Morphologies and Mechanical Properties of HDPE Induced by Small Amount of High-Molecular-Weight Polyolefin and Shear Stress Produced by Dynamic Packing Injection Molding

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Received 24 August 2007; accepted 15 April 2008
DOI 10.1002/app.28586
Published online 20 August 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: To better understand the effect of a small amount of high-molecular-weight polyethylene (HMWPE) on the mechanical properties and crystal morphology under the shear stress field, the dynamic packing injection molding (DPIM) was used to prepare the oriented pure polyethylene and its blends with 4% HMWPE. The experiment substantiated that the further improvement of tensile strength along the flow direction (MD) of high-density polyethylene (HDPE)/HMWPE samples was achieved, whereas the tensile strength along the transverse direction (TD) still substantially exceeded that of conventional molding. Tensile strength in both flow and TDs were highly enhanced, with improvements from 23 to 76 MPa in MD and from 23 to 31 MPa in TD, besides the toughness was highly improved. So, the samples of HDPE/HMWPE transformed from high strength and brittleness to high strength and toughness. The obtained samples were characterized via SEM and TEM. For HDPE/HMWPE, the lamellae of the one shish-kebab in the oriented region may be stretched into other shish-kebab structures, and one lamella enjoys two shish or even more. This unique crystal morphology could lead to no yielding and necking phenomena in the stress–strain curves of HDPE/HMWPE samples by DPIM. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2483–2487, 2008

Key words: shish-kebab; shear stress; induce; HDPE/HMWPE; self-reinforcement; dynamic packing injection molding

INTRODUCTION

Self-reinforcement of polyolefin resins was reported in many studies.[1–7] In recent years, more and more attentions have focused on the self-reinforcement through blending with a little another polymer by outside stress fields [Dynamic Packing Injection Molding (DPIM)] to reform the crystal morphology to further improve the mechanical property.[8–11] Under outside stress field, shear-stress results in the formation of nuclei by alignment of polymer chains in the cooling melt along the shear direction. In this case, lamellae would grow from these nuclei laterally due to their high aspect ratio. Crystal morphology was highly oriented by shear stress form in row. In this article, DPIM which was actuated by pistons in means of hydraulic pressure was applied to produce the shear stress. The main feature was that when the melt was injected into the mold, the melt was forced to move repeatedly in a chamber by two pistons that move reversibly with the same frequency as the solidification progressively occurs from the mold wall to the molding core part.[11] During this packing phase, the polymer chains between the static frozen layer and the flowing melt were stretched out in the direction of flow. It could be seen that there were three layers in cross sections of DPIM specimens: barely oriented skin regions, a highly oriented regions, and a core zone, shish-kebab structure is formed in oriented regions. Some studies have reported that the amount of shish crystal of high-density polyethylene (HDPE) can be promoted by adding second component.[11] This article is to report the effect of a small amount of high-molecular-weight polyethylene (HMWPE) blended into the HDPE on the mechanical property of samples and crystal morphology induced by a little HMWPE under shear-stress field.

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Contract grant sponsor: National Natural Science Foundation, China; contract grant number: 50473053.

Journal of Applied Polymer Science, Vol. 110, 2483–2487 (2008)

EXPERIMENTAL

Apparatus

The DPIM device used in this study is in Figure 1. It is a laboratory-scale hot-runner mold with hydraulic-driven pistons which is used to keep the polymer

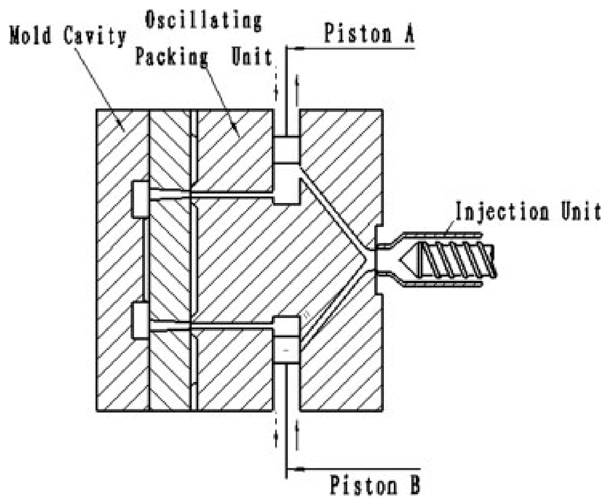

Figure 1 Dynamic packing injection molding device.

