Structure and transport properties of polyethylene terephthalate and poly(vinylidene fluoride-co-tetrafluoroethylene) multilayer films

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The morphologies of two crystalline polymers, polyethylene terephthalate (PET) and poly(vinylidene fluoride-co-tetrafluoroethylene) [P(VDF-TFE)], were probed under nanolayer confinement using forced assembly multilayer film coextrusion. This multilayer system was used as a platform to investigate the effect of nanolayer coextrusion, biaxial stretching, and isothermal melt recrystallization on the confined morphologies of both of these polymers. To determine the effect of each of these variables independently, three sets of PET/P(VDF-TFE) multilayer films were produced, each with comparable film thickness and layer thickness. The morphology and X-ray data of the extruded PET/P(VDF-TFE) multilayer films, which were taken directly from the coextrusion process, indicate that the morphologies of both PET and P(VDF-TFE) were relatively unaffected by nanolayer confinement. Biaxial stretching of multilayer films, produced from stretching micron thick layers down to nanolayers, facilitated the development of an on-edge P(VDF-TFE) crystal orientation in addition to an oriented PET fibrillar crystal structure. Finally, an approach of isothermal melt recrystallization was conducted on the biaxially stretched samples which revealed the formation of high aspect ratio in-plane P(VDF-TFE) crystals under nanolayer confinement while also further crystallizing the PET fibril crystals. Therefore, in the same multilayer system, three P(VDF-TFE) crystal orientations were achieved by utilizing nanolayer confinement, biaxial stretching, and isothermal melt recrystallization. Oxygen permeability was used as an additional structural probe for these confined PET and P(VDF-TFE) layer morphologies. From the transport data, it was determined that the PET layers possessed similar oxygen transport characteristics to the bulk materials, which was in good agreement with the morphology data of the PET layers in the various PET/P(VDF-TFE) multilayer films. In contrast, the on-edge P(VDF-TFE) orientation induced from biaxial stretching and in-plane P(VDF-TFE) crystal orientation induced from isothermal melt recrystallization of confined P(VDF-TFE) nanolayers yielded substantial reductions in the effective oxygen permeability of the P(VDF-TFE) layers in comparison to the bulk P(VDF-TFE) control. The various confined P(VDF-TFE) crystal orientations and subsequent enhanced barrier properties are enabled by the hard nanolayer morphologies, specifically the in-plane P(VDF-TFE) crystals, substantially reduced the WVTR in multilayer films opening new applications for this technology.

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1. Introduction

The properties of commercial polymer films are highly dependent on the processing conditions used to produce the final product. Careful control over these processing conditions provides an opportunity to tailor the final film properties to match a specific application. Semi-crystalline polymers such as poly(ethylene terephthalate) (PET) and polypropylene (PP) are widely used in food, electronic and medical packaging applications. The production of PP and PET thin films often involves a biaxial orientation step which is used to reduce the film thickness while also improving mechanical strength and dimensional stability [1–3]. In addition to improving mechanical properties, biaxial orientation also results in a 2–3 × reduction in gas permeability for both PP and PET [3,4]. The future
of advanced flexible packaging, especially for electronics packaging, requires much higher gas barrier properties than is obtainable from standard biaxially oriented monolith polymer films [5].

Researchers have turned to the field of nano-science to achieve the next level of innovation in polymer thin films [6,7]. Of particular interest is the area of nanoconfinement where the reduction of critical dimensions to the nano-scale can yield novel structures that impact bulk properties [8]. Techniques used to study nanoconfinement of polymers include spin coating thin films onto a substrate [8], block copolymers with at least one crystallizable block [9], patterned substrates [10], and more recently forced assembly nanolayer coextrusion [11,12].

Forced assembly micro and nanolayer coextrusion has proven to be a versatile and effective method of studying the nanoconfinement of a wide range of semi-crystalline and amorphous polymers [11–13]. Using this novel process, a variety of semi-crystalline polymers including poly(ethylene oxide) (PEO), poly(ε-caprolactone) (PCL), polyethylene (PE), and PP have been successfully confined which form unique crystalline morphologies under nanolayer confinement [11–15]. In the case of PEO and PCL, coextrusion against a hard confining layer resulted in the formation of high aspect ratio, in-plane crystals that resemble polymer single crystals grown from solution or confined in a very narrow channel. The formation of constrained, highly confined morphology in nanolayered films had a dramatic impact on the gas transport properties resulting in a 200–300 × reduction in bulk film permeability. Successful attempts have also been made to incorporate confined high aspect ratio PEO and PCL in-plane crystals into a potential commercial biaxially oriented PP (BOPP) film [16,17]. In these systems, the added benefit of enhanced barrier properties was achieved without sacrificing other important packaging properties such as optical clarity and mechanical toughness.

In order to gain additional understanding on the generality of this phenomenon, additional semi-crystalline polymers have been investigated including syndiotactic PP (sPP), poly(vinylidene fluoride) (PVDF), and a poly(vinylidene fluoride-co-tetrafluoroethylene) copolymer [P(VDF-TFE)] [18,19]. In contrast to PEO and PCL, coextrusion of sPP, PVDF, and P(VDF-TFE) against a hard confining polymer did not inherently produce a highly oriented crystalline structure under confinement. Instead, these materials required slow melt recrystallization in order to obtain high aspect ratio polymer crystals. It is speculated that the cause of this observation is due to the relatively high crystallization temperatures of these polymers and the rapid thermal quenching of the polymer film from the melt after it exits from the extruder die. The isothermal melt recrystallization process requires a temperature window between the melting of the confined semi-crystalline polymer and the glass transition or melting point of the confining polymer. As a result of this temperature window, the confined semi-crystalline polymer can be melted, while maintaining the hard nanolayer confinement, and crystallized or quenched to any temperature. Changing the crystallization or quench temperature will directly influence the confined polymer crystal orientation. In general, in-plane crystals form at higher temperatures whereas on-edge and/or isotropic crystals form at lower temperatures. This inherent flexibility over the confined morphology allows for the final film oxygen permeability properties to be tailored and controlled [18,19].

