



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

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## ABSTRACT

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, even in very thin 40 nm layers. 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 biaxially 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 confinement of the PET nanolayers during biaxial stretching at high draw ratios and isothermal melt recrystallization at high temperatures. Finally, the water vapor transport rate (WVTR) was evaluated for these confined systems which mimicked the trends observed for oxygen permeability. The confined 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

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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( $\epsilon$ -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 dilute solution. The formation of this confined morphology in nanolayered films had a dramatic impact on the gas transport properties resulting in a 200–300 $\times$  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<sup>-1</sup>, 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  $\mu$ m 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  $\mu$ m film thickness were produced for subsequent biaxial stretching. Additionally, both 10  $\mu$ m and 200  $\mu$ m 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.

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