



Breakup behavior of nanolayers in polymeric multilayer systems — Creation of nanosheets and nanodroplets

Jingxing Feng^{a,*}, Ziyou Zhang^a, Adrien Bironeau^b, Alain Guinault^b, Guillaume Miquelard-Garnier^b, Cyrille Sollogoub^b, Andrew Olah^a, Eric Baer^a

^a Center for Layered Polymeric Systems (CLiPS), Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH, 44106-7202, USA

^b PIMM, UMR 8006, ENSAM, CNRS, CNAM, 151bd de l'Hôpital, 75013, Paris, France

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ABSTRACT

Multilayer films comprising polystyrene (PS)/polymethyl methacrylate (PMMA) and PS/polycaprolatone (PCL) alternating nanolayers with varied layer thickness were fabricated by multilayer coextrusion. The nanolayers breakup phenomena of PMMA and PCL were characterized using atomic force microscopy (AFM), oxygen permeability, light transmission, wide-angle X-ray scattering (WAXS), and differential scanning calorimetry (DSC). The continuous layers started to break up into nanosheets and nanodroplets during the coextrusion process when the nominal layer thickness decreased to between 30 nm and 40 nm. Further decrease of the nominal layer thickness of PMMA and PCL resulted in less nanosheets and more nanodroplets. Oxygen permeability was effective for characterizing the onset thickness of layer breakup. The oxygen permeability for the PS/PCL system was modeled and demonstrated good correlation with estimated composition of continuous layers, nanosheets, and nanodroplets.

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1. Introduction

Forced assembly by multilayer coextrusion was proven by Dow Chemical to be a reliable technique for producing nanolayers and microlayers in a continuous process [1]. The past two decades witnessed the rapid development of multilayer coextrusion which evolved from uniform layers to gradient layers, from one-dimensional structure to two-dimensional structure and from two-component systems to more complex systems [2]. The nano/microlayered films demonstrated highly tunable gas barrier [3], mechanical [4], optical [5,6] and electrical [7,8] properties arising from scaling and layer-layer interaction.

For many polymer multilayer systems, there existed a layer thickness below which the polymer layers lost their integrity. In these cases, the polymer layers break and transform into nanosheets and nanodroplets, similar to the dewetting phenomenon observed in thin films [9,10]. Such nanostructures were observed on several polymer pairs (polypropylene (PP)/polyethylene oxide (PEO) [11], polycarbonate (PC)/polyethylene terephthalate (PET)

[12], PP/polystyrene (PS) [13] or PS/polymethyl methacrylate (PMMA) [14]). As such, the critical layer thickness was defined in a recent work by Sollogoub et al. as the smallest continuous layer observed in a given multilayer system, where they systematically studied the breakup behavior of nanolayers during coextrusion process of PS/PMMA [10,14]. They observed that this critical layer thickness was close to 7 nm for polystyrene and 10 nm for PMMA regardless of the processing route; suggesting it depends only on material parameters. It was speculated this critical layer thickness is due to small interfacial perturbations that are amplified by van der Waals disjoining forces that become dominant over stabilizing interfacial tension forces for thicknesses on the order of 10 nm.

In 2005, Baer et al. benefited from layer break-ups in nanolayered films to develop nanodroplets as polymer blends morphologies [12–14]. The nanolayered films were prepared from coextrusion and then thermally treated at high temperature. Even though the multilayer films had stable morphology at room temperature, the nanolayers were unstable at high temperature. The polymer nanodroplets were generated from the breakup and coalescence of nanolayers during thermal treatment. High density polyethylene and polypropylene were both made into well-dispersed nanodroplets in a PS matrix using this approach [15,16]. It was discovered that the size of the nanodroplets could be

* Corresponding author.

E-mail address: jxf309@case.edu (J. Feng).

controlled by changing the layer thickness of films before thermal treatment [15,17]. Thermal treatment of thicker films yielded larger nanodroplets and thinner films produced smaller nanodroplets.

In this paper, the possibility of using a macroscopic analysis technique, oxygen permeability measurement, to track breakup phenomenon of polymer nanolayers was investigated, using two different multilayer systems: glassy/glassy (PS/PMMA) and glassy/semi-crystalline (PS/polycaprolactone (PCL)). The multilayer composite films with different nominal layer thicknesses were prepared by varying the layer number and polymer compositions. When the layer thickness was lower than the thickness at which the layers start to break (onset thickness for layer break-up) nanosheets and nanodroplets were directly formed during the coextrusion process (as opposed to the nanodroplets formerly produced from the annealing of continuous multilayer films [16,17,21]). Oxygen permeability and light transparency of the composite films were performed on the extruded films and revealed the layer breakups in both systems. Coupling these measurements with an in-depth morphological analysis of the PCL (via AFM, Wide-angle X-ray scattering, Differential Scanning Calorimetry and optical light transmission), we showed that it was possible to model the effective oxygen permeability of PCL to quantitatively obtain the ratio of nanosheets and nanolayers in the PS/PCL films.

