

Alternating Multilayer Structure of Polyethylene/Polypropylene Blends Obtained Through Injection Molding

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ABSTRACT: The formation of multilayer structures in the high-speed thin wall injection-molded samples of high-density polyethylene/isotactic polypropylene blends is reported. Based on the morphology development in injection runner and mold, a possible formation mechanism of multilayer structure was proposed in this study. Injection molding could be used as a simple and an effective

method for the fabrication of multifunctional multilayer structure. This work is interesting and important for scientific research as well as several potential applications.

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Key words: injection molding; polypropylene; polyethylene; blends; alternating multilayer structure

INTRODUCTION

The morphology control of polymer blends is of great practical importance during industrial processing such as extrusion or injection molding. The multilayer structures in plastic products are becoming increasingly important for many applications, as a result of substantial improvements in gas permeability^{1–4} and electrical^{5,6} and thermal conductivities.⁷ There are several methods reported for the fabrication of multilayer polymer composites, including self-assembly of polyelectrolytes,^{4,8} self-assembly via hydrogen bonding,^{9,10} self-assembly of block copolymer,^{11–13} and coextrusion.¹ Generally, a regular array of periodic microlayers can be obtained through self-assembly technique.^{4,8–13} However, because of its special requirement for molecular structure and complicated processing method, self-assembly technique is significantly limited in practical applications. Recently, coextrusion is widely being used to fabricate multilayered composites. In contrast to the spontaneously created self-assembled multilayers, the alternating layers in coextruded samples are

formed by forced assembly. Moreover, the coextrusion method can fabricate uniform multilayer structure with a wide range of melt-processable polymers.¹ Injection molding as another melt processing method has a number of advantages over coextrusion, such as easy to fabricate complex shaped product and high production rates. Sheet-like morphology was reported in the skin layer of conventional injection-molded samples.¹⁴ In particular, thin wall injection molding is becoming increasingly more important because of the explosive growth of portable devices that require thinner and lighter plastic housings.¹⁵ A high injection speed is needed to overcome the melt flow resistance within the thin wall mold cavity. As the polymer melt is forced to flow into a narrow slit at high speed, melt breakage and unsteady flow may take place, and some unique structures may be formed by such a forced assembly. In this study, high-density polyethylene (HDPE)/isotactic polypropylene (iPP) blends were injection molded into a thin wall mold at high injection speed. Interestingly, a multilayer structure with alternating layers of HDPE and iPP in the sample was obtained. This work is important and provides a novel and simple way to fabricate multifunctional multilayer structure through thin wall injection molding.

Additional Supporting Information may be found in the online version of this article.

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EXPERIMENTAL SECTION

HDPE, supplied by Lanzhou Petrochemical Corp., (Lanzhou, China) has a melt flow index (MFI) of 7.5 g/10 min (2.16 kg, 190°C) and a density of 0.957 g/cm³. iPP, supplied by the Lanzhou Petrochemical

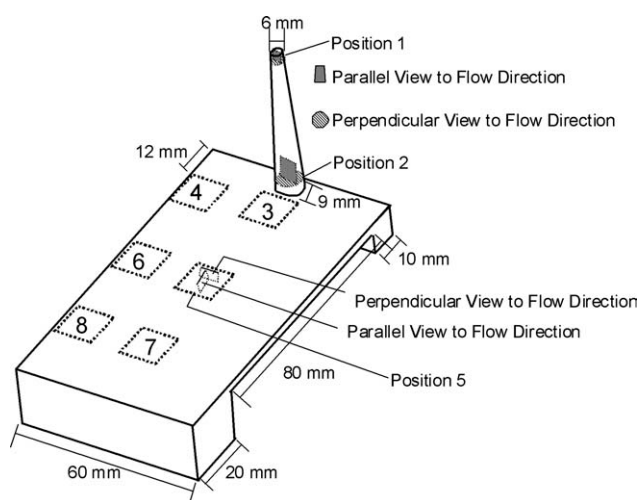


Figure 1 Schematic of injection molding sample. The position for parallel to flow direction and perpendicular to flow direction of specimens are indicated.

