeability continue decreasing when HDPE layer thickness becomes thinner than 290 nm? Again, in previous PEO/PS systems, researchers observed that the permeability continued decreasing as layer thickness decreased [1, 3, 4]. Let us note: when PEO layer thickness went down to about 110 nm, stacked PEO lamellae oriented majorly parallel to film surface [1, 3, 4]. In other words, PEO was in-plane oriented as layer thickness decreased. This implied that the crystal orientation may also contribute here.

Wide angle X-ray scattering (WAXS) was then utilized to check the possible crystal orientations of selected samples. The X-ray beam was aligned parallel to the transverse direction (TD) of the co-extruded films. 257-layer 1/3 skin HDPE/HP030 (75/25) film, 129-layer 1/3 skin HDPE/HP030 (75/25) film, 65-layer 1/2 skin HDPE/HP030 (75/25) film and 65-layer 1/3 skin HDPE/HP030 (75/25) film were selected for this study. All samples had overall film thickness of ~1 mil (~25.4 µm) which yielded nominal HDPE layer thickness of 99, 198, 290 and 380 nm respectively. Reflections from the thick HDPE skins could possibly mask the intensity from the HDPE in the layered-core. Fortunately, differences in the WAXS pattern were observed as shown in Figure 6.

On-edge orientation of HDPE crystals was observed as shown in Figure 6a and Figure 6b. This was confirmed by a pair of vertical reflection arcs for HDPE (200) plane and two symmetric pairs of reflections for HDPE (110) plane [10, 11, 14, 15]. Nominal HDPE layer thickness was 99 and 198 nm for these two samples respectively. When the HDPE layer thickness increased, the on-edge orientation
disappeared. Instead, isotropic reflection rings were observed in Figure 6c and Figure 6d, which implied that the HDPE lamellae were randomly oriented. Based on our previous experience, on-edge orientation is not favorable for gas barrier property because of the relatively larger voids between lamellae [1, 3-5, 12]. In other words, randomization of HDPE lamellae is more favorable for improving gas barrier properties.

Figure 6d and Figure 6e show the WAXS patterns of the extruded HP030 and the extruded HDPE controls. HP030, as a nearly amorphous COC (~2% crystallinity was claimed), showed halos in its WAXS pattern. The HDPE control also showed isotropic reflections implying random orientation of HDPE lamellae, which is similar to the samples with thicker HDPE layers ($\geq$ 290 nm based on our WAXS patterns).

The WAXS patterns suggested that when HDPE layer thickness was below 290 nm, on-edge orientation appeared which is not favorable for a barrier material. This answers why the permeability increases when HDPE layer thickness becomes thinner than 290 nm.

The combination of confined spherulite morphology and lamellar orientation should thoroughly explain why there is a maximum improvement for the effective HDPE layer’s permeability when HDPE layer thickness is ~290nm. When HDPE layers are thick, the confinement effect is moderate, so we start to observe only moderate decreases of both oxygen permeability and WVTR. When HDPE layer thickness continues decreasing to the level of ~290 nm, the lamellae are forced to tilt more, and the decreased gas permeability reaches its maximum. However, when the
HDPE layers become even thinner, lamellae start to orient perpendicular to the film surface (on-edge orientation), which gradually increases the permeability. The concave up trend is a result of these two competing effects.

3.3.2 Confinement of PP in PP/PC systems.

The effect of PP layer thickness on its gas barrier property.

It is interesting to discover that the confined spherulite morphology of HDPE has an effect on its gas permeability. We wonder whether this phenomenon only happens to HDPE or also works for other polyolefin materials. Polypropylene was selected to conduct the same study to verify this observation.

In a previous study, the lamellar morphology of PP was studied as a function of layer thickness in PP/PS multilayer films [13]. However, PS with Tg of 100 ºC is not a good confining substrate for PP (Tm=163 ºC, Tc=120 ºC). PP crystallized against a soft PS in that case. The relationship between PP’s confined spherulite morphology and its gas permeability was not completely built up.

PC was therefore chosen to co-extrude with PP in this study, as PC’s glass transition temperature (172 ºC) allows PP to crystallize under confinement. A series of PP/PC multilayer films with different PP layer thickness were investigated in this section. The layer structure of PP/PC was similar to HDPE/HP030 films. Thick PP skins were used to protect the layered-core and could not be removed. The details of these samples are listed in Table 3.

WVTR and oxygen permeability of the PP/PC multilayer films were tested by
a MOCON PERMATRAN-W® Model 3/33 unit and a MOCON OxTran ® Model 2/20 unit respectively. Similar to previous HDPE/HP030 multilayer film systems, effective PP layer’s water vapor permeability, \( P_{(\text{H}_2\text{O,PP,layer})} \) and oxygen permeability, \( P_{(\text{O}_2, \text{PP, layer})} \) showed lower values (better barrier property) compared to PP bulk control.

The measured overall film water vapor permeability values and calculated effective PP layer’s water vapor permeability values, \( P_{(\text{H}_2\text{O,PP,layer})} \) are shown in Table 3, 4th and 5th column respectively. The 65-layer 1/2 skin PP/PC (75/25) film with PP layer thickness of 290 nm has showed the lowest value. The effective PP layer’s water vapor permeability values, \( P_{(\text{H}_2\text{O,PP,layer})} \) are then plotted as a function of PP layer thickness in Figure 7. A concave up trend is shown in the figure, which is similar to what we have observed for HDPE.

Oxygen permeability was measured for PP/PC multilayer films as well. These results are also listed in Table 3. Similar trend are observed in Figure 8. The 65-layer 1/2 skin PP/PC (75/25) film with PP layer thickness of 290 nm again showed the best barrier property for oxygen as well.

**The relationship between PP layer morphology and its barrier properties.**

It is encouraging that PP has shown the same phenomenon as HDPE showed. When PP layer thickness is around 290 nm, it has the best gas barrier properties for both WVTR and oxygen. Naturally, since PP is quite similar to HDPE in many ways, the crystalline morphology is regarded to be responsible for these experimental
Following the same protocol, DSC was utilized to check the crystallinity of PP first. The overall crystallinity of PP in the PP/PC multilayer films remained the same, which are listed in Table 3. The $\Delta H_o$ (100% crystallinity $\Delta H$ value) used to calculate PP crystallinity is 209 J/g [27] in this study.

AFM cross section images in Figure 9 showed confined PP spherulite in the layers. The PP lamellae were forced to tilt down, which is similar to HDPE’s crystalline morphology in HDPE/HP030 multilayer films. The confined PP spherulites are expected to increase the tortuosity for gas to diffuse through the multilayer films.

WAXS was also used to check the crystal orientation of PP layers. Four multilayer films with PP layer thickness of 99, 145, 290 and 580 nm were investigated. Similar to HDPE in previous section, PP showed on-edge orientation when its layer thickness is smaller than 290 nm. However, when PP layer thickness is at 290 nm and above, isotropic reflections were observed, which suggested that the randomness of PP crystals increased (Figure 10).

These results have suggested that the same mechanism works for both HDPE and PP. The confined spherulite morphology is competing with the lamellar orientation. When PP layers are thin and confined by PC substrates, 3-D PP spherulite disappear. Instead, confined and squeezed PP spherulite form. This morphology increases the tortuosity for gas diffusion. Therefore, PP layers barrier property are improved. As PP layers become thinner and thinner, on-edge orientation of PP starts to be dominant, which gradually deteriorates the barrier properties.
It should be noted that HDPE showed different degree of improvements than PP. For WVTR, HDPE showed 5x improvements (the best one) compared to HDPE control, while PP showed just 2x improvements (the best one). This is possibly because the different crystallinity between HDPE (65-68%) and PP (38-39%). However, for oxygen permeability, both HDPE and PP showed 2x improvements even though they had different crystallinity. The reason remains unknown for this inconsistency. It may relate to the different transport characteristics between water vapor and oxygen when permeating through the HDPE and PP. In other words, the water vapor may be more sensitive to the change of crystallinity than oxygen (water vapor transport is complicated in terms of its solubility and diffusion). Especially, these two permeability tests were under different temperatures.

Based on the results of HDPE/HP030 and PP/PC systems, we can develop a general model to illustrate the relationship between polymer crystalline morphology and their permeability. **Figure 11** shows a schematic drawing of the confined polymer spherulite morphology in layered structures. As we can see, after squeezing in the layers, the spherulites are forced to become a 2-D shape. The lamellar bundles tilt down in order to fit into the thinner layers. This morphology improves polymer’s gas barrier properties.