in the melting state and at the same time to apply oscillating stress to solidify melt in the mold cavity. Pistons A and B are operated 180° out of phase. As soon as the mold cavity is alternately filled with polymer melt from two gates, the pistons reciprocate in their respective chambers according to the predetermined oscillating frequencies until the melt in the cavity is entirely solidified. To measure the mechanical properties in both MD and TD, the mold was designed to be a 60 mm × 68 mm × 4 mm thin square plate with two thickened fan gates (Fig. 2). After the square plates (60 mm × 60 mm × 4 mm) were obtained, the fan gates of the DPIM molding were cut off. Then the plates were machined to standard dumbbell tensile along the MD and TD.[11–14]

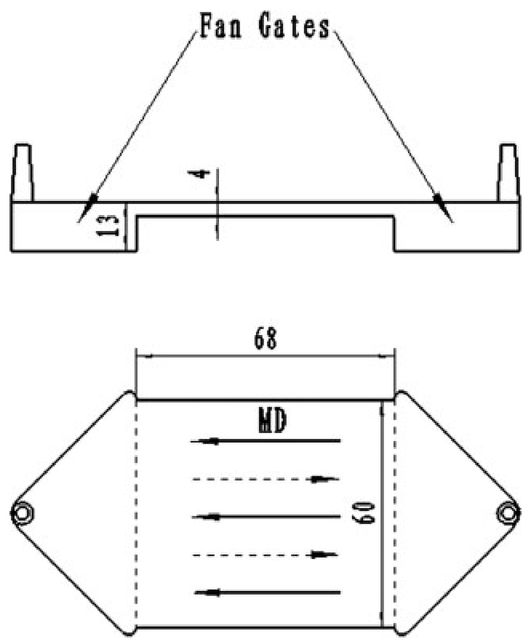

Figure 2 Outline of the square plate specimen with the dimensions (mm) as indicated.

Materials

HMWPE (DMDY1158) used in this study was provided by QiLu Petrochemical Corp., Shandong, China. It had a melt flow index (MFI) of 2.1 g/10 min (190°C, 21.6 kg); HDPE (5000S) was supplied by Lanzhou Chemistry Ltd. (China), and its MFI is 0.7 g/10 min (190°C, 2.16 kg) and a density of 0.954 g/cm^3.

Samples preparation

HDPE and HMWPE were applied in this work. The two components were blended by a corotating intermeshing twin-screw extruder with a barrel temperature of 160–190°C, and then cut into pellets using a plastic grain-cutting machine. Two blends prepared in this work were expressed as B0 and B4. B0 and B4 respectively, show the weight percentages of HMWPE in the blends as 0 and 4%. B0 blends were molded by DPIM and SPIM, and B4 blends were only molded by DPIM. For DPIM, packing pressure, mold temperature, and oscillating cycle were critical factors in determining the mechanical properties of the samples.[12,13] In this work, the processing parameters were shown in Table I. For B0 and B4 (blends), the difference of them was the content of HMWPE, the basic processing parameters were same.

Tensile testing

A Shimadzu tensile machine (model AG-10TA) was employed for tensile testing at room temperature, and the speed of the crosshead was 50 mm/min.

Scanning electronic micrograph (SEM) investigation

A small sample was cut from the tensile bar, ground and polished down to a flat plane on one side, which was 0.5 mm (skin region), 1.2 mm (oriented region), and 2 mm (core region) below the original surface respectively. The polished specimens were gold-sputtered after being etched in a solution of $KMnO_2$-H_3PO_3-H_2SO_4. In this experiment a Hitachi scanning microscope (Model *S*-450, Hitachi, Osaka, Japan) was used for SEM measurements.

TABLE I
Processing Parameters

Processing parameters	Value
Injection pressure (MPa)	45
Melt temperature (°C)	200
Mold temperature (°C)	60
Oscillating cycle (s)	6
Packing pressure (MPa)	25

