

A new method for achieving nanoscale reinforcement of biaxially oriented polypropylene film

Yijian Lin, Anne Hiltner*, Eric Baer

Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106-7202, USA

ARTICLE INFO

Article history:

Received 9 May 2010

Received in revised form

24 June 2010

Accepted 30 June 2010

Available online 7 July 2010

Keywords:

Biaxially oriented polypropylene

Gas barrier

Nanolayers

ABSTRACT

Nanolayers of poly(ethylene oxide) (PEO) produced by layer-multiplying coextrusion crystallize as single, high aspect ratio lamellae that resemble large single crystals. The confined crystallization habit imparts two orders of magnitude reduction in the gas permeability. We now demonstrate how the highly oriented lamellar nanolayers can be obtained with biaxial stretching. For this purpose, we chose biaxially oriented polypropylene (BOPP) film for modification and incorporated PEO nanolayers under conditions that mimicked the typical fabrication process. Sheet that contained a center core with 33 alternating layers of polypropylene (PP) and PEO was coextruded and subsequently biaxially oriented at 145 °C. Biaxial stretching reduced the PEO layer thickness from the spherulitic microscale to nanolayers of highly oriented PEO single lamellae. The nanolayers improved the oxygen barrier by an order of magnitude without sacrificing the high clarity and good tear resistance of BOPP film.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The demand for higher performance polymeric materials that can also meet today's environmental and energy requirements, has challenged researchers to innovate new materials systems and processes. Most strategies for enhancing the property window rely on the complex, hierarchical structures that are imparted to polymers by melt or solid state processing. A single polymer, or synergistic combinations of two (or more) polymers may be used to optimize the property spectrum; however, advances to existing materials and processes generally achieve only incremental improvements. Nanoscience promises a technology breakthrough that would define the next generation of advanced polymeric materials, particularly materials with an order of magnitude higher gas barrier [1,2].

Nanoparticles with high aspect ratio are an attractive candidate for this purpose. Following the initial success with nylon 6 [3,4], exfoliated organosilicate platelets received an extraordinary amount of attention as the reinforcement in polymer matrix nanocomposites [5], with literally thousands of papers published on the subject in the last 10 years. The combination of key property requirements (gas barrier, transparency and toughness) makes polymer film an ideal candidate for nanotechnology. Although success could transform the high volume polyolefin field,

a practical melt process for achieving good dispersion of exfoliated organosilicate platelets has proven an elusive goal [6]. The need exists for alternative approaches to achieving the property enhancements envisaged for polymer nanocomposites.

Recently, using layer-multiplying coextrusion, we discovered a morphology that emerges as confined polyethylene oxide (PEO) layers are made progressively thinner. When the thickness is confined to 25 nm by polystyrene or by poly(ethylene-co-acrylic acid) (EAA), the PEO crystallizes as single, high aspect ratio lamellae that resemble single crystals [7,8]. Unexpectedly, the confined crystallization habit imparts two orders of magnitude reduction in the gas permeability. The PEO nanolayers potentially can provide the barrier enhancement envisaged with exfoliated organosilicate platelets. However, adapting this discovery to commercial film processes presents certain challenges. Processing of polymer film often includes a post-extrusion stretching step that reduces the thickness and imparts orientation. For example, fabrication of biaxially oriented polypropylene (BOPP) films involves a biaxial stretching process that reduces the thickness of the polypropylene sheet by about 25× and transforms the opaque, brittle spherulites into a transparent, tough, fibrillar network [9]. Thus, although PEO nanolayers could be coextruded with the polypropylene sheet, the nanolayers would be destroyed in the subsequent stretching step and the barrier enhancement would be lost.

Rather than using layer-multiplying coextrusion to produce the nanolayers, we took an innovative approach in which the post-extrusion stretching process was used to produce the high barrier nanolayers in BOPP film. We coextruded a polypropylene (PP) sheet

* Corresponding author.

E-mail address: ahiltner@case.edu (A. Hiltner).

containing thick PEO layers. The micron-thick PEO layers crystallized with an essentially isotropic spherulitic morphology that did not enhance the barrier. However, the thickness of the PEO layers was chosen so that when the sheet was biaxially stretched under conditions typically used for BOPP film, the PEO microlayers melted and were reduced in thickness to nanolayers. At this size scale, the PEO layers recrystallized as oriented lamellar single crystals of very high aspect ratio.

2. Experimental

The PP (H105-03NA) and PEO (PolyOx WSR N80, $M_w = 200$ kg/mol) were obtained from the Dow Chemical Company. The PP and PEO were combined as alternating microlayers using layer-multiplying coextrusion. In the same process, thick monolithic PP skins were added to produce a 3-layer structure. The multilayer coextruded sheets were biaxially oriented using a Brükner Karo IV biaxial stretcher at 135, 140, 145 and 150 °C with a strain rate of 400% s⁻¹. The draw ratios were 5 × 5, 6 × 6 and 7 × 7.

The first heating thermogram was recorded by a Perkin–Elmer Series 7 differential scanning calorimeter (DSC) using a heating rate of 10 °C min⁻¹ from 60 to 190 °C. The crystallinity of the PEO was calculated from the melting enthalpy using the heat of fusion, ΔH_0 , of 197 J g⁻¹ for PEO crystals [10].

To view the layer structure, a small specimen was cut from the coextruded sheet or oriented film and microtomed at -85 °C through the thickness direction. The microtomed surface was examined in a Digital Laboratories Nanoscope IIIa atomic force microscope (AFM) operating in the tapping mode.