In **Figure 12**, the schematic drawings show the evolution of polymer layer morphology as layer thickness decreases. Polymer spherulites become more confined and more oriented as layers become thinner. Confinement of spherulite and lamellar orientation finally reach a balance when polymer layers are at a certain thickness.
That is the point where the HDPE and PP layers showed the best gas barrier property in our study.

3.4 Conclusions

Multilayer films of HDPE/HP030 and PP/PC were successfully fabricated through multiplication co-extrusion process. Different number of layers and different layer compositions were utilized to tailor the morphology of HDPE and PP layers.

Both HDPE/HP030 and PP/PC multilayer films showed improvements for oxygen and WVTR barrier properties. This is a result of confined spherulite morphology, which increases the tortuosity for gas diffusion.

It was also observed that there is a maxima improvement for both effective HDPE and PP layer, when their layer thickness is ~300 nm. At this layer thickness, effective HDPE layer yielded permeability improvements of ~5 times for water vapor and ~2 times for oxygen. Effective PP layer yielded permeability improvements of ~2 times for water vapor and ~2 times for oxygen. Two different effects are responsible for the maxima improvement point. Confined spherulite improves the barrier properties as layer thickness decreases. However, when layers become thinner and thinner, HDPE and PP lamellae start to orient perpendicular (on-edge) to the film surface, which then begins to diminish the material’s gas barrier properties.
3.5 References


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Table 3.2: Characteristics of HDPE/HP030 multilayered films
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**Table 3.3**

Chromatograms of ppC multi-layered films
Fig. 3.1 a) Schematic drawing of multilayer extrusion process showing how 3 layers become 9 layers with surface layer added by the end of extrusion.

b) Schematic drawing of 257 layer of HDPE/HP030 75/25 1/3 skin. The composition of layered-core is 75/25 as for HDPE/HP030 and the film has total 1/3 HDPE skin.
Fig. 3.2 The normalized HDPE layer WVTR value as a function of HDPE layer thickness.
Fig. 3.3 The normalized HDPE layer oxygen permeability as a function of HDPE layer thickness.
Fig. 3.4 AFM phase images of partial cross-sections of

a) 65 L 1/2 skin HDPE/HP030 75/25 25 µm film,

b) Zoom-in of 65 L 1/2 skin HDPE/HP030 75/25 25 µm film.
Fig. 3.5 AFM phase image of the surface of a HDPE layer in a 65 L 1/2 skin HDPE/HP030 75/25 25 µm film.
Fig. 3.6 Wide Angle X-ray Scattering patterns of extruded
a) 257 L 1/3 skin HDPE/HP030 75/25 25 µm film,
b) 129 L 1/3 skin HDPE/HP030 75/25 25 µm film,
c) 65 L 1/2 skin HDPE/HP030 75/25 25 µm film,
d) 65 L 1/3 skin HDPE/HP030 75/25 25 µm film,
e) HP030 25 µm control film,
f) HDPE 25 µm control film.
g) Schematic drawing for a and b
h) Schematic drawing for c, d and f,
Fig. 3.7 The normalized PP layer WVTR property as a function of PP layer thickness

Effective of PP layer WVTR

PP control: 0.50 g.mil/100in².day
Fig. 3.8 The normalized PP layer oxygen permeability as a function of PP layer thickness.
Fig. 3.9 AFM phase images of partial cross-sections of
a) 65 L 1/2 skin HDPE/HP030 75/25 25 µm film,
b) Zoom-in of 65 L 1/2 skin HDPE/HP030 75/25 25 µm film.
Fig. 3.10 2-D WAXS patterns of
a) 1/3 skin 257 L PP/PC multilayered film,
b) 1/2 skin 129 L PP/PC multilayered film,
c) 1/2 skin 65L PP/PC multilayered film,
d) 1/2 skin 33L PP/PC multilayered film.
Fig. 3.11 Schematic drawing of the possible morphology model of the confined spherullite morphology in the multilayered film.
Fig. 3.12 Schematic drawing of the possible mechanism for the permeability changes as a function of layer thickness.
Part II

Crystalline Polymers in Blend Systems
CHAPTER 4

Two-Dimensional Confined Crystallization of Linear Low Density Polyethylene in High Barrier Blend Systems

4.1 Introduction

Confined crystallization of semi-crystalline polymers was reported in many different systems [1-21], especially in co-extruded multilayer thin films [1-12]. In recent years, forced assembly, multilayer co-extrusion process [22] has come to be viewed as an effective way to study one-dimensional (1-D) confinement, because continuous and extremely thin layers can be easily prepared by this technique [1]. This multilayer co-extrusion technique offers us the flexibility of choosing polymers and the capability of tailoring the layer thickness. Thus, a structure-property relationship of polymers under confinement can be systematically studied in multilayered film systems [1-12].

However, the confined crystallization of polymers within multilayered films is usually only one-dimensional (1-D) [1-12]. Confined layers are commonly sandwiched by confining layers. The confinement effect is solely from the film normal direction (ND). It would be extremely interesting if we can combine the multilayer extrusion technique with polymer blends. When two or three polymers are blended together and then processed through the multilayer extrusion system, the blend morphology will be highly dependent on the process conditions and material composition. Cylinder or ribbon like morphology can therefore be achieved for
melt-extruded blends depending on the blend composition [21]. These cylinder or ribbon like domains will be surrounded by the confining materials from more than one direction. Along those lines, a 2-D confined crystallization should be achievable in the extruded blend films, which has been reported in block-copolymer systems [19, 21].

Polyethylene (PE), as a widely used polymer, has been studied in various systems for different purposes [9, 11, 12, 15, 17-20], including uses in multilayered systems [9, 11, 12, 15] and blend systems [23, 24]. Moreover, PE usually has a high barrier for both oxygen and water vapor [9]. In this study, a linear low-density polyethylene (LLDPE) was chosen to be compounded with another high barrier material, ethylene vinyl alcohol (EVOH) [25]. This blend will not only offer us the opportunity to study 2-D confined crystallization, it will also result in a high barrier material which can be useful for packaging applications.

In our study, a simple melt process by a single extruder system without any multipliers was used. Three compounded resins with different weight fractions of LLDPE-EVOH were melted and extruded through a 14-inch wide exit die to fabricate thin films. AFM results confirmed that for LLDPE-EVOH 50-50 blend film, ribbon like morphology was observed. For LLDPE-EVOH 70-30 and LLDPE-EVOH 30-70 films, cylinder like morphology was observed.

Regardless of the composition, both EVOH and LLDPE were found elongated along the extrusion direction (ED) in all three blend films due to the melt process. Since EVOH has higher melting temperature than LLDPE, EVOH behaved
as the confining material for LLDPE. LLDPE was physically confined by EVOH from film normal direction (ND) and film transverse direction (TD). This 2-D confined crystallization resulted in an on-edge oriented LLDPE crystal with the preferred elongation direction at extrusion direction (ED). This conclusion was supported by our WAXS and SAXS results.

As the composition changed, the domain size of LLDPE altered correspondingly. This resulted in different orientation functions.

4.2 Materials and experiments

Linear low density polyethylene (LLDPE), grade Exxon L3001 was obtained from Exxon Chemical Company, USA. Ethylene vinyl alcohol (EVOH), grade Eval E171 with 44% of ethylene group was obtained from Kuraray, USA. The resin information is listed in Table 4.1. The compounds of LLDPE-EVOH were prepared and generously offered by the A. Schulman Company, Akron, OH, USA. Three compositions of LLDPE-EVOH compounds (70-30, 50-50, 30-70) were prepared by the same twin-screw extruder.

The compound resins were dried in a vacuum oven for one day at 80 °C before the melt extrusion process. A single-screw extruder with feed-block and 16’ exit-die was used to fabricate thin films with thickness of ~25 μm. The process is demonstrated in a diagram shown in Figure 4.1. The extrusion condition was determined base on the thermal characteristics and viscosity match of LLDPE and EVOH. A Kayeness Galaxy 1 melt flow indexer (MFI) was used to investigate the
polymer viscosity as a function of temperature at a shear rate of 10 s⁻¹. The temperature of 250 °C was determined as the optimum temperature for extruding LLDPE-EVOH compounds.