This study aims not only to add additional understanding to the area of nanolayer induced confined crystallization but also to improve the final film properties. The approach is to combine the nanolayer confinement with solid state biaxial stretching and isothermal melt recrystallization in a manner not previously studied. Previous studies using PEO and PCL confined by BOPP conducted biaxial stretching with PEO and PCL in the molten state. Combining a PVDF based polymer and PET in a multilayer assembly opens the opportunity to biaxially stretch both materials in the solid state and produce unique confined structures that may also impact bulk film properties. In addition, the approach of isothermal melt recrystallization was also used as a means to further manipulate the structures of both layers. The thermal process can effectively change the crystal orientation of P(VDF-TFE) [19] while also further crystallizing the PET [20]. This system provides a unique platform for confined crystallization via forced assembly to optimize and tailor the confined structures to suit various applications and properties. Both of these polymers inherently possess high oxygen barrier properties and are attractive materials for confinement studies [1,21]. PVDF based polymers are attractive due to their wide range of commercial applications and crystalline phases, in addition to their unique energy storage, piezoelectric, and pyroelectric properties [22–24]. PET by itself is already commercially used as high barrier packaging. Finally, a second goal was to demonstrate the impact of nanolayer induced confined crystallization on other transport properties such as water vapor transport rate (WVTR). Fluoropolymers are commonly used as pipes or pipe linings for chemical processing due to their excellent chemical resistance properties [25]. For these applications, the performance properties i.e. corrosion resistance, solvent permeability etc., of these materials could potentially be improved through careful control over the polymer crystalline structure and/or orientation.

2. Materials and methods

Poly(vinylidene fluoride-co-tetrafluoroethylene) copolymer [P(VDF-TFE)] with 20 mol% tetrafluoroethylene (Neoflon VP-50) was obtained from Daikin Industries, Ltd. Poly(ethylene terephthalate) (PET) (Polyclear 1101q, IV: 0.83) was obtained from Invista Polymers and Resins. PET was dried under vacuum at 80 °C for 24 h prior to melt processing.

The coextrusion processing temperature was chosen based on the rheological compatibility of PET and P(VDF-TFE). Polymer melt rheological properties were measured as a function of temperature using a Kayeness Galaxy 1 melt flow indexer (MFI) at a low shear rate of 10 s⁻¹, chosen to simulate flow conditions during multilayer coextrusion. Using this technique, a processing temperature of 260 °C was determined for optimum multilayer coextrusion of PET and P(VDF-TFE). Multilayer films with alternating ABAB layers of PET/P(VDF-TFE) were produced using a “forced assembly” layer multiplying coextrusion process described previously [26,27]. All processing elements, including extruders, multiplier die elements and film die, were set at 260 °C to ensure matching melt viscosities of PET and P(VDF-TFE) as determined by MFI. All multilayer films produced were laminated with a polyethylene (PE) skin layer to improve the film quality and protect the film from damage. The PE skin layers were removed prior to any additional processing, characterization or testing. Films were cast onto a heated, stainless steel coated take-off roller at a temperature of 70 °C. Multilayer films with 32 and 256 alternating PET and P(VDF-TFE) layers were produced (Table 1). The relative composition [v/v, PET/P(VDF-TFE)] was varied by changing the volumetric melt pump rate of each polymer melt stream during film processing. The multilayer film thickness was varied by adjusting the take-off roll speed. Thin 10 μm films were produced and taken as extruded multilayer control films. The nominal P(VDF-TFE) layer thickness, calculated from the number of layers, volume composition, and the film thickness, was varied from 500 nm down to 24 nm. Thick multilayer films with a 200 μm film thickness were produced for subsequent biaxial stretching. Additionally, both 10 μm and 200 μm PET and P(VDF-TFE) control films were produced under identical processing conditions to that of the multilayer films.

Biaxial stretching was conducted using a Brückner (Greenville, SC, USA, Siegsdorf, Germany) Karo IV laboratory stretcher.
Unoriented plaques measuring 85 mm × 85 mm were cut from 200 μm thick extruded multilayered films. Before stretching, the plaques were marked using an ink grid pattern with a spacing of 6.5 mm × 6.5 mm to determine stretch uniformity after the stretching process was complete. Films were stretched simultaneously at a high draw ratio of 4.5−6.5 mm to determine previously [19]. The recrystallization condition was chosen in order to produce the uniformity and conformation of the printed ink pattern. All samples listed in Table 1 were evaluated for stretch uniformity indicated by the uniform deformation of the printed ink pattern. All samples listed in Table 1 were stretched under these conditions with the exception of the P(VDF-TFE) control.

Isotropical melt recrystallization was carried out on the biaxially stretched multilayer films, constrained in an aluminum mask, using two temperature controlled silicone oil baths. The oil bath temperature was regulated using an Fisher-Scientific (Waltham, MA) Series 988 controller. Films were placed into one oil bath at 140 °C for 20 min to melt the P(VDF-TFE) layers and then quickly transferred to the second bath at 120 °C and held isothermally for 3 h. This recrystallization condition was chosen in order to produce the maximum amount of highly oriented in-plane P(VDF-TFE) crystals as determined previously [19].

The PET and P(VDF-TFE) controls and multilayer film 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 PET and P(VDF-TFE) crystallinity was calculated from the melting enthalpies using the heat of fusion, ΔH0 of 104.7 J g−1 for PVDF and ΔH0 of 125 J g−1 for PET [28,29].

Extruded, biaxially stretched, and biaxially stretched recrystallized multilayer films were embedded in epoxy and cured at room temperature for 24 h. Multilayer film cross sections were microtomed at −100 °C perpendicular to the extrusion direction using a Leica Microsystems (Buffalo Grove, IL) EM FC6 ultramicrotome. Thick 200 μm multilayer film cross sections were examined using optical microscopy (OM) with an Olympus (Miami, FL) BH-2 optical microscope. Thin 10 μm multilayer films were examined using atomic force microscopy (AFM) to determine layer continuity, uniformity and confined PET and P(VDF-TFE) layer morphology. Phase and height images of the multilayer film cross sections were recorded using a Nanoscope IIIa Multimode scanning probe (Digital Instruments, Santa Barbara, CA) operating in the tapping mode, in air, and at ambient temperature.

Two dimensional wide angle X-ray scattering (WAXS) was used to characterize the structure and orientation of the PET/P(VDF-TFE) multilayer films in addition to the controls. WAXS patterns were obtained by aligning the incident X-ray beam parallel to the extrusion direction (ED) of the film. A highly focused monochromatic CuKα (λ = 0.154 nm) X-ray beam was generated using 45 kV and 0.88 mA with a Confocal Max-Flux optic with a sealed tube micro-focus X-ray source ( Rigaku, the Woodlands, TX, MicroMax-002). The sample to detector distance was 140 mm. A CaF2 standard was used to calibrate the diffraction angle. WAXS patterns were collected using a Fuji Film (Tokyo, Japan) image plate with a 50 μm pixel size.

The oxygen flux J(t) was measured using a MOCON OX-TRAN 2/20 ( Minneapolis, MN) at 23 °C, 0% relative humidity, and 1 atm pressure. NIST certified Mylar film of known oxygen transport properties was used as a calibrating standard measured at 23 °C. Film samples were masked using an aluminum sample mask with a testing area of 5 cm². Masked films were conditioned in the instrument as described previously [30]. The oxygen permeability P(O2) was calculated from the steady state flux, J, as

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

where Δp is the difference of the oxygen partial pressure across the film, which is 1 atm. The average reported P(O2) values were taken from a minimum of two samples. P values are reported in Barrers.

