Self-Reinforcement of High-Density Polyethylene/Low-Density Polyethylene Prepared by Oscillating Packing Injection Molding under Low Pressure

GONG ZHANG, LONG JIANG, KAIZHI SHEN, QING GUAN

Department of Plastics Engineering, Sichuan Union University, Chengdu 610065, People's Republic of China

Received 4 March 1998; accepted 31 July 1998

ABSTRACT: This article reports the toughness improvement of high-density polyethylene (HDPE) by low-density polyethylene (LDPE) in oscillating packing injection molding, whereas tensile strength and modulus are greatly enhanced by oscillating packing at the same time. Compared with self-reinforced pure HDPE, the tensile strength of HDPE/LDPE (80/20 wt %) keeps at the same level, and toughness increases. Multilayer structure on the fracture surface of self-reinforced HDPE/LDPE specimens can be observed by scanning electron microscope. The central layer of the fracture surface breaks in a ductile manner, whereas the break of shear layer is somewhat brittle. The strength and modulus increase is due to the high orientation of macromolecules along the flow direction, refined crystallization, and shish-kebab crystals. Differential scanning calorimetry and wide-angle X-ray diffraction find cocrystallization occurs between HDPE and LDPE. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 799–804, 1999

Key words: high-density polyethylene; low-density polyethylene; self-reinforcement; shish-kebab; injection molding

INTRODUCTION

The goal of the research in self-reinforcement of polyolefine is to improve the mechanical properties of general purpose polyolefine materials by a special processing method. With the theory of polyethylene forming a stretch chain under high pressure in injection molding, high modulus and strength structure parts can be made.¹ After that, much research has been conducted in polyolefine reinforcement in injection molding,² under high pressure,³ and shear control orientation technology.^{4–6}

In our previous articles, tensile strength and Young's modulus of high-density polyethylene (HDPE) increased from 27.8 MPa and 1.0 GPa to 108 MPa and 5.0 GPa, respectively.⁷ As for polypropylene, strength and modulus increased from 33.4 MPa and 1.4 GPa to 58.0 MPa and 3.0 GPa.⁸ Similarly, the strength of acrylonitrile-butyldiene-styrene (ABS), an amorphous material, increased from 46 MPa to 54 MPa.⁹ The tensile strength improvement is due to the high degree of macromolecule orientation along the flow direction under the shear stress field produced by the oscillating packing. A lot of the shish-kebab crystals can be observed. But, toughness of the specimens decreased with the increase of tensile strength and modulus.

Compared with the self-reinforced HDPE, the tensile strength of low-density polyethylene (LDPE) increased from 10.6 MPa to 20.9 MPa, and the toughness and elongation were kept at the same level.¹⁰

In this article, self-reinforcement of HDPE/ LDPE was studied using a similar processing method. LDPE was mainly used to increase the

Correspondence to: G. Zhang.

Journal of Applied Polymer Science, Vol. 71, 799-804 (1999)

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Paramatara	Values	
r arameters		
Injection pressure	90 MPa	
Packing pressure	50 MPa	
Mold temperature	$25^{\circ}\mathrm{C}$	
Melt temperature	$200^{\circ}\mathrm{C}$	
Holding time	2.5 min	
Oscillating frequency	0.3 Hz	
Oscillating packing pressure	45 MPa	
Osemaning packing pressure	40 WH a	

Table IProcessing Parameters in OscillatingPacking Injection Molding

toughness of self-reinforced HDPE. Characteristics of the blends were investigated by scanning electron microscopy, differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (WAXD).

EXPERIMENTAL

Materials

The materials used in this research were LDPE (1F7B; Yanshan Petrochemical Corp.; MFI (melting flow index) 7.0 g/10 min) and HDPE (7006 A; Qilu Petrochemical Corp.; MFI (melting flow index) 6.8 g/10 min).



Figure 1 Variations of the stress/strain behavior of HDPE/LDPE (80/20 wt %) prepared by oscillating packing and static packing. (A) Oscillating packing. (B) Static packing.



Figure 2 Variations of the stress/strain behavior of pure HDPE prepared by oscillating packing and static packing. (A) Oscillating packing. (B) Static packing.

Mold and Injection Molding

A dumbbell specimen mold according to ASTM-638M, as used in previous research, was used for injection molding. The injection molding machine was a SZ-100 g thermoplastic injection molding machine produced by Nanning No. 2 Light Industry Machinery Factory. The oscillating packing device equipped on the injection machine has been described in ref. 7. The processing parameters are listed in Table I. To compare the results with ordinary injection molding, we also conducted injection molding under static packing using the same processing parameters.

Table IIMechanical Propertiesof HDPE/LDPE Blends

	Tensile Strength (MPa)		
HDPE/LDPE (wt %)	Static Packing	Oscillating Packing	Strength Increase (%)
0/100	10.6	20.9	97
20/80	15.0	32.2	115
40/60	15.6	34.4	121
60/40	19.2	55.1	187
80/20	28.8	98.3	241
100/0	28.9	108.6	276



(a)



(b)





Figure 4 DSC endotherms of HDPE/LDPE blends prepared by static packing.