All thin films were collected by the film take-off roll to control the final film thickness. The film take-off roll temperature was held constant at 80 °C while collecting all films. Table 4.2 shows the information for the films that were produced.

Atomic force microscopy (AFM) was employed to investigate the morphology of extruded thin films. Small pieces of specimen were embedded in epoxy (5 Minute Epoxy, Devcon, Rivera Beach, FL) and cured for 24 hours at room temperature. Cross sections were prepared by microtoming at both ED and TD after cooling the samples to -120 °C in liquid nitrogen. AFM images were obtained with a commercial scanning microscope probe (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA) with normal tapping mode. The spring constant was 50 N/m and resonance frequency was in the 284-362 kHz.

Two-dimensional (2-D) Wide Angel X-ray (WAXS) and Small Angle X-ray (SAXS) patterns were obtained with a rotating anode X-ray generator (Rigaku, Woodlands, TX), which produced a beam of monochromatic Cu Kα radiation (λ=0.154 nm). The X-ray generator operated at 45 kV and 0.88 mA. X-ray beams were aligned parallel to both the extrusion direction and transverse direction of the extruded films. For WAXS, the distance between specimen and detector is 140 mm. For SAXS, the distance between specimen and detector is 1469 mm.

The thermal properties of extruded thin films were characterized using a
Perkin Elmer (Boston, MA) Pyris differential scanning calorimeter (DSC) unit at a heating/cooling rate of 10 °C/min.

Oxygen flux J(t) rates were characterized with a MOCON (Minneapolis, MN) OxTran 2/20 unit. The experiments were conducted in 1 atmosphere pressure at 23 °C (+0.1) with a 0% relative humidity. The instrument was calibrated at 23 °C with a NIST-certified Mylar film with known oxygen transport characteristics. Oxygen permeability, \( P(O_2) \), were calculated from steady-state flux, \( J \), rates.

\[
P(O_2) = J \frac{l}{\Delta p}
\]

Where \( l \) is the overall film thickness and \( \Delta p \) is oxygen’s partial pressure drop across the film. The average reported \( P(O_2) \) values were taken from at least two samples. \( P \) values are reported in Barrer units. One Barrer equals to \( 10^{-10} \) (cm³ O₂) cm cm⁻² s⁻¹ cmHg⁻¹.

4.3 Results and discussions

4.3.1 Blend morphology of the extruded films

Morphology plays an important role in determining other aspects of the extruded blend films. It would be interesting to study the morphology first. AFM was used to obtain the morphological information of these samples.

AFM images were taken from both the ED and TD shown in Fig. 2. The images of the upper row from Fig. 2 are the AFM results at the ED for LLDPE-EVOH 70-30, LLDPE-EVOH 50-50 and LLDPE 30-70 films respectively. As shown in Fig. 2 b, LLDPE-EVOH 50-50 film has a co-continuous morphology.
Both LLDPE and EVOH are elongated. For LLDPE-EVOH 70-30 and LLDPE 30-70 films (Fig. 2a and Fig. 2c), the minor group is dispersed as fillers in the major group. Regardless of the composition, both LLDPE and EVOH are more or less squeezed at the ND in all the extruded thin films. When EVOH is the minor group, the EVOH domains are in oval shapes (Fig. 2a). When LLDPE is the minor group, the LLDPE domains are in squeezed oval shapes (Fig. 2c).

The images in the lower row of Fig. 2 are the AFM results from the TD for LLDPE-EVOH 70-30, LLDPE-EVOH 50-50 and LLDPE 30-70 films respectively (Fig. 2d-2f). The morphology of all three films from the TD AFM is similar to layered structure. This is because both EVOH and LLDPE domains are elongated along ED under the shear force of the extruder. By combining the AFM images from both ED and TD, we found that the morphology of these extruded blend films is similar to block-copolymer but with much larger domain sizes [14, 15, 17, 18]. It has been well known that the blend of two immiscible homogenous polymers can have similar morphology as block-copolymers [21].

Regardless of the compositions, in all three extruded blend films, LLDPE domains are surrounded by EVOH domains from ND and TD. The schematic drawings of the blend morphology are shown in Fig. 3.

Since EVOH has a much higher crystallization temperature than LLDPE, it is reasonable to expect that LLDPE have been confined by EVOH. Usually, the confinement effect could result in specific crystal orientations of polymer. For LLDPE, on-edge orientation often shows up as a result of confined crystallization. As it is
shown in Fig. 3, the confining material of EVOH is squeezing LLDPE from both ND and the TD due to the ribbon or cylinder like morphology of LLDPE domains.

4.3.2 Crystalline orientation of LLDPE

The morphology of the extruded blend films suggested that the LLDPE are physically confined by EVOH from both ND and TD. This confinement effect should cause unique crystal orientation for LLDPE. In order to confirm this hypothesis, WAXS was first utilized to study the crystalline orientations of LLDPE.

The X-ray beam was aligned parallel to both ED and TD of these extruded films respectively. Fig. 4a and Fig. 4f are the X-ray patterns of LLDPE extruded control at ED and TD. Isotropic reflections of LLDPE (200) plane and (110) plane were observed in both patterns [9, 26]. This suggested that the LLDPE control yields isotropic orientation. In other words, the LLDPE crystals did not orient. For EVOH, isotropic halo rings were also observed (Fig. 4b and Fig. 4g), which implied that EVOH did not have a preferred orientation either.

Fig. 4c, Fig. 4d and Fig. 4e are the WAXS patterns at ED for LLDPE-EVOH 70-30, LLDPE-EVOH 50-50 and LLDPE-EVOH 30-70 films respectively. On-edge orientation of LLDPE was observed for all three films. This was confirmed by the concentrated reflections of (200) plane at meridional position [9, 11, 12, 17]. As the composition of LLDPE decreased in the extruded film, the orientation became stronger and sharper (Fig. 4e showed stronger orientations than Fig. 4c). This is the result of the decreased size of LLDPE domains, which is similar to decreasing the
layer thickness in multilayer film systems [5, 6].

Fig. 4h, Fig. 4i and Fig. 4j are the WAXS patterns at TD for LLDPE-EVOH 70-30, LLDPE-EVOH 50-50 and LLDPE-EVOH 30-70 films respectively. Interestingly, the reflections from LLDPE in the WAXS patterns were different from their counterpart at ED. It looks like both (200) and (110) planes had concentrated diffraction intensities at meridional positions in TD patterns. This is interesting, but we need to confirm that the reflections in the TD WAXS patterns are really from (200) and (110) planes of LLDPE. Selected 2-D WAXS patterns are plotted as 1-D profile in Fig. 5. Since the WAXS patterns are similar for all three extruded blend films, only LLDPE-EVOH 50-50 is presented here as an example. Fig. 5a and Fig. 5b are the curves for EVOH controls at ED and TD. Fig. 5c and Fig. 5d are the curves for LLDPE control at ED and TD. Fig. 5e and Fig. 5f are the curves for LLDPE-EVOH 50-50 film at ED and TD.

By comparing the 1-D X-ray profile curves, it is clear that the basic crystal unit of LLDPE should remain unchanged as orthorhombic, because the major reflections are still at 21.7° and 24.0°. Those two values are usual for LLDPE (110) and (200) planes.

Now that we know the major reflections observed in Fig. 4, are from LLDPE (200) and (110) planes, the interesting TD WAXS patterns must be from the specific orientation of LLDPE crystals. The meridional concentrated intensities of (200) planes in all LLDPE-EVOH blend films suggested that the a-axis of LLDPE crystals are aligned perpendicular to the film surface. In other words, the a-axis is at the ND of
the extruded films. This usually means it is an on-edge orientation of polyethylene [9, 11, 12, 15, 24]. For on-edge orientation, the c-axis is usually parallel to the film surface, while the b-axis is also parallel to the film surface for polyethylene [25]. Therefore, the b-c plane is parallel to the film surface. However, commonly, the WAXS patterns from ED and TD for the same sample should be the same. This is because, as an on-edge orientation, the b-c plane should be able to rotate freely along the a-axis. Hence, the reflections from (110) plane should yield at the same position no matter which way the X-ray was aligned. The difference between WAXS patterns at ED and TD in this study suggested that the b-c planes of LLDPE crystals are oriented, instead of randomly presenting.