The water vapor transport rate (WVTR) was measured using a MOCON Permatran-W (Model 3/33 SG-Plus, Minneapolis, MN) at 23 °C, 100% relative humidity, and 1 atm pressure. The humidity was generated by using a sponge wet with distilled water. Ultra-high purity, dry nitrogen was used as the carrier gas. The flow rate of the nitrogen gas was varied to acquire a constant water vapor flux and allowed to reach steady state for 24 h. NIST certified Mylar film of known water vapor transport properties was used as a calibrating standard measured at 23 °C. Film samples were masked using an aluminum sample mask with a testing area of 5 cm². The water vapor permeability P(H2O) was calculated from the steady state water vapor transport rate, WVTR, as

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

where Δp is the difference of the partial pressure of water across the film, which is 1 atm. The average reported P(H2O) values were taken from a minimum of two samples. WVTR values are reported in gm*mil/100*in²*day.

3. Results and discussion

3.1. Extruded PET/P(VDF-TFE) multilayer films

AFM was used to characterize the layer integrity, layer thickness, and confined PET and P(VDF-TFE) morphology of various extruded PET/P(VDF-TFE) microlayer films, Fig. 1. Cross-section AFM images of these films reveal continuous PET and P(VDF-TFE) layers with layer thicknesses that closely matched the nominal layer thickness calculated from the number of layers, composition and overall film thickness. The AFM phase images also revealed the confined PET and P(VDF-TFE) layer morphology in extruded PET/P(VDF-TFE) microlayer films. A random granular structure was observed in the P(VDF-TFE) layers for all of the samples. The PET layers possessed no apparent morphology as discerned from the AFM images, with only knife marks from the microtoming being observed which were considered artifact. The morphology within the extruded multilayer films was compared to extrusion direction (ED) WAXS images for the same samples, Fig. 1. The ED WAXS images of the extruded PET/P(VDF-TFE) multilayer films exhibit a single isotropic (110) and (200) P(VDF-TFE) reflection ring at 2θ = 20.1° irrespective of P(VDF-TFE) layer thickness. The observed reflection was also seen in the WAXS of the bulk P(VDF-TFE) control (not shown). The
crystal phase structure of this material was assigned to the low temperature ferroelectric phase of P(VDF-TFE) copolymers, which is similar to β-phase PVDF homopolymer [31,32]. No sharp PET crystal reflections were observed in the extruded PET/P(VDF-TFE) samples. Instead, a weak, isotropic PET amorphous halo was detected at 2θ = 20° indicating little to no PET crystallinity. Based on these results, it was determined that there was little to no effect of nanolayer confinement on the PET or P(VDF-TFE) morphology in the extruded multilayer films. This observation is consistent with previous results where the same P(VDF-TFE) copolymer was confined by an amorphous polycarbonate layer [19]. However, this result is in contrast with previous confinement studies using PEO and PCL where nanolayer confinement induced anisotropic lamellae orientation in extruded multilayer films. A stretching window was established for this system in the temperature range of 100–120 °C. This allows for stretching of glassy PET above its respective T_g of 75 °C and below the crystalline melting point for P(VDF-TFE) of 125 °C. Stretching in this temperature range will induce solid state structural changes in both polymers under multilayer confinement. A final biaxial stretching temperature of 105 °C was chosen for the PET/P(VDF-TFE) multilayer films, Fig. 2. It must be noted that a stretching condition to produce a biaxially stretched P(VDF-TFE) control was not found. For consistency and proper comparison, it was desired that the biaxially stretched films possessed a similar film thickness and layer thicknesses to the extruded films. This was accomplished by biaxial stretching thick 200 μm microlayer films down to thin 10 μm microlayer films, Fig. 3. A 200 μm microlayer film stretched at a 4.5 × 4.5 draw ratio resulted in a 20× thickness reduction yielding an approximately 10 μm thick biaxially stretched multilayer film, which is comparable to the film thickness and nominal PET and P(VDF-TFE) layer thickness of the extruded multilayer films listed in Table 1. Multilayer films before and after stretching are shown in

![Image](https://example.com/image.png)

**Fig. 1.** Top row: AFM phase images of extruded (a) 50/50, 32 layer (b) 70/30, 32 layer and (c) 50/50, 256 layer PET/P(VDF-TFE) multilayer films. The measured film thickness is around 9.6–10.5 μm. The darker layers are the P(VDF-TFE) layers. Bottom row: Corresponding ED X-ray WAXS images, with indicated P(VDF-TFE) layer thicknesses, of extruded (d) 50/50, 32 layer (e) 70/30, 32 layer and (f) 50/50, 256 layer PET/P(VDF-TFE) multilayer films.

3.2. Biaxially stretched PET/P(VDF-TFE) multilayer films

Biaxial stretching was used as a route to manipulate the confined structures of the PET/P(VDF-TFE) multilayer films. It is well known that stretching, either uniaxial or biaxial, can dramatically impact the structure of polymers including PET and PVDF based polymers [21,37]. In the case of PET, the nature of the structure depends on the stretching temperature. At stretching temperatures below T_g,PET, the PET forms a densified glass [34] where stretching above T_g,PET results in strain induced crystallization forming a fibrillar structure [35]. For semi-crystalline PVDF, stretching below T_m,PVDF results in the formation of a fibrillar morphology with ordering along the chain axis [21]. Multilayering P(VDF-TFE) with a stretchable polymer such as PET opens the opportunity to further manipulate the structure of both polymers through biaxial orientation under nanolayer confinement. A stretching window was established for this system in the temperature range of 100–120 °C. This allows for stretching of glassy PET above its respective T_g of 75 °C and below the crystalline melting point for P(VDF-TFE) of 125 °C. Stretching in this temperature range will induce solid state structural changes in both polymers under multilayer confinement. A final biaxial stretching temperature of 105 °C was chosen for the PET/P(VDF-TFE) multilayer films, Fig. 2. It must be noted that a stretching condition to produce a biaxially stretched P(VDF-TFE) control was not found. For consistency and proper comparison, it was desired that the biaxially stretched films possessed a similar film thickness and layer thicknesses to the extruded films. This was accomplished by biaxial stretching thick 200 μm microlayer films down to thin 10 μm microlayer films, Fig. 3. A 200 μm microlayer film stretched at a 4.5 × 4.5 draw ratio resulted in a 20× thickness reduction yielding an approximately 10 μm thick biaxially stretched multilayer film, which is comparable to the film thickness and nominal PET and P(VDF-TFE) layer thickness of the extruded multilayer films listed in Table 1. Multilayer films before and after stretching are shown in
Fig. 3. From these images, it can be seen that the layered structure remains intact following the biaxial stretching process. In addition, both the film thickness and layer thicknesses of these films match closely to the extruded films described earlier. The AFM phase image of the biaxial stretched multilayer film also reveals a change in the P(VDF-TFE) layer morphology. The confined P(VDF-TFE) layers appear as stacked granules that appear to be aligned in the stretching plane. The confined morphology of the confined PET layers is more difficult to elucidate from the AFM images. The PET layers do appear as short stacked platelets, aligned in the stretching plane, however, these structural features may be artifact from the microtoming process. Similar structural features were also observed in multilayer films with thinner P(VDF-TFE) layers (not shown).