Tensile Tests

Tensile strength was tested on a Universal Testing Machine (Shimadzu AG-10TA) at 20°C. The crosshead speed was 50 mm min⁻¹.

SEM Investigation

The tensile fracture surface of HDPE/LDPE specimens were observed on a Hitachi X-650 scanning electron microscope.

X-ray Measurement

Orientation of crystal graphic planes of specimens was determined by WAXD using a D/MAX-IIIA X-ray diffractometer.

DSC

For each specimen, three slices were cut from different location of the specimen to conduct DSC measurements on a Perkin-Elmer DSC-7. Slices were cut from the skin layer, shear stress layer, and central layer. The heating rate was 5°C min⁻¹.

RESULTS AND DISCUSSION

Figures 1 and 2 show that the tensile strength and Young's modulus of self-reinforced HDPE/

Figure 3 SEM micrographs of the fracture surface of self-reinforced HDPE/LDPE (80/20 wt %).



Figure 5 Peak temperatures versus blends composition.

LDPE (80/20 wt %) blends are almost the same as the self-reinforced pure HDPE, and toughness of the blends increases evidently. From Table II, with the increase of HDPE proportion, the tensile strength of the blends increases both under static packing and oscillating packing. Furthermore, the reinforcement efficiency of the oscillating packing rises with the increasing proportion of HDPE.

Scanning electron microscopic (SEM) pictures of the fracture surface are shown in Figure 3. Figure 3(a) is a low-magnification SEM photograph of the fracture surface, on which the mul-



Figure 6 Fusion heats versus blends composition.



Figure 7 DSC endotherms of HDPE/LDPE blends, pure HDPE, and pure LDPE. (A) HDPE/LDPE (80/20) prepared by oscillating packing. (B) HDPE/LDPE (80/ 20) prepared by static packing. (C) Pure HDPE. (D) Pure LDPE.

tilayer structure can be easily identified. Fig. 3(b) is a high-magnification SEM picture of shear layer on the fracture surface, which exhibits a brittle fracture. Figure 3(c) shows the fracture surface of the central layer, which breaks in a ductile manner and contributes to the toughness increase.

Melting behavior of the various LDPE/HDPE blends produced under static packing was studied by DSC. In Figure 4, only one endothermic peak is evident for each specimens. Peak temperatures of the blends are between the peaks of pure LDPE and HDPE, and the peak positions shift from LDPE to HDPE with the increasing proportion of HDPE. This behavior is clearer in Figure 5 (peak temperatures) and in Figure 6 (fusion heats vary with composition). Along with the WAXD curves (as shown in Fig. 9), in which there are no separate peaks and no peak broadening, this observation suggests that no segregation has taken place between LDPE and HDPE at the structural level of crystalline textures.



Figure 8 DSC endotherms of HDPE/LDPE (80/20 wt %) prepared by oscillating packing. (A) Shear layer. (B) Central layer.

As for the self-reinforced blends prepared by oscillating packing, DSC endotherms show two melting peaks of the self-reinforced specimen (Fig. 7), which means two kinds of crystalline structures exist in the specimens. The first peak temperature is almost the same as the peak temperature of LDPE/HDPE prepared by static packing, and the second peak is 6°C higher than the first one. If these two endothermic peaks stood for separate crystals from LDPE and HDPE, respectively, one might expect that, on the WAXD curves, two overlapping, closely spaced peaks or a broader peak may be observed. But, the actual WAXD curves do not comply with the expectation (as can be seen in Fig. 10). Thus, we think the first peak is the melting peak of colamellar and cospherulites of the shish-kebab structure of LDPE/ HDPE blends, and the second peak is attributed to shear-induced, stretched chain crystals of the blends, which has a higher melting point in the shish-kebab structure. This supposition needs our further study by transmission electron microscopy to testify.

Figure 8 shows two endotherms of the reinforced blends from different locations of the fracture surface. The second melting peak of the shear layer is larger than that of central layer. We can find similar results from any other reinforced



Figure 9 WAXD curve of HDPE/LDPE (80/20 wt %) prepared by static packing.

blends. This is attributed to a higher shear force applied on the melt in the shear layer and more stretched chain crystals induced by the shear force.

The WAXD curve is a key quantitative indicator of macromolecule orientation. The two strongest reflections in the curves are (110) and (200) planes of HDPE/LDPE. Comparing Figure 9 with Figure 10, we can see clearly the orientation degree of (110) and (200) is increased considerably



Figure 10 WAXD curve of HDPE/LDPE (80/20 wt %) prepared by oscillating packing.

in reinforced specimens. The highly oriented macromolecule chains is the prerequisite of tensile strength and modulus enhancement.

CONCLUSIONS

The poor toughness of self-reinforced HDPE was improved by adding LDPE, whereas tensile strength and modulus remained nearly unchanged. Self-reinforcement of HDPE/LDPE blends depends on high orientation of the macromolecule and shish-kebab crystals. Structural investigation also found cocrystallization between HDPE and LDPE.

The authors thank the Hong Kong Chiang Industrial Charity Foundation for financial support.

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