This difference can be more clearly seen in the Azimuthal scan curves of (110) plane of LLDPE in Fig. 6. There are two important pieces of information from Fig. 6. First, the shapes of the curves are completely different from ED to TD patterns, which confirm that the on-edge oriented LLDPE crystals have a preferred elongation direction. Second, as the LLDPE weight fraction decreases, the reflection intensity increases. This suggests stronger orientations due to smaller sizes.

Fig 6a shows the (110) Azimuthal scan from TD WAXS patterns. The intensity of diffractions concentrated at 180°. Fig 6b shows the (110) Azimuthal scan from ED WAXS patterns. The intensity of diffractions concentrated at 40° away from 180°, which is consistent with previous observations for Polyethylene [9, 11, 12, 26]. The LLDPE-EVOH 30-70 film showed sharpest reflection peaks. This is again, because it has the smallest domain size of LLDPE. In general, the smaller the size of
material domains, the stronger the crystal orientation is [5, 6].

Based on the discussions above, we know that the LLDPE crystals are on-edge oriented due to the confinement from ND. This is similar to what we have observed for PE in the layered films [9, 11, 12], in which confining layers apply the confinement effect from ND. As we mentioned earlier, the EVOH not only confine LLDPE from ND, but also confine the LLDPE from TD. The confinement from TD actually forced the b-c plane to face the extrusion direction. In other words, the c-axis is along the direction of ED. The on-edge oriented LLDPE crystals have lost the freedom of rotating along the a-axis here and are all elongated along the extrusion direction. This explains why WAXS ED patterns showed ordinary on-edge orientation, but WAXS TD patterns showed diffraction intensities at meridional positions for both (200) and (110) planes. The schematic drawings to illustrate the 2-D confinement are shown in Fig. 7.

SAXS was then utilized to confirm this orientation. The results are shown in Fig. 8. The images in the upper row are the SAXS results at ED. As we discussed above, the c-axis (as the molecule folding direction), is parallel to the ED. That is why when the X-ray beam was aligned at ED, no specific orientation was observed for all three samples. However, when the X-ray was aligned at TD, equatorial streaks were found in the SAXS images in the lower row. This confirmed that the c-axis is oriented or elongated at ED.

This phenomenon is different from what we have observed for extruded multilayered films. In multilayered films, when on-edge orientation of polyethylene is
achieved, the c-axis of LLDPE crystals is parallel to the film surface, but not necessarily parallel to ED. In other words, the on-edge oriented LLDPE crystals can freely grow in ED or TD or any directions between ED and TD in multilayered films. This is because only 1-D confinement from ND occurs between layers. The comparison between the extruded blend film and multilayered film is shown in Fig. 9.

Fig. 9b shows the WAXS patterns for a 33-layer LLDPE/EVOH multilayer film with volume fraction of 50/50. The layer thickness is 790 nm for both LLDPE layer and EVOH layer. The WAXS patterns from ED and TD were both isotropic, which suggested a random orientation of LLDPE crystals. Fig. 7c shows the WAXS patterns for 513-layer LLDPE/EVOH multilayer film with composition of 50/50. The layer thickness is 40 nm for both LLDPE layer and EVOH layer. As layer thickness decreased, the isotropic orientation of LLDPE crystals adopted on-edge orientation. Both WAXS patterns from ED and TD showed the same on-edge orientation, which suggested that the a-axis of LLDPE crystal is perpendicular to film surface, while b-axis and c-axis are random in the b-c plane.

Based on these results, we reach our conclusion that 2-D confined crystallization occurred in the extruded LLDPE-EVOH blend films. In the ND direction, the confinement effect resulted in an on-edge orientation. In TD direction, the confinement forced the on-edge oriented LLDPE crystals to elongate along the extrusion direction.

DSC curves for the extruded blend films are shown in Fig. 10. These curves show that, it is clear that the crystallization temperatures of both LLDPE and
EVOH remained unchanged. The crystallinity of LLDPE remained the same. This can be confirmed by the nearly identical melting enthalpy values.

4.3.3 The relationship between the morphology and the blend film’s permeability

The morphology of these extruded blend films should have effects on their properties. In this study we chose to study the gas permeability. Oxygen permeability of these extruded films were measured by the Oxtran Mocon units at 23°C and 0% relatively humidity.

Two model calculations were used to compare with the measured results. First, a miscible blend model was utilized here:

\[ \ln P_{\text{blend}} = \phi_1 \ln P_1 + \phi_2 \ln P_2 \]

Where \( P_1 \) and \( P_2 \) are the oxygen permeability of LLDPE control and EVOH control respectively; \( \phi_1 \) and \( \phi_2 \) are the volume fraction of LLDPE control and EVOH control respectively.

Since LLDPE and EVOH are not miscible blends, their permeability values were expected to be higher than the blend model calculations. However, only LLDPE-EVOH 70-30 sample showed higher gas permeability than the calculation. The LLDPE-EVOH 50-50 and LLDPE-EVOH 30-70 films both showed lower permeability values than the calculations. In other words, the barrier property of these two films was improved. The LLDPE-EVOH 50-50 showed 21X improvements compared to miscible blend model calculation. This is possibly because the layered-like morphology or lamella lying block-copolymer type morphology of
LLDPE-EVOH 50-50 extruded blend film.

In order to confirm the hypothesis above, we then used series model to do the calculation. This assembly shown below usually applies to multilayered film.

\[ \frac{1}{P_{Film}} = \frac{\phi_1}{P_1} + \frac{\phi_2}{P_2} \]

Interestingly, the LLDPE-EVOH 50-50 blend film showed very similar permeability value to the series model calculation. This result confirmed that this sample has co-continuous and layered-like morphology. This result also suggests that by using a co-continuous blend, it is possible to fabricate high barrier packaging material with a similar structure to layered films.

It would also be extremely interesting, if we introduce this blend into multiplication extrusion process. In other words, instead of using a simple melt-extrusion process, multipliers can be used to tailor the morphology of blend films. Since the multiplier can possibly physically change the domain size and domain length of the blend material, the increased number of multipliers could enhance the 2-D confined crystallization of LLDPE. The effect of multiplication process on the morphology and structure of LLDPE-EVOH blend films would be valuable. This will be discussed in another paper.

4.4 Conclusions

Extruded blended films of LLDPE-EVOH were successfully fabricated by an extrusion system. Due to the extrusion process, both LLDPE and EVOH domains were elongated along the extrusion direction. The LLDPE-EVOH 50-50 composition
film showed ribbon like, co-continuous morphology. The LLDPE-EVOH 70-30 and 30-70 films showed cylinder like blend morphology.

Higher crystallization temperature of EVOH over LLDPE enables the confined crystallization of LLDPE in the blend films. Due to the elongated ribbon/cylinder like morphology, a 2-D confined crystallization occurred. This 2-D confinement resulted in two way oriented LLDPE crystals. First, the confinement from ND forced the LLDPE crystal to orient on-edge. Second, the confinement from TD forced the on-edge oriented crystals to grow along the extrusion direction.

Our results suggested that by introducing blend polymers into extrusion systems, we can open new avenues for studying confined crystallization of polymers.

4.5 References


[20] Ting Li, Wan Juan Wang, Ran Liu, Wei Hao Liang, Guo Fang Zhao, ZhiYun Li, Qing Wu and Fang Ming Zhu, Macromolecules 42(2009), 3804-3810.


<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m / ^\circ C$</th>
<th>$T_c / ^\circ C$</th>
<th>Density g/cm$^3$</th>
</tr>
</thead>
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<tr>
<td>LLDPE (Exxon 3001)</td>
<td>124</td>
<td>115</td>
<td>0.917*</td>
</tr>
<tr>
<td>EVOH (E171)</td>
<td>159</td>
<td>140</td>
<td>1.14 *</td>
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* Data obtained from manufacturer.
Table 4.2
Blend films produced by extrusion system.