3.3. Biaxially stretched, recrystallized PET/P(VDF-TFE) multilayer films

An approach of isothermal melt recrystallization was utilized to further manipulate the confined morphologies of PET and P(VDF-TFE) under confinement. This technique was applied to the PET/P(VDF-TFE) system in order to produce in-plane P(VDF-TFE) lamellae crystals while also crystallizing the PET layers. A large temperature difference between the \( T_{m, P(VDF-TFE)} \) and the \( T_{m, PET} \) allowed melting of the P(VDF-TFE) layer under hard confinement from the PET layer, Fig. 4. Samples were held at 140 °C in order to melt the P(VDF-TFE) layers, for 20 min. Subsequently, the temperature was decreased to 120 °C and held for three hours to produce in-plane P(VDF-TFE) crystals. Cold crystallization of PET was also expected during this thermal treatment. It must be noted that this procedure was only effectively utilized in the biaxially stretched PET/P(VDF-TFE) films. Extruded samples had mostly amorphous PET layers that cold crystallized over a similar temperature range as the melting of P(VDF-TFE), which resulted into layer instability and even layer breakup to occur during the melt recrystallization process. AFM images reveal that the layer integrity remains intact following the thermal annealing, with measured layer thicknesses that match the calculated nominal layer thicknesses, Fig. 5. The confined structure of P(VDF-TFE) consisted of stacks of oriented crystals, lying in the plane of the layer, in 300 nm layers to large in-plane single oriented crystals in 60 nm P(VDF-TFE) layers. Interestingly for these samples, the P(VDF-TFE) layers appear as the brighter layer which qualitatively indicates an enhancement in the mechanical properties of the P(VDF-TFE) layers with in-plane crystals. Possible reasons for this observation may be related to the increased crystallinity of the P(VDF-TFE) after recrystallization and/or a potential enhancement in the mechanical stiffness as a result of the highly oriented in-plane structure, which was observed previously in multilayer films with PEO confined by polystyrene (PS) [36]. Even in the relatively thick P(VDF-TFE) layers, the majority of these platelet-like in-oriented crystals are predominantly lying parallel to the layered structure. The measured P(VDF-TFE) crystal widths from the AFM images appear to be as large as 1 μm. Additionally, the crystal thickness appears consistently around 20–25 nm regardless of the P(VDF-TFE) layer thickness. Similar to the previous samples, the apparent PET morphology was difficult to discern from the AFM images due to potential artifact from the microtoming. However, these layers did appear as short stacked platelets aligned in the stretching plane similar to the morphology observations in the biaxially stretched PET/P(VDF-TFE) system. No drastic morphology change in the PET layers was observed under these heating/annealing conditions.

Fig. 3. Top: Procedure for producing biaxially stretched multilayer films. Samples are prepared by stretching thick layers down to thin layers. Bottom: (a) optical microscopy image of a 200 μm thick 50/50 PET/P(VDF-TFE) 32 layer starting film before stretching. (b) AFM image of a 50/50 PET/P(VDF-TFE) 32 layer film after biaxial stretching at a 4.5 × 4.5 draw ratio. The measured film thickness is 10.4 μm.
3.4. PET/P(VDF-TFE) multilayer film thermal properties

DSC was used to characterize the thermal properties of the extruded, biaxially stretched, and biaxially stretched recrystallized 50/50 PET/P(VDF-TFE) 32 and 256 layer films, Fig. 6. For the extruded multilayer films, the $T_m$ of P(VDF-TFE) and $T_c$ of PET occur over the same temperature range making interpretations about the crystallinity of both polymer layers difficult using DSC. Therefore, the P(VDF-TFE) crystallinity was estimated using 2D WAXS images and was found to be approximately 28% which was close to the crystallinity of the P(VDF-TFE) control, $X_c = 32\%$ from DSC. Additionally, there was little change in P(VDF-TFE) crystallinity with decreasing...
layer thickness. The PET layer in the extruded multilayer films was assumed to be mostly amorphous, based on the absence of any crystalline reflections from WAXS and DSC results of the extruded PET control film, where a cold crystallization peak was observed, \( T_{cc,PET} = 126 \, ^\circ C \), in the first heating thermogram, Fig. 2. The \( \Delta H \) value for the cold crystallization peak (26.5 J g\(^{-1}\)) was close to the \( \Delta H \) value of the crystal melting peak (33.7 J g\(^{-1}\)) leaving around 6% crystallinity in the PET control films. Biaxial orientation results in an increase in the \( T_m \) of P(VDF-TFE) from 125 \(^\circ C\) for the extruded films to 132 \(^\circ C\) for the biaxially oriented films irrespective of layer thickness. The cold crystallization of PET was minimized in the biaxially stretched multilayer samples, due to the strain induced crystallization of PET during stretching, which allowed for determination of the P(VDF-TFE) crystallinity to be approximately 30–38%, matching the bulk crystallinity of P(VDF-TFE) control. With a stretch temperature that is 20 \(^\circ C\) below the \( T_m \) of P(VDF-TFE), the stretching process would transform the solid state structure of P(VDF-TFE) in extruded multilayer films into a fibrillar structure under high strain deformation [21]. A fibrillar like structure has been reported for PVDF under high strain uniaxial deformation which impacts properties such as gas transport [21,37]. In addition, fibrillar structures are extensively reported in the literature for biaxially oriented polypropylene [38]. Indeed, AFM phase images of the P(VDF-TFE) free surface in the biaxially stretched PET/P(VDF-TFE) 32 layer films reveal a fibrillar structure as a result of stretching (not shown). This apparent surface morphology may not be representative of the P(VDF-TFE) layer morphology inside the film; however, it is reasonable to assume a similar fibrill like structure would form under these orientation conditions, even under layer confinement. The highly ordered fibrill structure could also be responsible for the shift in \( T_m \) of P(VDF-TFE). Biaxially stretched, recrystallized films exhibit a further increase in both \( T_m \) of P(VDF-TFE), from 140 to 143 \(^\circ C\), and crystallinity of P(VDF-TFE), from 53 to 55%. Slow crystallization at higher temperatures, in nanolayers, would promote the formation of larger crystals, thus increasing \( T_m \), due to a reduction in area nucleation density and deactivation of surface nuclei [14,39]. Unlike P(VDF-TFE), the peak \( T_m \) of PET was unaffected by stretching or thermal treatment, however, the PET layer crystallinity was significantly altered. Stretched multilayer samples showed little to no cold crystallization peak with overall crystallinities ranging from 30 to 40% for the PET layer. This was in good agreement with DSC results for the PET control under the same stretching and thermal annealing conditions.