Corp., has a MFI of 2.6 g/10 min (2.16 kg, 230°C) and a density of 0.91 g/cm³. Melt blending of HDPE/iPP was conducted using a corotating twin-screw extruder (TSSJ-25 corotating twin-screw extruder, the L/D ratio of the screws is 32, and $D = 25$ mm) with a barrel temperature of 160–200°C and a screw speed of 120 rpm. The dried HDPE/iPP pellets were then subjected to injection molding (with a screw diameter of 25 mm) at a barrel temperature of 200°C and a mold temperature of 23°C. An injection speed of 600 mm/s without holding pressure was used in the current study. The as-obtained samples were labeled according to the weight content of iPP. For example, EP20 represents the samples containing 20 wt % iPP and 80 wt% HDPE. The mold for the injection molding in rectangular shape with a size of 80 mm × 60 mm and a thickness of 0.4 mm was used. To achieve high injection speed before mold is completely filled by polymer melt, a cavity with a larger thickness is attached to the end of rectangular plate (as shown in Fig. 1).

The specimens were cryogenically fractured in the direction parallel and perpendicular to the flow direction in liquid nitrogen. Then they were etched chemically with 3% solution of potassium permanganate in a 2 : 1 (by volume) mixture of concentrated sulfuric acid and 85% orthophosphoric acid. After the surface was coated with gold, the phase morphologies of the specimens were studied with an FEI Inspect F scanning electron microscope (SEM) at 20 kV.

RESULTS AND DISCUSSION

Injection-molded samples of polymer blends are known to show an inhomogeneous structure over

their thickness due to temperature and shear gradient during injection.¹⁶ The morphological studies of the injection-molded specimens were carried out after chemical etching to improve the contrast. iPP phase was etched in these specimens as a result of its weaker resistance to the mixed acid.^{17,18} Both phase morphology parallel and perpendicular to the melt flow direction were investigated for each layer. Three layers can be distinguished in the cross

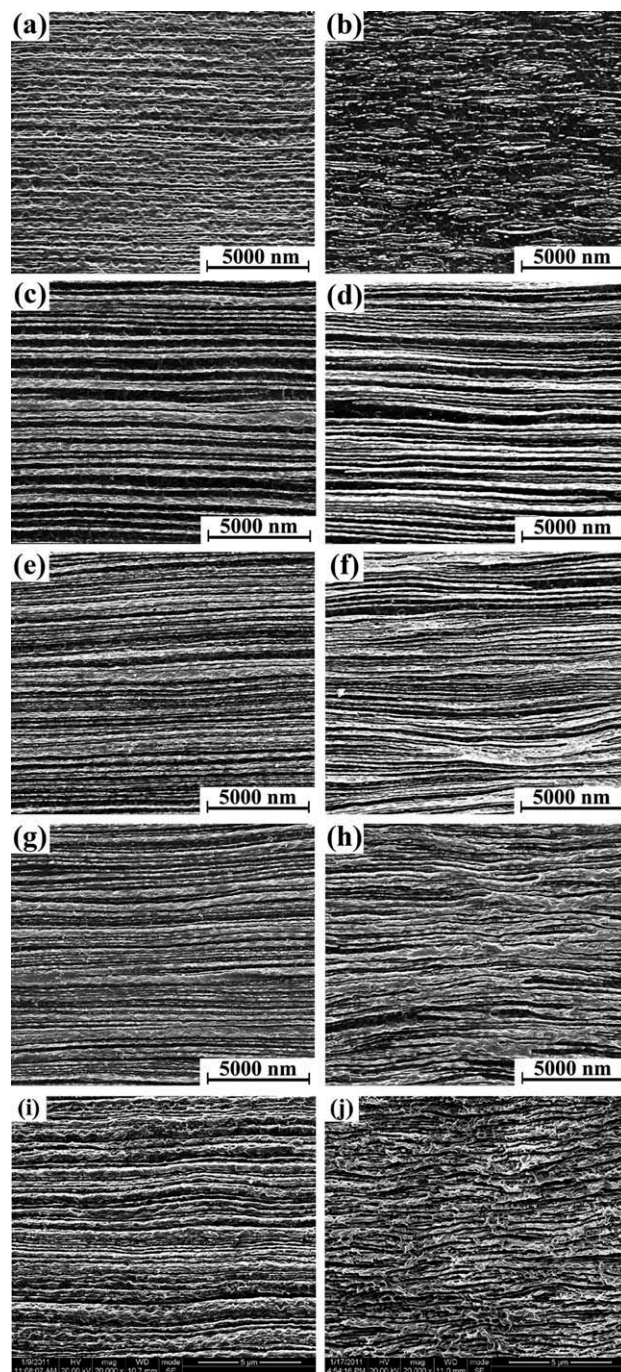


Figure 2 SEM micrographs of samples at position 5 with parallel (left column) and perpendicular (right column) to the flow direction: (a, b) EP80, (c, d) EP60, (e, f) EP50, (g, h) EP40, and (i, j) EP20.