<table>
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<tr>
<th>Sample name</th>
<th>Weight fraction of LLDPE over EVOH w/w</th>
<th>Volume fraction of LLDPE over EVOH v/v</th>
<th>Film thickness/µm</th>
</tr>
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<tbody>
<tr>
<td>LLDPE-EVOH 70-30</td>
<td>70/30</td>
<td>65/35</td>
<td>25</td>
</tr>
<tr>
<td>LLDPE-EVOH 50-50</td>
<td>50/50</td>
<td>46/54</td>
<td>25</td>
</tr>
<tr>
<td>LLDPE-EVOH 30-70</td>
<td>30/70</td>
<td>26/74</td>
<td>25</td>
</tr>
<tr>
<td>Extruded blend film (EVOH-LLDPE composition)</td>
<td>$P_O^2$ / Barrer</td>
<td>$P_O^2$/ Barrer based on miscible blends model</td>
<td>Improvement ratio</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>------------------</td>
<td>-----------------------------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>LLDPE control (0-100)</td>
<td>3.7 ± 0.1</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>EVOH control (100-0)</td>
<td>0.0015 ± 0.0001</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>EVOH-LLDPE blend (70-30)</td>
<td>0.0020 ± 0.0001</td>
<td>0.016</td>
<td>8</td>
</tr>
<tr>
<td>EVOH-LLDPE blend (50-50)</td>
<td>0.0034 ± 0.0001</td>
<td>0.070</td>
<td>21</td>
</tr>
<tr>
<td>EVOH-LLDPE blend (30-70)</td>
<td>1.5 ± 0.1</td>
<td>0.36</td>
<td>0.26</td>
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**Fig 4.1** Extrusion system to fabricate the blend control films.
Fig 4.2 AFM images of partial cross section of
a) Extruded LLDPE-EVOH blend control with composition of 70-30 at ED,
b) Extruded LLDPE-EVOH blend control with composition of 50-50 at ED,
c) Extruded LLDPE-EVOH blend control with composition of 30-70 at ED,
d) Extruded LLDPE-EVOH blend control with composition of 70-30 at TD,
e) Extruded LLDPE-EVOH blend control with composition of 50-50 at TD,
f) Extruded LLDPE-EVOH blend control with composition of 30-70 at TD.
Fig 4.3 Schematic Drawings of the blend films based on the AFM images.
Fig 4.4 WAXS pattern of
a) Extruded LLDPE control at TD,
b) Extruded LLDPE control at ED,
c) Extruded EVOH control at TD,
d) Extruded EVOH control at ED,
e) Extruded LLDPE-EVOH 70-30 blend film at TD,
f) Extruded LLDPE-EVOH 70-30 blend film at TD,
g) Extruded LLDPE-EVOH 50-50 blend film at TD,
h) Extruded LLDPE-EVOH blend 50-50 film at TD,
i) Extruded LLDPE-EVOH 30-70 blend film at TD,
j) Extruded LLDPE-EVOH blend 30-570 film at TD,
The arrows are showing the reflection planes from LLDPE.
Fig 4.5  1-D WAXS profile for
a) Extruded LLDPE control at TD,
b) Extruded LLDPE control at TD,
c) Extruded EVOH control at TD,
d) Extruded EVOH control at TD,
e) Extruded LLDPE-EVOH 50-50 blend film at TD,
f) Extruded LLDPE-EVOH 50-50 blend film at ED.
Fig 4.6 Azimuthal scan of LLDPE 110 plane for extruded LLDPE-EVOH blend films with different compositions.

a) from TD X-ray patterns,

b) from ED X-ray patterns.
Fig 4.7 Schematic drawing shows how the LLDPE crystals orient after extrusion process.
Fig 4.8 SAXS patterns for the LLDPE-EVOH blend films:
   a) Extruded LLDPE-EVOH 70-30 ED,
   b) Extruded LLDPE-EVOH 50-50 ED,
   c) Extruded LLDPE-EVOH 30-70 ED,
   d) Extruded LLDPE-EVOH 70-30 TD,
   e) Extruded LLDPE-EVOH 50-50 TD,
   f) Extruded LLDPE-EVOH 30-70 TD.
Fig 4.9 Comparison of LLDPE-EVOH blend film with LLDPE-EVOH layered film.
Fig 4.10 DSC heating curves of LLDPE-EVOH (50-50) blend films fabricated by different number of multipliers.
CHAPTER 5
The Structure-Property Relationships of LLDPE-EVOH Blend Films
Fabricated by Multiplication Extrusion

5.1 Introduction

Polymer blends have been extensively studied by many scientists for various applications [1-7], especially the blends with so called co-continuous morphology [3-7]. The co-continuous blends usually have outstanding properties due to the favorable combination of each component [7]. The formation of co-continuous blend highly depends on the blend composition and processing conditions [6, 7]. It would be extremely interesting if we can introduce the co-continuous blends into a multiplication extrusion process. The multiplication co-extrusion has been reported in recent years as an extremely effective processing technique to tailor polymer’s morphology [8]. By using multiplication co-extrusion process, structure-property relationships of various polymers were thoroughly investigated [9-19]. When the co-continuous blends are melt-process through the multiplication extrusion, the effect of multiplication on the blend morphology can be systematically studied. The multipliers are expected to act like mixers that can physically break the blend components into tiny phases. Therefore, the number of multipliers used is critical in this study. The combination of blends and multiplication extrusion technique offers us a new opportunity to explore polymer’s morphology-property relationship. Moreover, polymer blends with desired high performance can be fabricated through this new
method.

Instead of using two or three extruders at the same time, only one extruder followed by a series of multipliers is required to produce thin blend films. The different numbers of multipliers play an important role in determining the morphology of the blend films. It is well known that co-continuous structure is easier to fabricate within a composition range [7]. The blend material of LLDPE and EVOH with weight fraction of 50-50 is therefore selected in this study.

LLDPE is physically and mechanically different from EVOH. The blending of these two immiscible materials offers us the access to study the gradual evolution of their morphology through the multiplication process. Every time of multiplication, the melt blend is spitted and recombined by the multiplier. The extruded blend film with no multipliers shows elongated and co-continuous morphology, which is somehow similar to block-copolymers [20-22]. After several times of multiplication, the immiscible blend of LLDPE-EVOH finally exhibited like homogenous blends with indistinctive tiny phases.

We also found that the properties of the extruded LLDPE-EVOH eluted as the film morphology changes. As the morphology changes, the gas permeability, optic property and mechanical properties of the blend film change dramatically.

The co-continuous morphology, which is similar to layered structure, is preferred for gas barrier properties. Hence when the number of multipliers increased, both oxygen permeability and water vapor transport rate of the extruded blend film increased. However, with the blend morphology turns into more homogenous
characteristics, the transmission rate of the blend film is improved. More interestingly, the homogenous blend morphology eventually eliminates the anisotropic features in the blend films in terms of its mechanical behaviors. These results suggest that by introducing co-continuous blends into multiplication extrusion process, new materials with desired properties can be fabricated.

AFM and WAXS were employed in this paper to investigate the morphology and crystalline structure of these extruded blend films. MOCON units, UV-vis and MTS were used to study the gas permeability, optic property and mechanical properties of these samples.

5.2 Materials and experiments

Linear low density polyethylene (LLDPE), grade Exxon L3001 was obtained from Exxon Chemical Company, USA. Ethylene vinyl alcohol (EVOH), grade Eval E171 with 44% of ethylene group was obtained from Kuraray, USA. The resin information is listed in Table 5.1. The compound resin of LLDPE-EVOH with weight fraction of 50-50 was prepared by a twin-screw extrusion system and was generously offered by the A. Schulman Company, Akron, OH, USA.

The LLDPE-EVOH compound was dried in a vacuum oven for one day at 80°C before the melt extrusion process. A single-screw extruder of the 3-component co-extrusion system was utilized to melt process the compound resin and fabricate thin film through a 14’ exit-die with final film thickness of ~25 μm. Different numbers of multipliers were employed during this process to tailor the film
morphology. The process is demonstrated in a diagram shown in Figure 5.1. The extrusion condition was determined based on the thermal characteristics and viscosity match of LLDPE and EVOH. A Kayeness Galaxy 1 melt flow indexer (MFI) was used to investigate the polymer viscosity as a function of temperature at a shear rate of 10 s\(^{-1}\). The temperature of 250 °C was determined as the optimum temperature for extruding LLDPE-EVOH compounds.

All thin films fabricated by different number of multipliers were collected by the film take-off roll to control the final film thickness. The film take-off roll temperature was held constant at 80 °C while collecting all films.

Atomic force microscopy (AFM) was employed to investigate the morphology of extruded thin films. Small pieces of specimen were embedded in epoxy (5 Minute Epoxy, Devcon, Rivera Beach, FL) and cured for 24 hours at room temperature. Cross sections were prepared by microtoming at both ED and TD after cooling the samples to -120 °C in liquid nitrogen. AFM images were obtained with a commercial scanning microscope probe (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA) with normal tapping mode. The spring constant was 50 N/m and resonance frequency was in the 284-362 kHz.