### 3.5. WAXS of biaxially stretched and recrystallized PET/P(VDF-TFE) multilayer films

The nature of the PET and P(VDF-TFE) chain orientation in the biaxially stretched, and biaxially stretched recrystallized PET/P(VDF-TFE) multilayer films was investigated using 2-dimensional WAXS. Analysis of the ED WAXS patterns for the PET/P(VDF-TFE) multilayer films reveals that biaxial orientation has a large effect on the confined P(VDF-TFE) crystal orientation, Fig. 7a–d. The WAXS data also confirm that the crystal phase of P(VDF-TFE) in the biaxially stretched multilayer samples is that of the low temperature ferroelectric phase, indicating that the P(VDF-TFE) crystal phase is unaffected by the biaxial stretching process. The appearance of sharp P(VDF-TFE) (200) arc reflections at the meridian indicates that the c-axis of the P(VDF-TFE) lamellae is oriented parallel to the layers thus forming on-edge P(VDF-TFE) lamellae crystals. Further proof of on-edge P(VDF-TFE) lamellae is indicated by the appearance of a four-point P(VDF-TFE) (110) arc pattern in the WAXS images. The formation of the on-edge lamellae was not significantly affected by layer thickness with similar reflection patterns being observed for multilayer films with 300, 120, 40 and 24 nm P(VDF-TFE) layer thicknesses. In a previous study using P(VDF-TFE) confined by PC in multilayers [19], only isotropic and in-plane P(VDF-TFE) orientations were achieved. Biaxial stretching allows for the formation of on-edge P(VDF-TFE) crystals under PET confinement. The effect of biaxial stretching in confined layers was not as prominent in the PET layers. Weak but highly oriented PET crystalline reflections were seen in all the biaxially stretched multilayer samples. These PET reflections were nearly identical to those observed in the WAXS patterns of the biaxially stretched PET control, Fig. 7e. Biaxial stretching above the \( T_g \) of PET results in strain induced crystallization which forms a network of PET fibril crystals randomly oriented in the stretching plane [35]. This same structure is evident in both the PET control and PET layers in multilayer films.

The ED WAXS patterns for the biaxially stretched recrystallized PET/P(VDF-TFE) multilayered samples confirm that the crystalline phase of P(VDF-TFE) is that of the low temperature ferroelectric phase, indicating the crystal phase of P(VDF-TFE) was unaffected by the recrystallization process. However, the P(VDF-TFE) crystal orientation is significantly affected by this thermal process. These recrystallized multilayer samples exhibit a single pair of P(VDF-TFE) (110) and (200) reflection arcs at the equator confirming the

![Fig. 7. Extrusion direction 2D WAXS patterns for various 10 µm PET/P(VDF-TFE) multilayer films with indicated P(VDF-TFE) layer thicknesses and PET controls. Top row: biaxially stretched films (a) 50/50, 32 layers (b) 80/20, 32 layers (c) 50/50, 256 layers (d) 70/30, 256 layers and (e) PET control. Bottom row: biaxially stretched, 120 \(^\circ C\) heat set/recrystallized films (f) 50/50, 32 layers (g) 80/20, 32 layers (h) 50/50, 256 layers (j) 70/30, 256 layers and (j) PET control.](image-url)
presence of in-plane P(VDF-TFE) crystals with the c-axis oriented perpendicular to the layer plane, Fig. 7f–i. Like the extruded and biaxially stretched systems, this in-plane P(VDF-TFE) orientation was not significantly affected by the layer thickness. The intensity of the oriented PET reflections in the WAXS images of the multilayer films after annealing appears sharper, indicating that the PET layers are effectively being crystallized during annealing. This observation is similar to a biaxially oriented PET film which was identified to have an oriented fibril structure with lamellae crystals forming perpendicular to the fibril crystals seen in the literature [35]. The thermal process crystallizes the amorphous segments of the PET layers and allows them to form lamellar crystals and bridge the oriented fibril crystals, thus increasing the intensity of the PET reflections in the WAXS images. Through multilayer coextrusion, biaxial stretching, and thermal annealing, three possible crystal orientations (isotropic, on-edge, and in-plane) can be obtained. This inherent flexibility does not extend to the PET layers, where a different confining layer and higher annealing temperatures would likely be needed in order to manipulate the confined PET orientation [40].

Azimuthal intensity profiles of the P(VDF-TFE) (110) and (200) reflections for the extruded, biaxially stretched, and biaxially stretched recrystallized 50/50 PET/P(VDF-TFE) 32 layer films reveal the three crystalline structures obtained through nanolayer confinement, biaxial stretching and, thermal annealing in this system, Fig. 8. Comparing all three samples, it can be clearly seen that this system allows for unique and systematic control over the confined P(VDF-TFE) crystal orientation. Using an orthorhombic unit cell for β-PVDF and unit cell dimensions of $a = 0.858$ nm, $b = 0.491$ nm, and $c = 0.256$ nm [41], the predicted (110) and (200) peak positions for the on-edge P(VDF-TFE) crystals with the a-axis perpendicular to the layers and c-axis parallel to the layers match those seen experimentally in the biaxially stretched PET/P(VDF-TFE) multilayer films: 60.2°, 119.7°, 240.2°, 299.8° for (110) and 0°, 180° for (200). The predicted (110) and (200) peak positions for perfect in-plane crystals would be 90° and 270°, however, the azimuthal scan appears broad with an almost four-point pattern. In-plane P(VDF-TFE) reflections were not entirely sharp which is characteristic of single crystal lamellae under confinement [11,13] and was seen previously when P(VDF-TFE) was confined by PC [19]. It was hypothesized that the chain axis is tilted with respect to the lamellae fold surface ND. This observed phenomena is also unaffected by the confining substrate as it was observed for both PC and PET. Two additional small peaks were observed at 0° and 180° for the biaxially stretched recrystallized multilayer film. These small peaks were attributed to remnant on-edge crystals that were not completely melted during the recrystallization process. It is possible that these remnant on-edge crystals may be disrupting the formation of in-plane crystals. Based on the morphology and structure analysis from AFM and WAXS, a schematic of the confined PET and P(VDF-TFE) structures in extruded biaxially stretched, and biaxially stretched recrystallized P(VDF-TFE) multilayer films is proposed, Fig. 9.