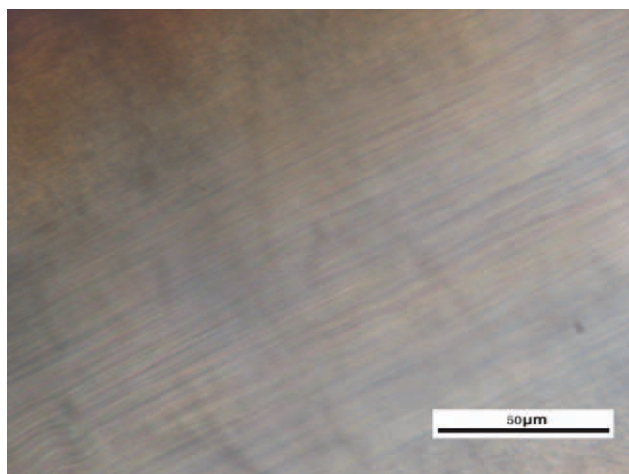


Figure 3 The PLM image of the multilayered structure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

section of these specimens: skin layer, intermediate layer, and core layer as shown in Supporting Information (Fig. S1). The core layer has a width of around 100 μm and is accounted for nearly 25% of the whole cross section. The images in Supporting Information Figure S2(a,b) are taken from the skin layer of EP50. One can see that shear in the skin layer leads to a discontinuous sheet structure. This could be caused by a balance between high shear rate and fast cooling rate. A co-continuous structure is observed in the intermediate layer, as shown in Supporting Information Figure S2(c,d). In the core layer [see Fig. 2(e,f)], a fine multilayer structure with alternating HDPE and iPP phase is formed. The thickness of each layer is around 70–500 nm. Please note that the thickness of the layers in all samples is not uniform, as injection molding can lead to local inhomogeneity in the flow field.¹⁶ To obtain an overall review of the multilayer structure, the core layer with lower magnification is shown in Supporting Information Figure S2(g). From this figure, one can observe that the layers are well arranged along the flow direction; almost all the layers are continuous with high aspect ratio. In contrast with the sheet-like morphology in the skin layer of conventional injection-molded samples,¹⁴ the alternating multilayer structure in the core layer of thin wall injection-molded samples have regular arrangement, uniform thickness of each single layer, and high length to thickness ratio. More importantly, the high ratio of multilayer structure in the whole cross section makes it have the possibility to be widely used in industrial application, for example, the products with good gas barrier fabricate directly through injection molding.

To further investigate the multilayer structure observed in injection-molded samples, more studies

were carried out on the core layer of blends in different composition ratios. SEM was used to investigate the composition dependence of phase morphology of the core layer, with iPP content ranging from 20 to 80 wt %, and these results are shown in Figure 2. It is obvious to note that iPP is a major component in EP80 sample and HDPE is dispersed in iPP matrix. One can observe discontinuous sheet or incomplete layer structure as shown in Figure 2(a,b). In this case, the content of HDPE is too low to form a complete alternating multilayer structure. EP60 [Fig. 2(c,d)], EP50 [Fig. 2(e,f)], and EP40 [Fig. 2(g,h)] samples consist of the alternating layers of HDPE phase and iPP phase. While iPP is dispersed in the HDPE matrix, discontinuous sheet structure is observed again for sample EP20 [Fig. 2(i,j)]. It can be concluded that the different layer structures always show up for different compositions. Continuous multilayer can be obtained in these samples of iPP content in the range of 40–60 wt %. It should be noted that the morphology of samples at position 5 (see Fig. 1) has only been examined in this study. To perform systematic study on the morphology of these thin wall samples, SEM study was carried out on several positions of sample EP50 at core layer. Selected micrographs are shown in Supporting Information Figure S3. Multilayer structure is observed in the whole thin wall sample. However, the layer structure at positions 5 and 7 is slightly more regular than the one observed at positions 4, 6, and 8. To confirm the multilayered structure observed, polarized light microscope (PLM) study is carried out. The result confirms the presence of multilayered structure in the injection-molded part (see Fig. 3).