Two-dimensional (2-D) Wide Angle X-ray (WAXS) was conducted with a rotating anode X-ray generator (Rigaku, Woodlands, TX), which produced a beam of monochromatic Cu K\(\alpha\) radiation (\(\lambda=0.154\) nm). The X-ray generator operated at 45 kV and 0.88 mA. X-ray beams were aligned parallel to both the extrusion direction and transverse direction of the extruded films.
The thermal properties of extruded thin films were characterized using a Perkine Elmer (Boston, MA) Pyris differential scanning calorimeter (DSC) unit at a heating/cooling rate of 10 °C/min.

Oxygen flux \( J(t) \) rates were characterized with a MOCON (Minneapolis, MN) OxTran 2/20 unit. The experiments were conducted in 1 atmosphere pressure at 23 °C (+0.1) with a 0% relative humidity. The instrument was calibrated at 23 °C with a NIST-certified Mylar film with known oxygen transport characteristics. Oxygen permeability, \( P(O_2) \), were calculated from steady-state flux, \( J \), rates.

\[
P(O_2) = J \frac{l}{\Delta p}
\]

(5.1)

Where \( l \) is the overall film thickness and \( \Delta p \) is oxygen’s partial pressure drop across the film. The average reported \( P(O_2) \) values were taken from at least two samples. \( P \) values are reported in Barrer units. One Barrer equals to \( 10^{-10} \) (cm³ O₂) cm cm⁻² s⁻¹ cmHg⁻¹.

Water vapor transport rate (WVTR) was all measured with a MOCON (Minneapolis, MN) PERMATRAN-W® Model 3/33 unit. The measurements were carried out in 1 atmosphere pressure at 37.8 °C (+0.1) with a 100% relative humidity for all samples. The instrument was calibrated at 37.8 °C with a NIST-certified Mylar film with known water vapor transport characteristics.

\[
P(H_2O) = WVTR \frac{l}{\Delta p}
\]

(5.2)

Again, \( l \) is the overall film thickness (in units of ‘mil’, 1 mil=25.4 µm) and \( \Delta p \) is water vapor’s partial pressure drop across the film, which is 1 here. The average
reported water vapor permeability, $P(H_2O)$ values were taken from at least two samples. $P(H_2O)$ values are normalized by the actual measured thickness and reported in the unit of g.mil/100in$^2$.day

The transmission rate of the extruded blend films was measured by an ultraviolet-visible spectrometer [23]. The diameters of the light source beam and the detector were approximately 3 mm. The distance between film and detector was 6 mm. Five different spots on each film were selected to perform the measurement.

Tensile test was conducted by using a mechanical tensile stretcher (MTS) system by the method of ASTM D882 for thin films [24]. The samples were prepared in rectangular shape with the width of 10 mm and the gauge length of 100 mm. The strain rate was set at 10%/min for obtaining the young’s modulus. At least five measurements for every sample were conducted.

5.3 RESULTS AND DISCUSSION

5.3.1 Morphology evolution as a function of multipliers.

The LLDPE-EVOH 50-50 compound resin was melt-processed through 0, 4, 6 and 8 multipliers respectively. The morphology changed as we increased the number of multipliers. In order to investigate the evolution of morphology, AFM images were taken from both extrusion direction (ED) and transverse direction (TD) for all samples. The images are shown in Fig. 5.2.

The upper row of Fig. 5.2 shows the images taken from ED. From left to right, the number of multipliers increased from 0 to 8. As the number of multipliers
increased, the co-continuous and elongated morphology of the blend gradually disappeared. When 0 multiplier was used, the extruded film showed elongated and layered-like morphology. When 8 multipliers were used, the extruded blend film showed homogenous mixture morphology (Fig 5.2d). The tiny domains in Fig 5.2d were below 100 nm in thickness and indistinctive of which materials they were. During the process, the multipliers split and recombined the melt flow, every time of which the melt was mixed. More multipliers were used, more times of mixing happened. Therefore, After 8 times of multiplication, the domains of both LLDPE and EVOH became small enough to lose their characteristics.

AFM images at TD were also taken for all samples. From Fig. 5.2e to Fig. 5.2h, the number of multipliers increased from 0 to 8. It is clear that both EVOH and LLDPE were elongated at the extrusion direction due to the melt process. At beginning, when no multiplier was used, the morphology was similar to layered structure. However, as the number of multipliers increased, the size of each material became smaller and smaller. Eventually, the size of both materials became small enough to be indistinctive from each other.

This morphology evolution is interesting. When less number of multipliers was used, the elongated, co-continuous and layer-like blend morphology is similar to block-copolymers [7, 20-22]. When the number of multipliers increased to 6, the morphology transformed into net-work like co-continuous structure [7] (Fig. 5.2c). When even more number of multipliers was used, homogenous blend morphology became dominant. In other words, the multipliers physically or mechanically
transformed the elongated, co-continuous, block-copolymer like morphology into homogenous mixture by reducing the domain size. Simply changing the number of multipliers, completely different morphology of LLDPE-EVOH blend was achieved. The schematic drawings of the morphology as a function of the number of multiplier are shown in Fig. 5.3.

WAXS was then utilized to study the crystalline orientation within the extruded blend films. In a previous study, we found that in the extruded blend films, a 2-D confined crystallization happened due to the co-polymer like morphology (that work was submitted to Polymer as another paper). In that study, blends of LLDPE-EVOH with different weight fractions were melt processed without multipliers. LLDPE was found to be confined by EVOH from both film normal direction (ND) and TD.

In this study, similar WAXS pattern was observed, which again confirmed the 2-D confined crystallization in the extruded blend films. WAXS patterns taken from both ED and TD are shown in Fig. 5.4. Both LLDPE extruded control (Fig. 5.4e and Fig. 5.4k) and EVOH extruded control (Fig. 5.4f and Fig. 5.4i) exhibited isotropic orientation irrespective of X-ray beam direction.

For all blend films fabricated by different number of multipliers, the ED WAXS patterns showed ordinary on-edge orientation. This is confirmed by the concentrated reflections of (200) plane at the meridional position. The TD WAXS patterns for the extruded blend films showed different concentrated reflections from ED patterns. Both (200) and (110) planes showed concentrated intensities at
meridional position. This is because on-edge oriented LLDPE crystals were elongated at the ED, which is the result of the 2-D confined crystallization. The details of determining the 2-D confinement was discussed in another paper submitted to polymer.

The important information we can obtain from these WAXS patterns is how the crystalline orientation evolves as a function of the number of multipliers. As the number of multipliers increased, the domain size of both LLDPE and EVOH became smaller and smaller. The decrease of size usually resulted in stronger orientations under confinement []. This is confirmed by our observations that as the number of multipliers increased, the reflections intensities became shaper. This trend can be more clearly seen in Fig 5.5.

Azimuthal scan of the LLDPE (200) plane from WAXS ED patterns are plotted in Fig. 5.5. From bottom to top, the curve shape became shaper and shaper, which suggested that as the number of multipliers increased, the LLDPE crystals gained stronger and stronger orientations. These results supported our observation from AFM that the size of both materials within the blend films turned smaller as a result of multiplication process.

DSC was also used to determine whether the crystallinity of either LLDPE or EVOH had changed under the confinement. The DSC curves for the first heating were plotted in Fig. 5.6. Similar curves with nearly identical meting enthalpy values were obtained for all extruded blend films. This suggested that the crystallinity did not change during the multiplication process.
5.3.2 Structure-property relationships.

Gas permeability-morphology relationship.

The morphology of LLDPE-EVOH blend film evolved as a result of multiplication process, which was confirmed by AFM and WAXS. The dramatic change of morphology should result in a considerable change of physical properties for these extruded blend films.

EVOH, as a high barrier material is widely used in packaging applications. Gas barrier properties are therefore important aspects for these extruded films. Oxygen permeability and water vapor transport rate were measured by an Oxtran 2/20 and PERMATRAN 3/33 units at 23°C and 37.8°C respectively.