### 3.6. Oxygen barrier properties of PET/P(VDF-TFE) microlayer films

Oxygen permeability, $P$, was measured for the various PET/P(VDF-TFE) multilayer films, Table 2. As expected, biaxial stretching reduced $P$ for all multilayered films in addition to the PET control. Comparing extruded and biaxially stretched films of the same composition and number of layers, for example 70/30 v/v, 32 layers, a two times decrease in $P$ is seen as a result of stretching. Reducing the layer thickness while maintaining the same PET/P(VDF-TFE) composition had little effect on $P$ in both extruded and biaxially stretched films. Consistent with previous reports on nanolayer confined multilayer films with in-plane lamellae [12], the biaxially stretched recrystallized samples with in-plane P(VDF-TFE) crystals exhibit a tremendous improvement in oxygen barrier properties compared to the bulk controls. In the films with thinnest 40 and 24 nm P(VDF-TFE) layers, the overall oxygen permeability dropped to 0.001 barrer representing a 30× improvement in overall film oxygen barrier properties compared to the PET control. At this time, this is the lowest oxygen permeability system obtained using nanolayer confined crystallization facilitated by forced assembly coextrusion. For the biaxially stretched recrystallized films, comparing films with the same composition and different number of layers, the permeability also decreases slightly with decreasing P(VDF-TFE) layer thickness. The higher degree of confinement combined with the slow melt recrystallization may facilitate the formation of larger in-plane crystals, even though the structural features observed in AFM and WAXS appear similar. Considering that biaxial stretching and thermal annealing effectively manipulate the solid state structure of both PET and P(VDF-TFE) in multilayers, the decrease in $P$ most likely results from the contributions of both of these polymers under multilayer confinement. The barrier properties of the PET control films decrease with biaxial stretching and thermal annealing. The stretching process crystallizes the PET due to strain induced crystallization while thermal annealing further develops the microstructure by producing additional lamellae crystalline domains that grow perpendicular to the fibril crystalline domains [35]. Both of these structural features are reported to reduce the permeability properties in PET [20,42]. These structural features were verified in the PET controls for this study using WAXS and DSC, however, this reduction in permeability does not fully account for the large permeability reductions for the biaxially stretched and biaxially stretched recrystallized PET/P(VDF-TFE) multilayer films.

The overall film $P$ of the various PET/P(VDF-TFE) multilayer films was compared to a calculated series model permeability $P_M$ based on the oxygen permeability of the single layer controls according to

$$\frac{1}{P_M} = \frac{\phi_{P(VDF-TFE)}}{P_{P(VDF-TFE)}} + \frac{1 - \phi_{P(VDF-TFE)}}{P_{PET}}$$

where $\phi_{P(VDF-TFE)}$ is the volume fraction of P(VDF-TFE), and $P_{PET}$ and $P_{P(VDF-TFE)}$ are the permeability of the single layer extruded PET and P(VDF-TFE) controls respectively. Since a biaxially stretched or a biaxially stretched recrystallized P(VDF-TFE) control could not be produced under the described conditions, $P_{P(VDF-TFE)}$ was estimated as will be explained later. $P$ for the 32 layer extruded, biaxially
sustained, and biaxially stretched recrystallized PET/P(VDF-TFE) films were plotted as a function of PET volume fraction and compared to their respective calculated series permeability models, Fig. 10. Permeability of the extruded PET/P(VDF-TFE) multilayer films match closely to the series model prediction. This strong correlation suggests that the inherent morphology and transport properties of both PET and P(VDF-TFE) in extruded multilayer films are consistent with that of the single layer controls. AFM and WAXS results shown previously are in good agreement with this conclusion.

The $P_{(VDF-TFE)}$ input variables for the biaxially stretched and biaxially stretched recrystallized films were determined by evaluating the effective permeability of the $P(VDF-TFE)$ layers $P_{(VDF-TFE)}$ as calculated from the series model according to

$$P_{(VDF-TFE)} = \frac{\phi_{P(VDF-TFE)} \left( \frac{1}{P_{\text{film}}} - \frac{1}{P_{\text{PET}}} \right)^{-1}}{1 - \phi_{P(VDF-TFE)}}$$

where $P_{\text{film}}$ is the film permeability and $P_{\text{PET}}$ is the permeability of the PET layer, under various processing conditions, which was assumed to be independent of the layer thickness and matched that of the bulk PET control. This approach allows for direct calculation of the $P_{(VDF-TFE)}$ layer thickness and processing condition were compared to the extruded PET/P(VDF-TFE) control, Fig. 11. $P_{(VDF-TFE)}$ for the extruded PET/P(VDF-TFE) films, as a function of $P_{(VDF-TFE)}$ layer thickness, closely matched $P$ determined for the single layer $P(VDF-TFE)$ control independent of the $P(VDF-TFE)$ layer thickness. The $P_{(VDF-TFE)}$ values for the biaxially stretched PET/P(VDF-TFE) samples are two to four times lower than the bulk P(VDF-TFE) control and are also independent of the P(VDF-TFE) layer thickness. The biaxially stretched recrystallized multilayer samples with in-plane P(VDF-TFE) crystals possessed $P_{(VDF-TFE)}$ values 400× lower than those of the extruded PET/P(VDF-TFE) multilayer films and the P(VDF-TFE) control and 130× lower than those of the biaxially stretched PET/P(VDF-TFE) films with on-edge P(VDF-TFE) crystals. These large, high aspect ratio impermeable crystals lying in the plane of the layers act as barriers for oxygen diffusion and thus increase the tortuosity pathway of oxygen through the film. The biaxially stretched recrystallized samples also exhibit a minor layer thickness dependence on $P_{(VDF-TFE)}$, indicating that recrystallizing P(VDF-TFE) in thinner layers is more effective at producing larger and/or a higher percentage of in-plane P(VDF-TFE) crystals. This behavior has been observed in other confined systems and was explained based on a decrease in the area nucleation density, thus producing more highly oriented crystals with a higher length to thickness aspect ratio [33].