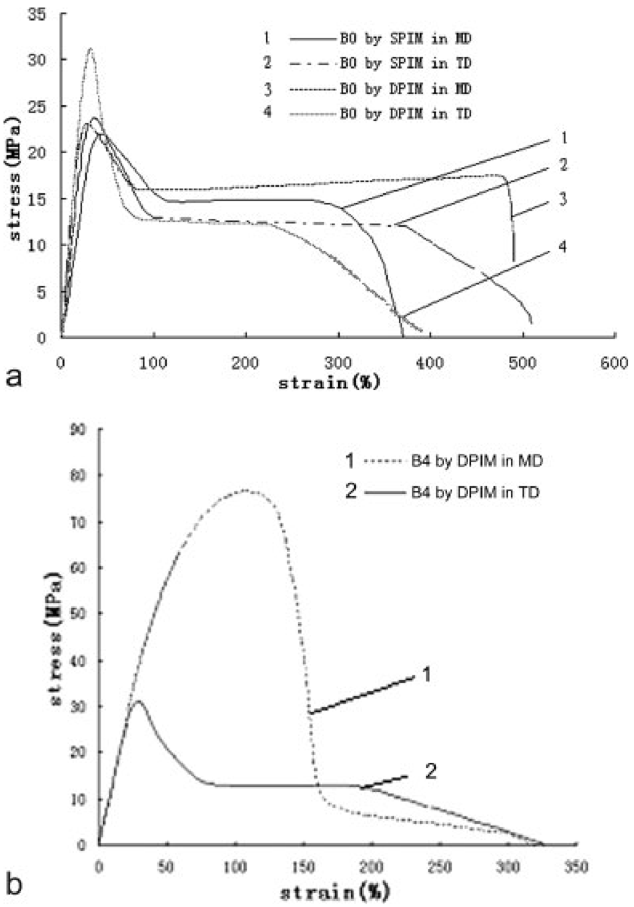

Figure 3 (a) (B0) Stress–strain curves of DPIM, and SPIM samples of B0 and B4 and (b) (B4) Stress–strain curves of DPIM and SPIM samples of B0 and B4.

Transmission electron microscope (TEM)

The oriented layers (1.2 mm below the original surface) of B0 and B4 were frozen in liquid nitrogen, sliced parallel to MD, and stained with ruthenium tetraoxide (RuO_4). Then, the morphologies of these superthin slices were observed on a Hitachi H-800 SE microscope.[14,15]

RESULTS AND DISCUSSION

Mechanical properties

Figure 3(a) shows the stress–strain curves of DPIM and SPIM samples of B0 blends prepared by DPIM and SPIM. These curves are the typical stress–strain curves, which are subdued. Compared with SPIM samples, the DPIM samples obviously improve their tensile strengths along both TD and MD. This illustrates that pure HDPE can be biaxially self-reinforced by DPIM technology.[14] Figure 3(b) gives another stress–strain curve, which has no yielding and necking phenomenon during tensile testing. When the 4% HWMPE is mixed into the HDPE, the stress–strain curve of the blends samples has a wonderful change, which expresses that the samples have higher tensile-stress and larger elongation (about 325%) in MD. At the same time, the tensile-stress of B4 samples keep no fall compared with the