The LLDPE-EVOH blend film fabricated without multiplier (0 multipliers) showed similar to layered-structure morphology as we mentioned before. However, as the number of multipliers increased, the co-continuous, elongated and layer-like morphology was gradually replaced by the homogenous and isotropic mixture morphology. During this transformation, the gas permeability was expected to increase. This is because, only when the high barrier component has high aspect ratio, it could result in good barrier properties for the overall film.

The gas permeability values measured by MOCON units are listed in Table 5.3. As we can see, both oxygen permeability and WVTR increased as the number of multipliers increased. This further confirmed that the multipliers had broken the co-continuous and elongated morphology into tiny domains. The elongated morphology is preferred for gas barrier property, losing of which will result in
increased gas permeability.

As we mentioned above, the blend film fabricated by 0 or 4 multipliers showed very similar morphology to layered-structure. This can be verified by a series model calculation for gas permeability. The series equation below predicts the permeability of layered structure:

\[
\frac{1}{P_{\text{film}}} = \frac{\phi_1}{P_1} + \frac{\phi_2}{P_2}
\]  

(5.3)

Where \(P_{\text{film}}, \ P_1\) and \(P_2\) are the permeability values of the total film, layer LLDPE and layer EVOH respectively. \(\phi_1\) and \(\phi_2\) are the volume fractions of LLDPE and EVOH.

The calculated oxygen permeability value is 0.0030 Barrer, which is very similar to our measured value of 0.0034 for LLDPE-EVOH 50-50 blend film fabricated through 0 multiplier. This suggests that the morphology of LLDPE-EVOH film fabricated by 0 multiplier is very similar to layered-structure.

If we assume our samples are miscible blends, then the gas permeability of the overall blend film follows the correlation below:

\[
\ln P_{\text{blend}} = \phi_1 \ln P_1 + \phi_2 \ln P_2
\]  

(5.4)

Where \(P_{\text{blend}}, \ P_1\) and \(P_2\) are the permeability values of the overall blend film, LLDPE control and EVOH control respectively. \(\phi_1\) and \(\phi_2\) are the volume fractions of LLDPE and EVOH. The calculated value for oxygen permeability of the 50-50 blend is 0.07 Barrer. This is closer to the measured value for the film fabricated through 8 multipliers.
These calculations again confirmed that as the number of multipliers increased, the morphology of the extruded film evolved from co-continuous, elongated and layered-like to homogenous mixtures.

**Transparency-morphology relationship.**

As the domain size changed greatly during the multiplication process, the optic property of these extruded blend films was expected to change accordingly. At beginning, when no multiplier was used, the morphology was elongated and co-continuous with thickness of several hundred of nanometers. When the number of multipliers increased, the domain size decreased to several nanometers. By looking at the AFM images (Fig. 5.2d and Fig. 5.2h), the thickness of these domains are below 100 nm in this film fabricated through 8 multipliers. As we know, when the size of fillers or blends is below a quarter of the visible light wavelength, the scattering of light will be reduced dramatically. This makes us believe that the film fabricated through 8 multipliers should yield higher transmission rate than that of the film fabricated through 0 multipliers.

The transmission rate was measured by a UV-vis spectrometer at an atmosphere environment. The sample surface was not further treated post extrusion. As we expected, the film fabricated through 8 multipliers showed the highest transmission rates at all wavelength from 400 nm to 800 nm. Every film was measured at 5 different spots; the average value of the transmission rate was plotted as a function of wavelength in Fig. 5.7a.
The more multipliers we used, the higher transmission rate of the extruded film was. (Except 0 multiplier film and 4 multiplier films, this is possibly due to the film surface roughness of the extruded film.) This is consistent with our observations of the morphology change in our extruded blend film.

**Mechanical behavior-morphology relationship.**

The mechanical properties usually are directly related to the samples’ morphology and composition [7]. When the extruded blend films showed such a tremendous change in morphology, it is reasonable to expect dramatic alterations in the mechanical behaviors for these extruded films.

A tensile test using the ASTM D882 was conducted on these extruded blend films by a MTS. The deformation was applied to both ED and TD. Samples were in rectangular shape with a width of 10 mm and the gauge length of 100 mm. The strain rate was set at 10%/min for getting the young’s modulus results. At least five repeats were conducted for every sample.

The tensile test was first conducted at the ED. EVOH and LLDPE controls were also tested. The representative stress-strain curves are shown in Fig. 5.8. Young’s modulus of every sample was calculated at 1% strain. Both young’s modulus and yield stress results are listed in Table 5.4.

By looking at Fig. 5.8, the EVOH control behaved like a tough material with yield stress around 30 MPa, while the LLDPE behaved like an elastomer, which was gradually yielding. The distinctive mechanical behaviors between LLDPE and EVOH
controls make their blends interesting. The LLDPE-EVOH 50-50 blend films showed intermediate mechanical behaviors between the two controls independent of the number of multipliers used.

As we observed in AFM images, film fabricated through 0 multipliers showed elongated and continuous morphology. This morphology is similar to a block-copolymer. As the number of multipliers increased, the continuous, elongated and block-copolymer like morphology gradually disappeared. In other words, when the tensile test was applied to the film fabricated through 0 multipliers, it was similar to stretch a block-copolymer. However, as the number of multipliers increased, it was similar to stretch a homogeneous blend. Hence, as the number of multipliers increased, both young’s modulus and yield stress of the extruded blend films decreased as shown in Fig. 5.8 and Table 5.4. This is because: when the morphology is laminar composite like/block-copolymer like, the stress was distributed in both LLDPE and EVOH elongated domains. However, when the laminar composite like/block-copolymer like morphology disappeared, the stress then concentrated in the interface between LLDPE and EVOH small domains. LLDPE and EVOH are actually immiscible, so losing the co-continuous morphology actually deteriorated their mechanical strength.

It is well known that the mechanical properties for blends usually depend on their morphology. However, the parallel model and series model are commonly used as the upper bound limit and lower bound limit by many scientists for polymer blends [3].
The film fabricated through 0 multiplier therefore is expected to be close to the upper limit, while the film fabricated through 8 multipliers is expected to be close to the lower limit. The yield stress actually decreased nearly 2X from film fabricated through 0 multipliers to film fabricated through 8 multipliers, which is consistent as the difference between the upper limit and lower limit. The extruded film became less strong and less rigid. This is somehow attractive in packaging industry, as customers preferred softer packaging materials.

Then, the tensile test was conducted at TD as well. As we mentioned above, the film fabricated through 0 multipliers was similar to a laminar composite/block-copolymer. The elongation of the ‘laminar composite’ is at ED. When deformed at TD, the stress again concentrated at the interface between LLDPE domains and EVOH domains. At this point, the size of the domains became less important. The modulus followed the lower bound of a series model again for all samples. That is the reason why all films showed similar stress-strain curves shown in Fig. 5.9.

However, the stress-strain curves from ED and TD are nearly identical for film fabricated through 6 and 8 multipliers. Because as the number of multipliers increased, the morphology of the extruded film gradually became similar to homogenous blends.
In other words, the morphology of the blend film turned into isotropic. But for films fabricated through 0 and 4 multipliers, due to the anisotropic morphology, we observed a decrease of young’s modulus and yield stress when deformed at TD compared to ED. LLDPE control and EVOH control showed similar stress-strain curves deformed at ED and TD, because LLDPE and EVOH control are isotropic in terms of morphology.

The comparison for stress-strain curves between ED and TD is shown in Fig. 5.10. Fig. 5.10a and Fig. 5.10b are the curves for films fabricated through 0 multipliers and 4 multipliers respectively. For those two films, deformation at ED yielded higher modulus as well as higher yield stress. However, when the number of multipliers increased to 6 and 8, the curves from ED and TD were nearly identical (Fig. 5.10a and Fig. 5.10b). As the number of multipliers increased, the mechanical behaviors became more and more isotropic. This is consistent with the morphology in terms of the AFM images.

Based on our discussions above, two interesting points were raised after the investigation for mechanical properties of the LLDPE-EVOH 50-50 extruded blend films. 1) As the number of multipliers increased, the morphology transformed from elongated, co-continuous and layered-like feature to homogenous and well dispersed feature. Along with this morphological evolution, the young’s modulus and yield stress of the extruded blend films decreased. 2) As the morphology became isotropic, the mechanical behaviors of the extruded blend films also became isotropic. These isotropic characteristics allowed these specific films to be used in many different
applications, like food packaging and medical packaging.

