



# The effect of confined crystallization on high-density poly(ethylene) lamellar morphology



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## ABSTRACT

High-density polyethylene (HDPE) was co-extruded against high glassy transition temperature ( $T_g$ ) 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 coextruded with another high  $T_g$  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.

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## 1. Introduction

As a widely used material, 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 investigated in various systems [1–5,7–17]. Confined crystallization of polyethylene block copolymers has been reported [16,17]. However, long range one-dimensional (1-D) confined crystallization of polyethylene by a hard polymer in coextruded thin multilayer film systems has not been systematically studied.

Layer multiplying coextrusion as a complementary way to study polymer crystallization confinement has been reported recently [18]. A variety of polymers were coextruded to fabricate multilayer films with hundreds or thousands of alternating layers [19–24]. 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( $\epsilon$ -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  $T_g$  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  $T_g$  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  $T_g$  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

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**Table 1**  
Thermal properties of polymers used in this study.

Material	Melting/glassy transition temperature °C	Crystallization temperature °C
HDPE	131	120
PSF	184	/
PC	172	/

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. Materials and experiments

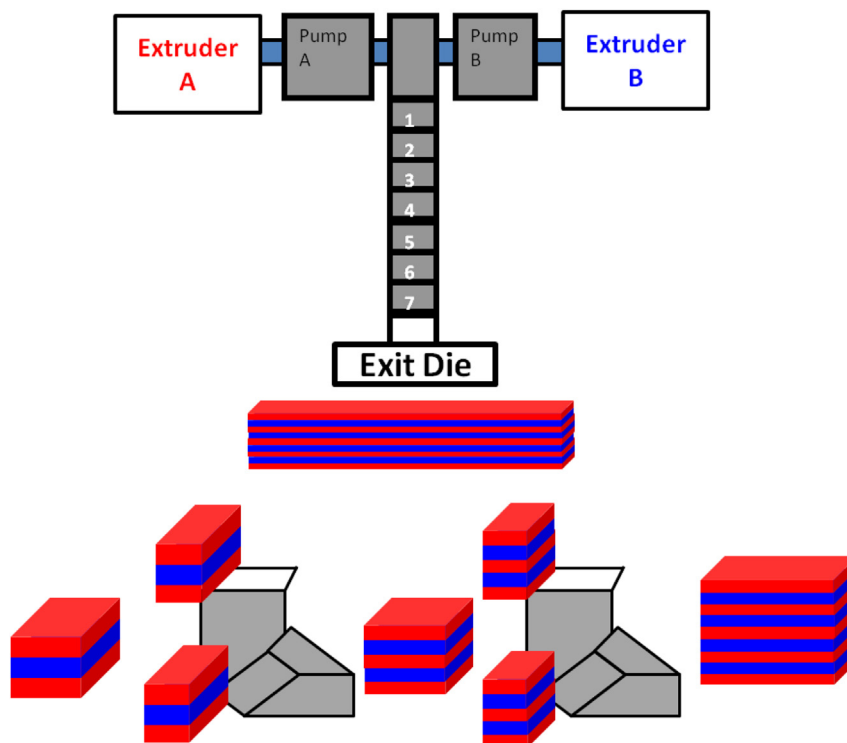
High-density polyethylene (grade Surpass 167) with density of  $0.967 \text{ g/cm}^3$  (HDPE) was produced by Nova Chemical USA. Polycarbonate (PC) (grade number Apec 1745) was obtained from Bayer Material Science. Polysulfone (PSF) (grade Udel 3700) was obtained from Solvay Company, USA. The thermal properties of these resins are listed in Table 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 Fig. 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  $10 \text{ s}^{-1}$ . These measurements determined that the optimum multilayer coextrusion temperature for PC/HDPE systems is  $285 \text{ }^\circ\text{C}$  and the optimum temperature for PSF/HDPE systems is  $290 \text{ }^\circ\text{C}$ .

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  $80 \text{ }^\circ\text{C}$  while collecting all films. The film thickness and corresponding HDPE layer thickness are listed in Table 2.

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 h at room temperature. Cross sections were microtomed after cooling the samples to  $-120 \text{ }^\circ\text{C}$  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  $50 \text{ N/m}$  and resonance frequency was in the  $284\text{--}362 \text{ kHz}$ . Both phase and height images of the cross sections were recorded simultaneously.



**Fig. 1.** Schematic of multilayer extrusion process showing how 3 layers become 9 layers [18].

Source: Reference: [18] M. Ponting, A. Hiltner, and E. Baer, *Macromolecular Symposia*, (2010) 294, 19.

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