To understand the formation mechanism of the multilayer structure, the phase morphology of EP50 at different location in injection runner and mold was examined. The results are shown in Figure 4 for positions 1, 2, and 3 as illustrated in Figure 1. To illustrate the formation process of such a multilayer structure, the morphology evolution in the core layer of thin wall injection-molded samples is schematically represented in Figure 5. iPP is the dispersed phase forming discontinuous fiber with a larger domain size at position 1 than the rest. The fibers become smaller in diameter while the polymer melt flow to position 2. This is probably due to flow-induced morphology change or mixing between iPP and HDPE. The fibrillar shape is deformed into discontinuous layer structure at position 3 due to confined flow in the thin wall mold. Discontinuous sheet structure can be observed in Supporting Information Figure S2(a,b) as a result of high shear rate and rapid cooling in the skin layer. In the core layer, the discontinuous layer structure can be formed [Fig. 4(e,f)], and these discontinuous layers are able to merge into each other forming wide continuous

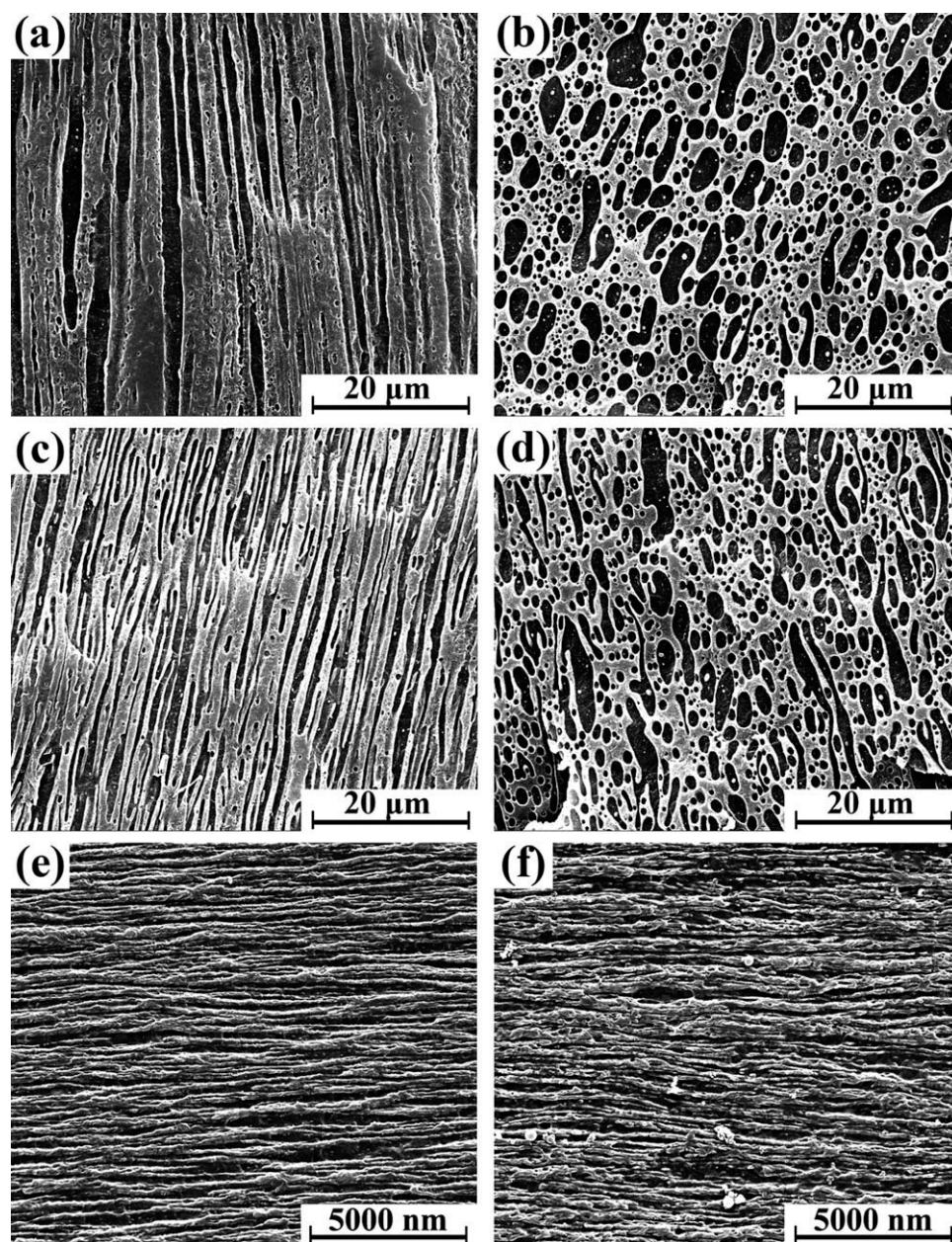


Figure 4 SEM micrographs of EP50 view parallel (left column) and perpendicular (right column) to the flow direction: (a, b) position 1, (c, d) position 2, and (e, f) position 3.

multilayer structure. During injection molding, shear and temperature gradient are often observed. The co-continuous structure of intermediate layer may attribute to the “break up behavior” at a special shear and temperature.¹⁹ Further study is needed to understand such an effect.