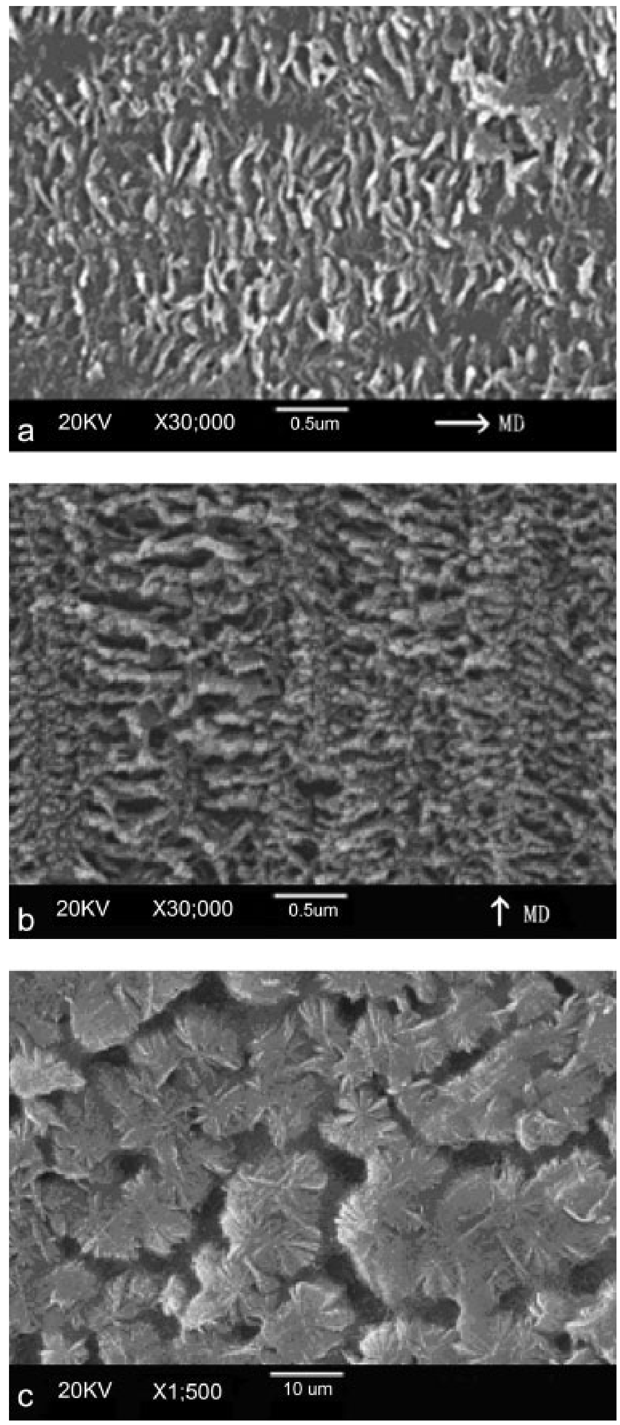

Figure 4 (a) (oriented region) SEM micrographs of the etched surfaces from DPIM samples of B0, (b) (skin region) SEM micrographs of the etched surfaces from DPIM samples of B0 and, (c) (core region) SEM micrographs of the etched surfaces from DPIM samples of B0.

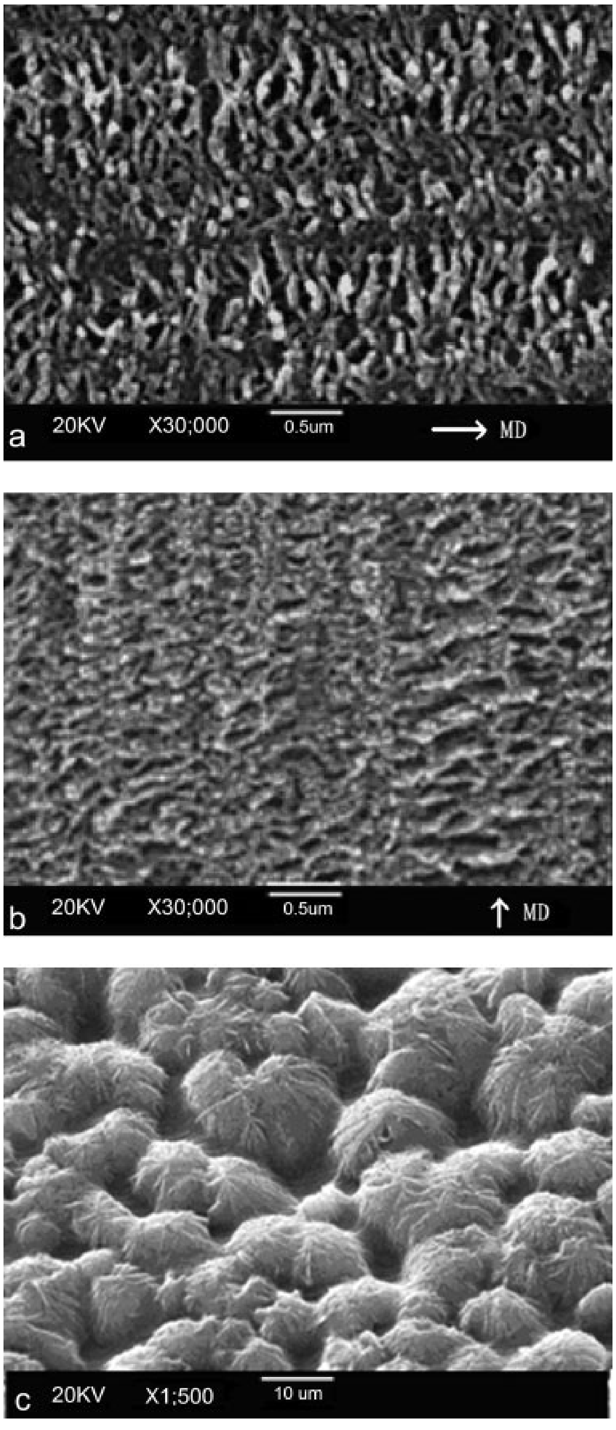

Figure 5 (a) (oriented region) SEM micrographs of the etched surfaces from DPIM samples of B4, (b) (skin region) SEM micrographs of the etched surfaces from DPIM samples of B4, and (c) (core region) SEM micrographs of the etched surfaces from DPIM samples of B4.

samples of B0 by DPIM in TD. In fact, all DPIM samples of blends, which mixed with HWMPE, show the same types of tensile failure as blends B4,[14] but B4 samples have the best mechanical properties among this blends.