The oxygen permeability $P(O_2)$ was measured with a MOCON OX-TRAN 2/20 at 23 °C, 1 atm and 0% relative humidity. Two films prepared under the same conditions were tested to obtain the average permeability. The carbon dioxide permeability $P(CO_2)$ was measured with a MOCON PERM-TRAN C4/40 at the same conditions. The CO_2/O_2 selectivity was calculated as the ratio $P(CO_2)/P(O_2)$.

Wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS) measurements were carried out using a rotating anode X-ray generator (Rigaku RU 300, 12 kW) equipped with two laterally graded multilayer optics in a side-by-side arrangement, giving a highly focused parallel beam of monochromatic CuK α radiation ($\lambda = 0.154$ nm). For the SAXS measurements, the X-ray beam was aligned at an angle of about 3° relative to the film surface to avoid total reflection. The scattering vector q was calibrated using a silver behenate (AgBe) standard, which had the (001) peak position at $q = 1.076$ nm⁻¹. On the basis of the intensity of the direct beam, all WAXS and SAXS images were corrected for background scattering.

The clarity was characterized by a light transmission measurement [11], in which a film was placed between a light source and a detector. The light transmission T was calculated as

$$T = \frac{\sum_{\lambda=400}^{700} I_{\lambda}}{\sum_{\lambda=400}^{700} I_{\lambda,0}} \quad (1)$$

where I_{λ} is the light intensity at wavelength λ , $I_{\lambda,0}$ is the reference light intensity without the film, and 400–700 is the wavelength range of the visible light. To remove the surface scattering effect, mineral oil with refractive index of 1.500 was spread on both surfaces of the films. The diameters of the light source beam and the detector were both approximately 3 mm. The distance between film and detector was 6 mm. Five spots on each film were selected to perform this measurement.

In a standard trouser tear test, the tear energy G_t was calculated as

$$G_t = 2F/t \quad (2)$$

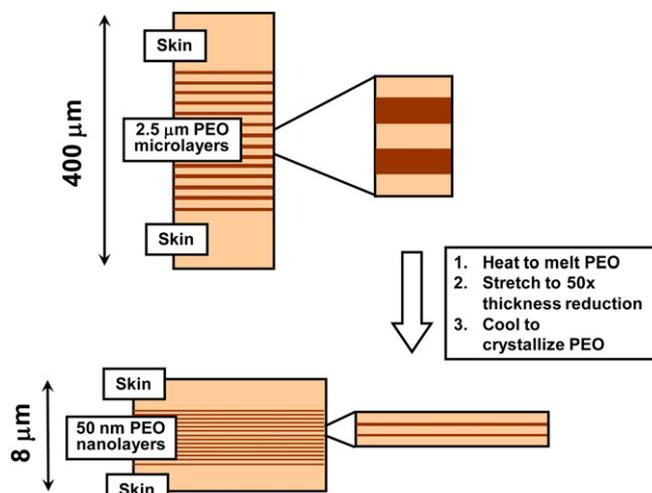


Fig. 1. Schematics showing how polymer microlayers are reduced to nanolayers by biaxial orientation.

where F is the steady force during the tear test and t is the thickness of the film. An Instron 1122 tensile testing machine equipped with a 500 g load cell was employed to record the tear force at a speed of 250 mm min⁻¹.

3. Results and discussion

A 3-layer sheet was produced for biaxial orientation. A 130 μm core layer was prepared by combining PP and PEO as 33 alternating microlayers (17 PP microlayers and 16 PEO microlayers) using layer-multiplying coextrusion [12]. The composition in the core layer was PP/PEO-90/10, 80/20 and 70/30 vol/vol. Two thick 130 μm PP skin layers were added before the melt was spread through a sheet die. The composition of the final 3-layer sheet was PP/PEO 96.7/3.3, 93.3/6.7 and 90/10 vol/vol. The entire architecture was created in a continuous coextrusion process.

The *in situ* transformation of spherulitic PEO layers into impermeable, highly oriented lamellar single crystals is shown in Fig. 1. The typical stretching temperature window for PP film was

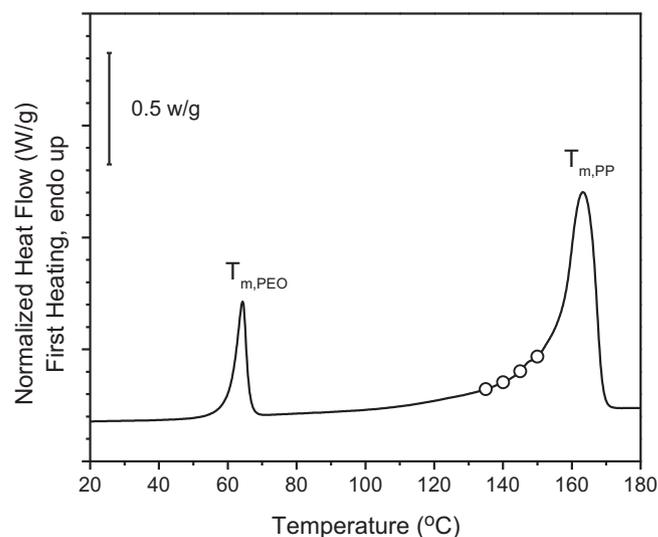


Fig. 2. DSC heating thermogram of extruded PP/PEO sheet with 10 vol.% PEO. The circles indicate the biaxial stretching temperatures that were used to obtain the nano-BOPP films.

Download English Version:

<https://daneshyari.com/en/article/5186785>

Download Persian Version:

<https://daneshyari.com/article/5186785>

[Daneshyari.com](https://daneshyari.com)