CONCLUSION AND REMARKS

The morphology of the polymer blends is strongly dependent on the viscosity ratio,²⁰ interfacial interaction, volume ratio, shear and temperature conditions during processing, and so forth.²¹ In this work, a multilayer structure with alternating layers of HDPE

and iPP in the core layer has been obtained through high-speed thin wall injection molding. It is seen that this result is interesting and important for scientific research as well as several potential applications. More work needs to be carried out to better understand the formation mechanism and to realize precise control on the multilayer structure. The following issues could be interesting to be investigated: the effect of injection speed and mold thickness on the thickness and the thickness distribution of the layers; the possibility of improving gas barrier properties of injection-molded parts (such as beer bottles) through the formation of such multilayer structure; the crystallization behavior of these confined

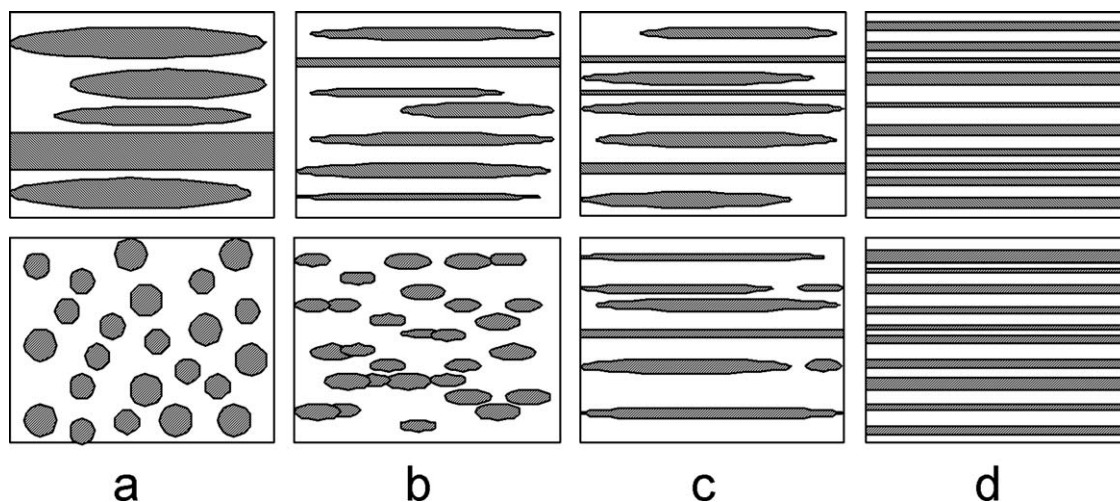


Figure 5 Schematic of morphology at core layer representation in (a) position 1, (b) position 2, and (c, d) the thin wall mold, view parallel (upper column) and perpendicular (bottom column) to the flow direction.

polymer crystals between these layers; and the possibility of incorporating nanofillers into such a structure. More importantly, as the continuous multilayer structure was prepared through an efficient processing method, that is, thin wall injection molding, our work could pave a new way for the preparation of multifunctional and high-performance materials.

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