Interfacial instabilities in Multilayer Extrusion

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ABSTRACT

Polymeric alternating multilayer laminates have been prepared by coextrusion, utilizing a specially designed feedblock to combine the two incoming materials from different extruder. Layer multiplying elements (LME) were used to split the melt stream, divide it, and then bring the two polymeric melt streams together, increasing the number of layers, while decreasing the thickness of each layer.

Polycarbonate (PC) and polypropylene (PP) were extruded to form alternating structures by repeated layer multiplications. The materials were characterized by optical microscopy (OM) and atomic force microscopy (AFM) to study layer instabilities.

Zig-zag type instabilities were found at the interfaces, predominantly in the center of the samples, which originated from the interfaces near the walls. Instabilities could be reduced by increasing the temperature of the LMEs and decreasing the total flow rate of both materials.

Keywords: multilayer, interfacial instabilities, coextrusion, feedblock, AFM, layer multiplying element.

INTRODUCTION

Numerous applications have appeared for nanolayered materials, which are often produced using layer by layer deposition. One attractive method to create nanolayered materials employs coextrusion technologies. [1, 2, 3] This method offers the potential to develop extruded multicomponent thin films for conformable, high-density data or energy storage.

The coextrusion technique has been used in many applications, including those utilizing transparent materials. In the manufacture of films or sheets where appearance is important, product uniformity is critical. Coextrusion techniques, using two incompatible materials, typically require adhesive materials in between the layers or interfaces [4]. These adhesive materials act as a bonding layer and stress reliever at the interface, so that the layers show good uniformity. Without the use of adhesive layers in incompatible compositions, interfacial stresses will be increased as the number of layers increases, generating interfacial irregularities, especially near the walls in the flow channel. Interfacial instabilities result in decreased performance and aesthetics.

Thus, multilayer coextrusion requires the manufacture of uniform layered structures, which can be problematic as a result of these interfacial instabilities caused by differences in chemical or rheological properties between materials. In addition, as the number of layers increases and the thickness of each layer decreases, the individual layers often became discontinuous due to these flow instabilities. This change in behavior as the thickness decreases is an example of the issues unique to maintaining layer identity and uniformity at the nanoscale.

Much of the multilayer instability studies have been based on systems with three to five layer structures, using two or three different polymeric materials [13, 14, 15]. Two major interfacial instabilities have been found; zig-zag and wave instabilities [5]. The zig-zag type (high frequency, low amplitude) instability is driven by high interfacial shear stresses, while the wave type (low frequency, high amplitude) instability is generated by an extreme extensional deformation of the minor layer at the merge point [6 – 12].

This work investigates the role of polymer properties in the development of flow instabilities in mulitlayered films. In this research, multilayer coextrusion experiments were carried out with a semi crystalline and an amorphous material to produce multilayered structures containing tens or thousands of alternating layers.

EXPERIMENTAL

1.1 Materials

Polycarbonate (PC) (ECM Plastics, molding grade) and polypropylene (PP) (Huntsman WL-313) were used in this study. Prior to processing the PC was dried at 120^{o}C. Shear viscosities of the materials were measured using a capillary rheometer.

1.2 Processing

Multilayer layer coextrusion equipment with two single screw extruders having a conventional 25.4 mm single screw (L/D = 24) were used to produce sheets, 25.4 mm wide and 3mm thick. These sheets consisted of three to several thousands of alternating layers, using specially designed layer multiplying elements as shown in Figure 1. Each layer multiplying element (LME) was composed of three plates, where the melt stream was split into two parts, each part was compressed, restretched, and then restacked together. These LMEs were added, one by one, up to 10 sets, until nanoscale layers were obtained. The extrusion temperature was 280°C for PC/PP compositions in most experiments because these two materials showed similar viscosities at this temperature. PC was used as the skin layer as seen in Figure 2, which resulted in PC being 80 % by volume of the total composition in the samples. Extruded samples were quenched in a water bath immediately after processing.

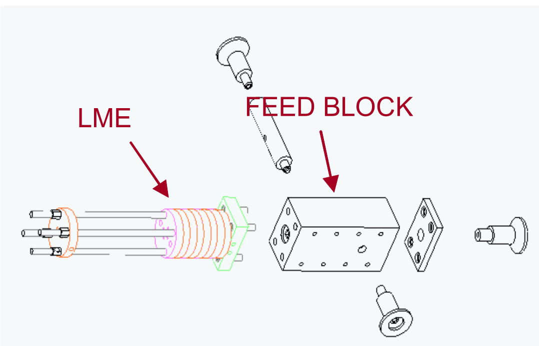


Figure 1. Multilayer coextrusion system.