The LLDPE-EVOH 50-50 blend film fabricated through 8 multipliers with isotropic mechanical behaviors and improved transmission rate is a major finding of this paper. Although both young’s modulus and yield stress decreased as the number of multipliers increased, the isotropic mechanical behaviors of the extruded blend film made it valuable for many applications. Especially, due to the high oxygen barrier of EVOH and high water vapor barrier of LLDPE, this blend film of LLDPE-EVOH is interesting for packing applications.

By exploring the structure-property relationship of the extruded blend film, we proved that 1) by using multipliers, two immiscible polymers can be physically made homogenous; 2) by simply changing the number of multipliers, completely different morphology (from block-copolymer like to homogenous blend) of polymer films can be achieved.

5.4 Conclusions

Extruded blend films of LLDPE-EVOH with weight fraction of 50-50 were successfully fabricated through different number of multipliers. Due to the extrusion process, elongated, o-continuous and layered-like morphology was observed for film fabricated through 0 multipliers. As the number of multipliers increased, the elongated, co-continuous and layered-like morphology gradually became isotropic and homogenous. This is because the multipliers physically broke the domains of both materials into tiny phases. By using this way, two miscible polymers can form
homogenous blends.

As the morphology changed, the properties of the extruded LLDPE-EVOH 50-50 blend film also changed dramatically. When layered-like, elongated morphology turned into homogenous mixture, both oxygen and WVTR increased. The transparency was improved. More interestingly, the mechanical behaviors became isotropic as well. The LLDPE-EVOH 50-50 blend film fabricated through 8 multipliers showed great potential for packaging applications due to its tangency and soft mechanical behaviors.

The last but not the least, our results suggested that multiplication extrusion process can be used to fabricate homogenous blends regardless of the miscibility of polymer pairs. This really opens new avenue for both extrusion technique and compounding industry.
5.6 Reference


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Table 5.1
Thermal characteristics of LLDPE and EVOH studied in this paper.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m$ / °C</th>
<th>$T_c$ / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE control</td>
<td>124</td>
<td>115</td>
</tr>
<tr>
<td>EVOH control</td>
<td>159</td>
<td>140</td>
</tr>
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</table>
Table 5.2

Gas permeability of extruded EVOH-LLDPE (50-50) blend films fabricated through different number of multipliers.

<table>
<thead>
<tr>
<th>Sample (~1mil)</th>
<th>P O₂ / Barrer</th>
<th>P H₂O / g.mil/100in².day</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE control</td>
<td>3.7 ± 0.1</td>
<td>/</td>
</tr>
<tr>
<td>EVOH control</td>
<td>0.0015 ± 0.0001</td>
<td>/</td>
</tr>
<tr>
<td>0 multiplier</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EVOH-LLDPE 50-50</td>
<td>0.0034 ± 0.0001</td>
<td>0.38</td>
</tr>
<tr>
<td>4 multipliers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EVOH-LLDPE 50-50</td>
<td>0.0049 ± 0.0001</td>
<td>0.50</td>
</tr>
<tr>
<td>6 multipliers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EVOH-LLDPE 50-50</td>
<td>0.0055 ± 0.0001</td>
<td>0.59</td>
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<tr>
<td>8 multipliers</td>
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<tr>
<td>EVOH-LLDPE 50-50</td>
<td>0.011 ± 0.001</td>
<td>0.64</td>
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Table 5.3

<table>
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<tr>
<th>Sample/TD</th>
<th>EVOH control</th>
<th>LLDPE-EVOH 50-50 (0 multiplier)</th>
<th>LLDPE-EVOH 50-50 (4multiplier)</th>
<th>LLDPE-EVOH 50-50 (6multiplier)</th>
<th>LLDPE-EVOH 50-50 (8multiplier)</th>
<th>LLDPE control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus/Gpa</td>
<td>1.8±0.09</td>
<td>0.74±0.05</td>
<td>0.70±0.04</td>
<td>0.68±0.06</td>
<td>0.65±0.03</td>
<td>0.16±0.03</td>
</tr>
<tr>
<td>Yield Stress/Mpa</td>
<td>28±4</td>
<td>11±2</td>
<td>10±2</td>
<td>10±2</td>
<td>8±2</td>
<td>4±0.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample/ED</th>
<th>EVOH control</th>
<th>LLDPE-EVOH 50-50 (0 multiplier)</th>
<th>LLDPE-EVOH 50-50 (4multiplier)</th>
<th>LLDPE-EVOH 50-50 (6multiplier)</th>
<th>LLDPE-EVOH 50-50 (8multiplier)</th>
<th>LLDPE control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus/Mpa</td>
<td>1.8±0.09</td>
<td>0.84±0.03</td>
<td>0.73±0.04</td>
<td>0.69±0.05</td>
<td>0.67±0.05</td>
<td>0.17±0.05</td>
</tr>
<tr>
<td>Yield Stress/Mpa</td>
<td>30±3</td>
<td>14±2</td>
<td>11±2</td>
<td>10±2</td>
<td>7±1</td>
<td>4±0.3</td>
</tr>
</tbody>
</table>

Mechanical properties of LLDPE-EVOH blend films.
**Fig 5.1** Multiplication extrusion system to fabricate the blend films.
Fig 5.2  AFM images of partial cross section of
a) Extruded EVOH-LLDPE (50-50) blend film using 0 multiplier at ED,
b) Extruded EVOH-LLDPE (50-50) blend film using 4 multiplier at ED,
c) Extruded EVOH-LLDPE (50-50) blend film using 6 multiplier at ED,
d) Extruded EVOH-LLDPE (50-50) blend film using 8 multiplier at ED,
e) Extruded EVOH-LLDPE (50-50) blend film using 0 multiplier at TD,
f) Extruded EVOH-LLDPE (50-50) blend film using 4 multiplier at TD,
g) Extruded EVOH-LLDPE (50-50) blend film using 6 multiplier at TD,
h) Extruded EVOH-LLDPE (50-50) blend film using 8 multiplier at TD.
Fig 5.3. Schematic drawing shows the morphology of the LLDPE-EVOH (50-50) blend films after fabricated through different numbers of multipliers.
Fig 5.4 WAXS pattern of

a) Extruded EVOH-LLDPE (50-50) blend film using 0 multiplier at ED,
b) Extruded EVOH-LLDPE (50-50) blend film using 4 multiplier at ED,
c) Extruded EVOH-LLDPE (50-50) blend film using 6 multiplier at ED,
d) Extruded EVOH-LLDPE (50-50) blend film using 8 multiplier at ED,
e) Extruded LLDPE control at ED,
f) Extruded EVOH control at ED,
g) Extruded EVOH-LLDPE (50-50) blend film using 0 multiplier at TD,
h) Extruded EVOH-LLDPE (50-50) blend film using 4 multiplier at TD,
i) Extruded EVOH-LLDPE (50-50) blend film using 6 multiplier at TD,
j) Extruded EVOH-LLDPE (50-50) blend film using 8 multiplier at TD,
k) Extruded LLDPE control at ED,
l) Extruded EVOH control at ED,

The arrows are showing the reflection planes from LLDPE.
Fig 5.5 Azimuthal scan of LLDPE (200) plane from selected WAXS pattern of (from bottom to top):
Extruded EVOH-LLDPE (50-50) blend film using 0 multiplier at ED,
Extruded EVOH-LLDPE (50-50) blend film using 4 multiplier at ED,
Extruded EVOH-LLDPE (50-50) blend film using 6 multiplier at ED,
Extruded EVOH-LLDPE (50-50) blend film using 8 multiplier at ED.
**Fig 5.6** DSC heating curves of LLDPE-EVOH (50-50) blend films fabricated by different number of multipliers.
**Fig 5.7** Transmission rate of extruded blend films fabricated by different multipliers as a function of wavelength.
Fig 5.8 Stress-Strain curves of LLDPE-EVOH blend films deformed at extrusion direction.
Fig 5.9 Stress-Strain curves of LLDPE-EVOH blend films deformed at transverse direction.
Fig 5.10 Comparison of the Stress-Strain curves of LLDPE-EVOH blend films deformed at ED and TD fabricated by different number of multipliers:
a) Film fabricated through 0 multipliers,
b) Film fabricated through 4 multipliers,
c) Film fabricated through 6 multipliers,
d) Film fabricated through 8 multipliers.
Chapter 1


Chapter 2


Chapter 3


Chapter 4


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Chapter 5