Since no statistically significant layer thickness dependence was observed for the $P_{(VDF-TFE)}$ of the biaxially stretched PET/P(VDF-TFE) multilayer films, an average effective P(VDF-TFE) layer permeability was calculated from these data. A permeability value of 0.072 ± 0.024 Barrer was calculated for a biaxially stretched P(VDF-TFE) control. Using this value in Equation (3) and comparing permeability data from Fig. 10, it can be seen that the series model, using this control assumption, now adequately describes the permeability behavior of the biaxially stretched multilayer films. For the biaxially stretched recrystallized system, same analysis was applied. In this case, a minor layer thickness dependence was observed but not considered large enough to make the analysis invalid. An average $P_{(VDF-TFE)}$ value of 0.0015 ± 0.0001 barrer was

<table>
<thead>
<tr>
<th>Number of layers</th>
<th>Composition PET/P(VDF-TFE)</th>
<th>$P_{(VDF-TFE)}$ nominal layer thickness (nm)</th>
<th>Overall film $O_2$ permeability (barrer)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Extruded</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Biaxially stretched</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Biaxially stretched, recrystallized</td>
</tr>
<tr>
<td>1</td>
<td>PET control</td>
<td>–</td>
<td>$0.059 \pm 0.002$</td>
</tr>
<tr>
<td></td>
<td>P(VDF-TFE) control</td>
<td>10,000</td>
<td>$0.204 \pm 0.002$</td>
</tr>
<tr>
<td>32</td>
<td>20/80</td>
<td>500</td>
<td>$0.147 \pm 0.002$</td>
</tr>
<tr>
<td></td>
<td>30/70</td>
<td>440</td>
<td>$0.116 \pm 0.005$</td>
</tr>
<tr>
<td></td>
<td>40/50</td>
<td>380</td>
<td>$0.106 \pm 0.004$</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>300</td>
<td>$0.089 \pm 0.002$</td>
</tr>
<tr>
<td></td>
<td>60/40</td>
<td>250</td>
<td>$0.080 \pm 0.006$</td>
</tr>
<tr>
<td></td>
<td>70/30</td>
<td>190</td>
<td>$0.080 \pm 0.001$</td>
</tr>
<tr>
<td></td>
<td>80/20</td>
<td>120</td>
<td>$0.071 \pm 0.001$</td>
</tr>
<tr>
<td></td>
<td>90/10</td>
<td>60</td>
<td>$0.064 \pm 0.001$</td>
</tr>
<tr>
<td>256</td>
<td>50/50</td>
<td>40</td>
<td>$0.095 \pm 0.001$</td>
</tr>
<tr>
<td></td>
<td>70/30</td>
<td>24</td>
<td>$0.075 \pm 0.003$</td>
</tr>
</tbody>
</table>
determined and taken as the assumed permeability of the biaxially stretched recrystallized P(VDF-TFE) control. The calculated series model using this value compared well with the experimental values for the biaxially stretched recrystallized samples. Fig. 10. Using this analysis, the series permeability model was fit to all systems effectively, even without the ability to produce controls under identical processing conditions. From these data, it is clear that the ability to manipulate the structure and morphology of both polymers is directly responsible for the substantial improvement in oxygen barrier properties. Interestingly, it appears that the P(VDF-TFE) layer morphology has a much larger influence on the final film permeability properties compared to the PET layer morphology.

The observed decrease in the effective P(VDF-TFE) layer permeability in the biaxially stretched and biaxially stretched recrystallized multilayer films is related to the confined morphologies of the P(VDF-TFE) layers as revealed by WAXS and AFM images. Both the stacked granules in the P(VDF-TFE) layers of the biaxially stretched films and the high aspect ratio in-plane crystals in the P(VDF-TFE) layers of the biaxially stretched recrystallized multilayer films are oriented in the stretching plane, with an inherent length to thickness aspect ratio, and act as impermeable barriers to oxygen diffusion through the film [43]. The Cussler model was used to quantify the aspect ratio of these confined morphologies in the biaxially stretched and biaxially stretched recrystallized PET/P(VDF-TFE) multilayered films [44]. This model considers the gas diffusion, \( P \), through a composite matrix with a dispersion of impermeable platelets and is given as

\[
P = P_a \left( 1 + \frac{\phi_c^2}{4(1 - \phi_c)} \cos^2 \theta \right)^{-1}
\]

where \( P_a \) is the matrix permeability, taken as the amorphous phase permeability of the P(VDF-TFE) layer, \( \phi_c \) is the volume fraction of impermeable crystals in the P(VDF-TFE) layer, \( \alpha \) is the crystal aspect ratio, and \( \theta \) is the angle between the gas flux and the normal to the P(VDF-TFE) crystals, which was taken as 0° because the majority of the granules or platelets were aligned in the stretching plane. The volume fraction of impermeable crystals in the P(VDF-TFE) layer, \( \phi_c \), was determined from the bulk crystallinity given as

\[
\phi_c = \langle X_c \rangle \left( \frac{\rho_c}{\rho_{\text{cr}}} \right)
\]

where \( X_c \) is the weight fraction crystallinity of the P(VDF-TFE) layer, \( X_c,P(VDF-TFE),\text{Biax} = 37% \) and \( X_c,P(VDF-TFE),\text{Recry} = 53% \) as determined by DSC, \( \rho \) is the density of the P(VDF-TFE) polymer, taken as 1.78 g/cc (obtained from resin manufacturer), and \( \rho_c \) is the P(VDF-TFE) crystal density taken as 1.97 for pure \( \beta \)-phase PVDF crystals [41]. The amorphous phase permeability of the P(VDF-TFE) layer was estimated as \( P_{\text{Am}} = (P_{\text{tot}}(1 - \phi_c))^{-2} \) where \( P_{\text{tot}} \) is the oxygen permeability of the extruded P(VDF-TFE) control [45]. The extracted aspect ratio from the Cussler model for the biaxially stretched 50/50 PET/P(VDF-TFE) 32 layer film was 11. The estimated aspect ratio of the stacked granules observed in the AFM images was determined to be approximately 10 which is very close to the Cussler model prediction. For the biaxially stretched recrystallized system, the extracted aspect ratio for the 50/50 PET/P(VDF-TFE) 32 layer film was 45. This estimated aspect ratio is consistent with those reported previously for P(VDF-TFE) confined by PC under the same heat treatment procedure [19]. This result was interesting, considering the semi-crystalline nature of the PET confining layer may introduce additional surface nucleation sites [46] in addition to the presence of remnant on-edge crystals from the biaxial stretching process. Using an approach described previously [13], small angle X-ray scattering (SAXS) was used to determine a long period of 13.5 nm and subsequent P(VDF-TFE) crystal thickness of 7.2 nm for the biaxially stretched recrystallized 50/50 PET/P(VDF-TFE) 32 layer sample. Using the measured crystal thickness from SAXS and the calculated aspect ratio from the Cussler model, the lateral dimension of the in-plane P(VDF-TFE) crystals is estimated to be greater than 300 nm. This value is smaller than the measured P(VDF-TFE) crystal widths from the AFM images which range anywhere from 300 to 1000 nm, however considering this predicted aspect ratio represents an average value and does not take into account any tilting of the in-plane crystals, the value is reasonable. The inclusion of confined P(VDF-TFE) morphologies in the PET/P(VDF-TFE) multilayer films can dramatically impact oxygen diffusion and reduce the effective permeability of the P(VDF-TFE) layer.