SEM analysis

The samples of B4 molded by DPIM have the especial mechanical properties, for the sake of uncovering the relationship between the mechanical properties and microcosmic structures, the above micrographs of samples by DPIM of B0 and B4 were obtained by SEM measurements. They indicate that the crystal structures of the B0 and B4 samples molded by DPIM technology are variational because of different shear stress. As is well known, three basic region of injection molding are distinguished. Close to the surface, the layer is called the skin region, which is orientated due to the shear flow. The shear region, actually a multilayer structure, is orientated by the shear stress during solidifying.[16,17] The other layer is barely orientated core region which is lastly frozen.

The micrographs of Figs. 4(a) and 5(a) obtained from the oriented region of sample by DPIM technology show that there are shish-kebab crystals, and the arrangement of lamellae in Figure 5(a) is more regular than that in Figure 4(a). The reason perhaps is that the HDPE blended with 4% HMWPE (B4) was more prone to form the regular shish-kebab crystals under the same shear-stress condition than pure HDPE. The regular arrangement of lamellae contributes to the enhanced strength, and the relatively close connection of interlamellae was in favor of the back-up trend of elongation at break. In addition, with the regular arraying long lamellae of samples becoming more and more, the tensile strength and the toughness of the sample would be both improved. So, we can see from the Figure 5(a) that there were more and longer lamellae, which contribute to enhanced tensile strength and toughness in orientated region, as a result, the samples of B4 by DPIM had a remarkable stress–strain curve compared with that of B0. Furthermore, the reason of these lamellae forming is that HWMPE blended into the HDPE, which induced the crystal of HDPE by shear stress during solidification.

Figures 4(b) and 5(b) show the micrographs obtained from skin region, the micrographs of Figures 4(c) and 5(c) were obtained from core region. From the Figures 4(b) and 5(b), it indicated that there were only a few orientated lamellae because of the shear flow during injection molding. The other side of shield, for the core region in Figures 4(c) and 5(c), because of barely shear stress there was enough time to form the spherulites during solidification. They would make against the toughness of samples.

TEM analysis

Figure 6 shows the TEM micrographs of biaxially self-reinforced samples of B0 and B4 by DPIM. The

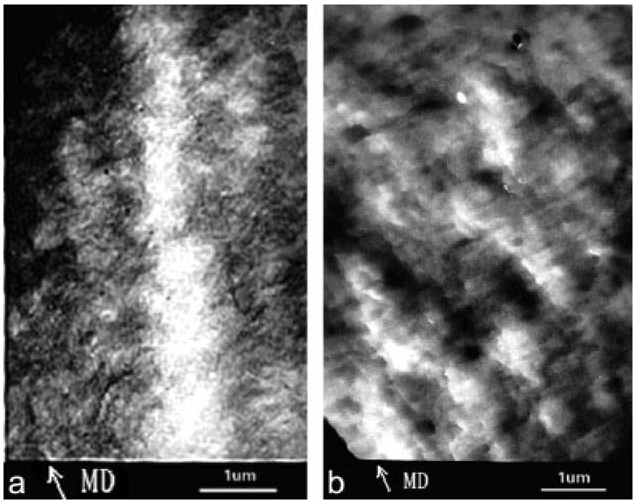

Figure 6 (a) (B0) TEM micrographs from orientated region of DPIM samples of B0 and B4 and (b) (B4) TEM micrographs from orientated region of DPIM samples of B0 and B4.

bright areas stand for crystalline phases, and the dark areas belong to amorphous phases.[18] In correspond to the SEM micrographs of the orientated region of B0 and B4, TEM micrographs can further prove the shish-kebab crystal existing in the samples of B4 by DPIM. From the Figure 6(b), the lamellae of shish-kebab crystal in the orientated region arrayed tidily along the melt flow direction. At the same time, the lamellae of shish-kebab crystal grown laterally from these nuclei, and the size of this direction was longer than the conventional lamellae so as to stretch into the other shish-kebab crystal, namely the same lamellae simultaneity possess of two central filament (shish). From the Figure 6(a), the lamellae of B0 samples were thicker than that of B4. Obviously, the enhancement of tensile strengths in both MD and TD are mainly resulted from this structure.[12]

CONCLUSIONS

In summary, the oriented HDPE/HMWPE samples prepared by DPIM technology have greatly improved both toughness and tensile strength, they were characterized through SEM and TEM. The shish-kebab structure could be found in the oriented region, and the improvement of toughness and tensile strength was strongly dependent on the longer, more and thinner lamellae of shish-kebab which forms in HDPE induced by HMWPE by DPIM. In the core region the spherulite were found and lightly oriented lamellae in the skin region.

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