Steps
1: Split melt stream
2: Compression of melt streams
3: Recombination of melt streams
4: Stabilization of melt stream
5: Repeat

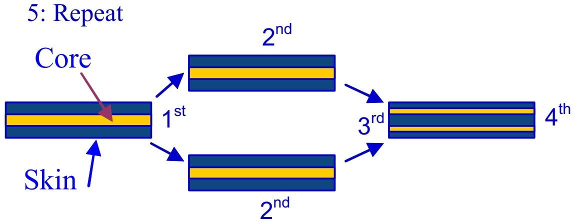


Figure 2. Schematic diagram of skin-core structure.

To prevent the formation of wave type instabilities, the volumetric flow rates were adjusted to give the same velocities for the two materials at the first merge point in the feedblock. The output ratio of skin to core layers from the extruders was set at 4 to 1 based on the ratio of the cross sectional areas of the two flow channels in the feedblock. Since the skin layer material was split and placed on either side of the core layer, the actual velocity ratio of skin and core layers in the feedblock was 2 to 1. Prior to taking samples at least 20 minutes of purging was performed.

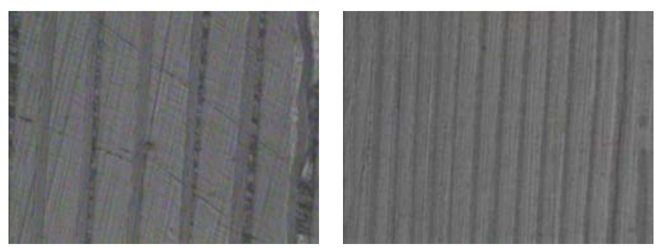
1.3 Characterization

Multilayer laminate thicknesses were measured using optical microscopy (OM) and atomic force microscopy (AFM). The samples were prepared by embedding the extrudate in epoxy resin to hold each layer tightly and avoid delamination. After curing the epoxy, the surface of the sample was polished using a mechanical grinder with fine-mesh sandpaper (1200 grit) to reduce the surface roughness for AFM measurements. All samples were examined by optical microscopy, and for selected samples, followed by AFM (XE-100 AFM, PSIA Corp) to study the interface using a scan rate of 1Hz [16]. A non-contact ULTRASHARP silicon cantilever (NSC15 series) with Al coating on the laser-reflection side was used in this study. The dimensions of the cantilever were 125 μm × 35 μm × 4 μm. Non-contacting mode was used for the AFM scan, followed by image processing to measure the thickness of each layer.

RESULTS AND DISSCUSSION

In order to avoid the viscous encapsulation behavior [17], PC was extruded as the skin layer and PP as the core layer, due to the lower viscosity of PC over PP at the processing temperatures. Since the PP and PC were incompatible with each other, they delaminated easily, which aided in the investigation of layer uniformity.

As the number of layer multiplications increased, the thickness of layers decreased as seen in Figure 3. When five and seven LMEs were used, the thicknesses of PP layers were about 19 and 4 μm, respectively.



(a) (b)

Figure 3. Optical micrographs (600x) of multilayers using five (a) and seven (b) LMEs with PC and PP.

As the number of layers increased, interfacial stresses near the wall would be higher than those near the center of samples. Thus, interfacial deformation caused by instabilities was greater in layers nearest the wall, as compared to those in the center as seen in Figure 4.

Wall ← Center → Wall

Figure 4. Digital photo image of delaminated layers for three LMEs; flow rates PC (50.3 g/min), PP (30 g/min).

This increase in interfacial stresses would be expected to cause zig-zag type instabilities [11]. To avoid these instabilities, interfacial stresses should be decreased by either increasing the temperature of LMEs or decreasing the total flow rate of materials, while keeping the flow rate ratio constant.

After five layer multiplying elements were used, instability appeared, showing merged layers in the center of the cross section of the extrudates. The merged layers were found to originate from the layers closest to the walls, which were brought to the center of the sample during the splitting and recombination of the melt streams. These instabilities were reduced by increasing the temperature of the layer multiplying elements, which would act to decrease the critical interfacial shear stress [18]. This is seen in Figure 5, where delamination occurs more easily in samples with more uniform layers (Figure 5b).

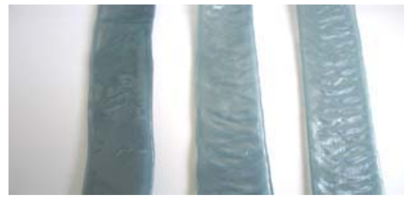
(a) (b)

Figure 5. Digital photo images of alternating layered structures produced by five LMEs for LME temperatures of (a) 280^{o}C and (b) 302^{o}C.

As the number of LMEs increased over five, most of interfaces were uniform except for layers near the center of samples where two layers merged, which had originated from interfaces close to the walls. Figure 6 shows an image of a merged layer from the center of a sample, where PP layers appear darker and thinner (due to lower volumetric flow rate of PP compared to that of PC). This merged layer results in mechanical interlocking between layers, reducing the ability to delaminate the extrudates. This behavior was previously observed by Ranjbaran and Khomami [12].

Figure 6. Optical micrograph (600x) of instability using six LMEs at 280^{o}C.