Based on the structure/morphology and permeability data, it was concluded that the PET layers possessed similar morphological features and oxygen barrier properties to the bulk PET control. Even though biaxial stretching and thermal annealing change the structure and morphology of PET, the analysis did not indicate that the PET layers were substantially benefitting from the layer confinement in the same manner as the P(VDF-TFE) layers. This result was unexpected considering that previous studies on the confinement of PET in multilayers have established the development of unique microstructures with thermal annealing [40]. The variation
is likely due to the nature of the confinement of the PET layer. Previously reported results consisted of a PC/PET multilayer system where thermal annealing was conducted below the \( T_m \) of PC which allowed for a hard confinement of the PET layer. In this PET/P(VDF-TFE) system, thermal annealing was conducted at temperatures mostly above the \( T_m \) of P(VDF-TFE) resulting in a soft confinement of the PET layer. Additionally, during biaxial film stretching, the PET layers are confined by semi-crystalline P(VDF-TFE) layers with a relative crystallinity around 32%. With the majority of the P(VDF-TFE) material in the flexible amorphous state, little confinement effects are to be expected during biaxial stretching. The nature of the confinement is vitally important to manipulating the structure of the confined polymer layers. This has also been observed previously in PEO nanolayers confined by a soft Ethylene Acrylic Acid copolymer (EAA) vs. a hard PS layer [12,47].

### 3.7 Water vapor transport properties of confined P(VDF-TFE) layers

In an effort to expand the applicability of the confined crystallization via force assembly technology, additional property improvements needed to be identified beyond oxygen permeability. WVTR was of interest, due to some of the commercial applications of PVDF based polymers in piping, pipe lining, and moisture barrier applications. The WVTR for all extruded, biaxially stretched, and biaxially stretched recrystallized PET/P(VDF-TFE) multilayer films was evaluated, Table 3. Comparing extruded and biaxially stretched samples of the same composition and number of layers, for example 50/50 v/v, 32 layers, the WVTR drops by a factor of two in the stretched samples. The biaxially stretched recrystallized samples, containing in-plane P(VDF-TFE) lamellae crystals, possess substantially lower WVTRs. For the 50/50 v/v, 32 layer sample, the WVTR dropped to 0.04 gm·mil/100 in²·day representing a 25 decrease as compared to the extruded samples and a 12 decrease compared to the biaxially stretched samples. From these data it is evident that the confined morphologies of PET and P(VDF-TFE) in nanolayers significantly impact the WVTR in a manner similar to that detailed for oxygen permeability. The orientation and crystallization of the PET layers in addition to the confined morphologies in the P(VDF-TFE) layers, either on-edge or in-plane crystals, effectively disrupt the diffusion pathway for both \( O_2 \) and \( H_2O \) through the film.

The effective WVTR of the P(VDF-TFE) layer, \( \text{WVTR}_{\text{P(VDF-TFE)}}^{\text{eff}} \), was calculated using the series model modified from Equation (4) and plotted as a function of layer thickness for all extruded, biaxially stretched and biaxially stretched recrystallized samples, Fig. 12. The overall trend in the WVTR for the various PET/P(VDF-TFE) multilayer samples closely resembles that observed for P(\( O_2 \)). In the extruded samples, the P(VDF-TFE) layers possess WVTR values that are virtually identical to the bulk P(VDF-TFE) control. With biaxial stretching, the stacked granular morphology in the P(VDF-TFE) layer results in a 3–4 decrease in the \( \text{WVTR}_{\text{P(VDF-TFE)}}^{\text{eff}} \). Finally, with the inclusion of confined in-plane P(VDF-TFE) crystals, the \( \text{WVTR}_{\text{P(VDF-TFE)}}^{\text{eff}} \) in the biaxially stretched recrystallized PET/P(VDF-TFE) samples was 100–150 lower as compared to the extruded PET/P(VDF-TFE) samples. It is also important to note, a tortuosity factor or aspect ratio calculated from the WVTR data using the Cussler model for the biaxially stretched and biaxially stretched recrystallized 50/50 PET/P(VDF-TFE) 32 layer films yields virtually identical values to those obtained for the P(\( O_2 \)) data. From this observation, the confined P(VDF-TFE) morphologies are just as effective for blocking water vapor as they are for blocking oxygen. This additional property enhancement opens the door for new applications as effective water barriers for confined crystallization facilitated by force assembly coextrusion.

### 4. Conclusions

Forced assembly multilayer coextrusion in combination with biaxial stretching and thermal treatment were used to study the confined nanolayer morphology of PET and P(VDF-TFE). Extruded multilayered films containing 32 and 256 alternating layers of PET and P(VDF-TFE) were produced with individual P(VDF-TFE) layer thicknesses ranging from 500 down to 24 nm. A second set of thick 200 μm multilayer films were produced that were biaxially stained.
stretched at a 4.5 × 4.5 draw ratio to produce films with comparable film thicknesses and layer thicknesses. Finally, an approach of isothermal melt recrystallization was used to further manipulate the confined structures of PET and P(VDF-TFE). The structure and morphology of these various multilayered films were examined using atomic force microscopy (AFM), wide angle x-ray scattering (WAXS), and oxygen permeability. In the extruded PET/P(VDF-TFE) films, layer confinement had little effect on the morphology of each polymer layer, even under the highest degree of confinement, resulting in oxygen barrier properties that matched those predicted from a series permeability model based on the permeability of the single layer controls. In contrast, biaxially stretched multilayer films exhibited an on-edge P(VDF-TFE) crystal orientation and an oriented fibrillar PET structure under nanolayer confinement. These confined structures reduced the overall oxygen permeability by a factor of 2 or 3 over the extruded samples and were attributed to the confined structures of both PET and P(VDF-TFE). Melt recrystallization produced highly oriented in-plane P(VDF-TFE) crystals while also improving the crystalline microstructure of the oriented PET. The high aspect ratio in-plane P(VDF-TFE) crystals act as barriers for oxygen diffusion which greatly reduce the bulk film oxygen permeability properties. Layer confinement combined with biaxial stretching and thermal annealing facilitated the formation of various nanolayer confined crystal morphologies in the P(VDF-TFE) layers. The nature of the layer confinement is vitally important in order to successfully manipulate the morphology of polymers in nano-layered films via forced assembly. Due to the nature of the "soft" layer confinement, the morphology and subsequent transport characteristics of the PET layers were similar to that of the single layer controls. In addition, the confined PET and P(VDF-TFE) morphologies were probed using water vapor transport rate (WVTR), which produced a similar trend to that observed for oxygen permeability and opens the door for new water barrier applications for the confined crystallization facilitated by forced assembly coextrusion technology.

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