2. Materials and methods

2.1. Materials

The polystyrene (PS) used in this study was supplied by Americas Styrenics LLC (MC3650). It had a glass transition temperature of 95 °C and melt flow index of 13.0 g/10 min measured at 200 °C under a load of 5 kg. The poly (methyl methacrylate) (PMMA) was a poly (methyl methacrylate-co-ethyl acrylate) which contained 5%–10% ethyl acrylate to prevent depolymerization during extrusion, purchased from Arkema (Plexiglas VS). The glass transition temperature (T_g) of the PMMA was measured as 95 °C (due to the presence of ethyl acrylate in the PMMA) and its melt flow index was 27.0 g/10 min measured at 230 °C/3.8 kg. The polycaprolactone (PCL) was acquired from Perstorp (CAPA 6800). Its melting temperature, glass transition temperature, and crystallization temperature respectively were measured as 58 °C, –60 °C, and 35 °C. The melt flow index of PCL was 2.4 g/10 min measured at 160 °C under a load of 2.16 kg. The materials' information is shown in Table 1.

The melt viscosity of PS, PMMA and PCL was determined as a function of temperature using a Kayeness Galaxy 1 melt flow indexer at a shear rate of 10 s⁻¹. The extrusion temperature was selected to ensure the polymeric material's rheological compatibility for extrusion and to maximize layer uniformity. Before the coextrusion process, the PMMA was dried in a vacuum oven for 24 h at 80 °C. The PCL was dried for 48 h at 40 °C. Films with 513 and 2049 alternating PS/PMMA and PS/PCL layers were produced through continuous coextrusion process [23,24]. The composition of the films in volume was changed to vary the individual layer thickness. The extruder and layer multiplication elements were 200 °C and the 14-inch exit die temperature was 190 °C. The takeoff

temperature of the chill roll was 60 °C. A sacrificial polyethylene skin layer was coextruded with the PS/PMMA, PS/PCL multilayers. The skin layer was peeled off before characterization. Other parameters of the coextrusion process were identical to previous setups.

2.2. Atomic force microscopy

The extrusion direction morphologies of the as-extruded films were characterized by atomic force microscopy (AFM). The film was embedded in epoxy (Loctite Heavy Duty Epoxy, Loctite Inc.) and cured at room temperature for 24 h. The film cross-sections were prepared perpendicular to the extrusion direction at –100 °C (for PS/PCL system) and –80 °C (for PS/PMMA system) by an ultramicrotome equipped with a cryogenic chamber (Leica EM UC7, Leica Microsystems). The height variance of the samples after microtoming was controlled to be less than 30 nm. The AFM images were acquired at room temperature in air with a scanning probe microscope (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA) operated in the tapping mode. A rectangular type silicon tapping mode probe was used to record height and phase images simultaneously. The tip radius was 10 nm and the spring constant was 50 N/m with a resonance frequency of around 320 kHz. To acquire high-quality images of the layered morphology and to capture the breakup behavior of the PMMA layers, a low scan rate was used for AFM. The number of layers, nanosheets, and nanodroplets were counted from at least three AFM scans with a size of 10 μm by 10 μm. The areas for imaging were randomly selected from the cross-section. If the layers were continuous throughout the 10 μm image, the layer was defined as a continuous layer. Otherwise, the layer was defined as a breakup layer.

2.3. Oxygen permeability

Oxygen flux $J(t)$ at 0% relative humidity, 1 atm, and 23 °C was measured with a MOCON OX-TRAN 2/20. Permeability was calculated from the steady flux J_0 according to Equation (1).

$$P(O_2) = J_0 l / \Delta p \quad (1)$$

where Δp is the oxygen pressure drop and l is the film thickness. The permeability values in this work were reported in Barrer. One Barrer is equivalent to 10⁻¹⁰ (cm³ O₂) cm cm⁻² s⁻¹ cmHg⁻¹.

Oxygen permeability of the film was affected by both polymer phases. For example, in the case of the PS/PCL system, the effective PCL permeability could be calculated using Equation (2) as follows,

$$\text{Film Permeability} = \left(\frac{V_{PCL}}{P_{PCL}} + \frac{V_{PS}}{P_{PS}} \right)^{-1} \quad (2)$$

where V_{PCL} and V_{PS} were the volume fraction of PCL and PS in the film.

Similarly, the effective PCL permeability consisted of the permeability of the PCL layers, nanosheets, and nanodroplets as shown in Equation (3). The modeling of oxygen permeability will be discussed later in this paper.

$$P_{PCL} = \left(\frac{V_{PCL \text{ Layers}}}{P_{PCL \text{ Layers}}} + \frac{V_{PCL \text{ Sheets}}}{P_{PCL \text{ Sheets}}} + \frac{V_{PCL \text{ Droplets}}}{P_{PCL \text{ Droplets}}} \right)^{-1} \quad (3)$$

where $V_{PCL \text{ Layers}}$ and $V_{PCL \text{ Sheets}}$ and $V_{PCL \text{ Droplets}}$ were the volume fraction of PCL layers, nanosheets, and nanodroplets.

Table 1
Properties of materials for coextrusion process.

Materials	Trade Name	T_m (°C)	T_g (°C)	T_c (°C)	Density (g/cm ³)	Refractive Index
PS	AmSty MC3650	–	95	–	1.04	1.58
PMMA	Arkema Plexiglas VS	–	95	–	1.18	1.49
PCL	Perstorp CAPA 6800	58	–60	35	1.14	1.48

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