When the two materials were recombined with each other in the feedblock, the velocity difference at this first merge point caused stress at the interface, generating non-uniformity at this interface. Experiments indicated that the flow ratio between PC and PP was a critical factor in the generation of wave type layer instabilities [8]. Balancing the flow rate ratio of the two materials in the feedblock helped to delay the occurrence of the layer instabilities as seen in Figure 7 and Table 1. When the average velocity ratios of PC/PP were less than 0.4, wave type instabilities occurred. Samples including wave type instabilities were rather easy to delaminate, indicating the amplitude of the wave type instabilities was low.



(a) (b) (c)

Figure 7. Digital photo images of instabilities appearing on the surfaces of samples prepared with three LMEs with a temperature of LMEs of 280^{o}C and average velocity ratio of PC/PP, (a) 0.4, (b) 0.2 and (c) 0.1, respectively.

As more than six sets of LME were used, the number of merged layers increased as seen in Figure 8 (OM and AFM images of samples from seven LMEs). In addition, the size of the merged layers was increased. Instabilities located in the center of the sample, formed in the most recent combination of the melt streams, showed the greatest size. Layers in between these instabilities were rather uniform.

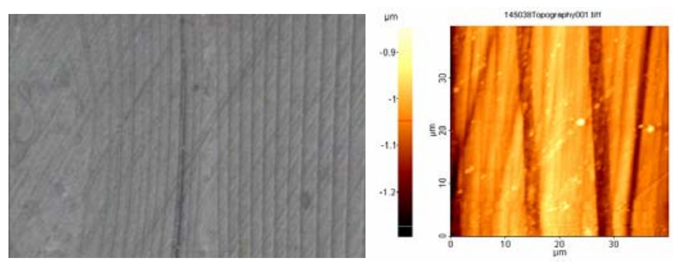


Figure 8. Optical microscope (600x) and AFM image for a sample prepared using seven LMEs at 302ºC.

Figure 9 shows a cross sectional view of a sample using 10 LMEs. Most of the interfaces near the center area were disrupted, yielding small PP droplets in the PC domain. Interfaces close to the surface of the samples were stable, and fairly uniform with layers about 500 nm thick.

CONCLUSIONS

We have investigated the effect of layer multiplication on interfacial instabilities in multilayer coextrusion. Interfacial shear stress was found to be a critical parameter controlling the development of zig-zag type instabilities between layers. As the number of layers increased, the amount of instability also increased. Interfacial instabilities could be reduced by increasing the temperature of LMEs, resulting in lowered interfacial stresses. The velocity ratio of materials was also found to be an important factor in wave-type interfacial instabilities. There was a critical value of velocity ratio required to produce uniform layers. The size of instabilities grew as the number of LMEs increased, causing layer breakdown in the center area of samples. After ten LMEs were used, uniform layer structures were only detected near the surfaces.

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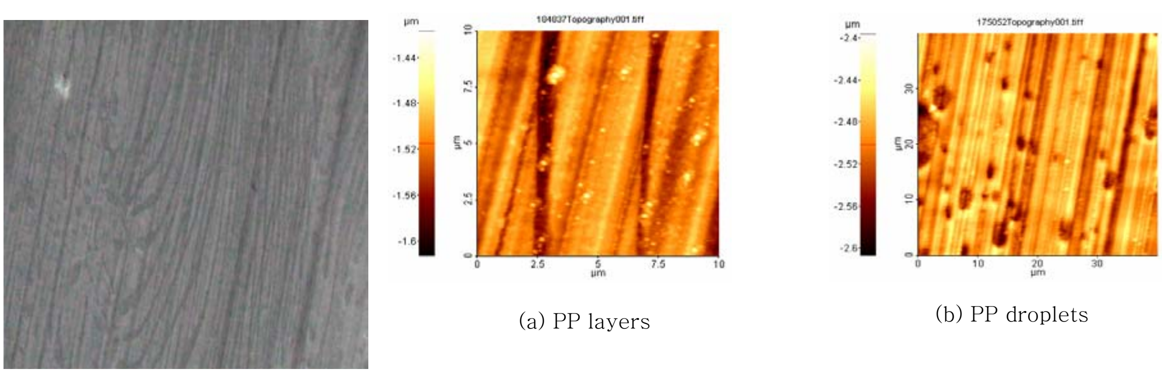
Screw Speed Ratio (PC/PP)	Flow Rate of PC	Flow Rate of PP	Average Velocity Ratio (PC/PP)	Pressure Drop	Wave Instabilities
[-]	[g/min]	[g/min]	[-]	[MPa]	
45/20	74	18	1.0	1.86	None
30/30	50.3	30	0.4	1.72	None
20/45	34.5	45	0.2	1.79	Yes
20/60	28	60	0.1	2.2	Yes

Table1. The effect of flow rate ratios on wave type instabilities.



(a) PP layers

(b) PP droplets

Figure 9. Optical microscope (600x) and AFM images for a sample prepared using 10 LMEs at 302ºC.