폴리에틸렌의 모세관 용융흐름에 Boron Nitride Powder 와 Die 의 적용에 의한 가공성의 향상

이상명, 양현석, 이재욱
서울시 마포구 신수동 1번지
서강대학교 화학공학과, 121-742

The Improvement of the Processability by Applications of Boron Nitride Powder and Die to the Capillary Melt Flow of Polyethylene

Sang Myung Lee, Hyun Suk Yang, Jae Wook Lee
Dept. of Chemical Engineering, Sogang University,
1 Shinsu-dong, Mapo-ku, Seoul, Korea, 121-742

Introduction

Various kinds of polyethylene resins are extensively used in many commercially important polymer processings such as pipe, film casting, film blowing, continuous blow molding extrusion, and various coating flows. It is well known that productivity of these polymer processes is limited by the onset of melt fracture. Various melt fracture phenomena are related to complex flows that involve the occurrence of vortex at an entrance region and the flow instability in a die. The first limiting factor affecting the production rates is a surface or sharkskin defects. Therefore, some researchers used fluoro elastomer as an additive, which essentially acts as a lubricant and forms a slip layer between the metallic surface of die wall and the polymer [1, 2]. Their experimental results show that the addition of a small amount of fluoro elastomer to the pure resin delays the onset of melt fracture until much higher shear rates. Moreover, the power requirement for extrusion is significantly reduced. But, the main disadvantage of the use of fluoro elastomer is its high cost. It has been recently reported that compositions containing fine Boron Nitride (BN) particles of low cost can be successfully used as processing aids to eliminate or delay surface melt fracture or sharkskin, and substantially delay gross melt fracture until much higher shear rates in the extrusion of polyolefins [3, 4].

In this research, two kinds of BN powders were used to study the effect of BN powder on the rheological properties and processability of metallocene catalyst based LDPE. The considered BN powders differ from their crystal and agglomeration sizes. This causes the difference in dispersed crystal size and size distribution on final extrudates, and finally leads to the difference in processing performance. Slip velocities of resins with and without BN powders have been measured. Finally, the effects of hot-pressed BN and Composite dies on the processability of capillary flow have been investigated. To the author's knowledge, the use of BN die as a processing aids utility is the first work. The synergetic effects of BN powder, hot-pressed BN and Composite dies will also be explained.

Experimental

Materials

Metallocene catalyst based ethylene/octene copolymer (m-LDPE, grade name PL1850) from Dow Plastics was used in this study. It has a weight average molecular weight (M_w) of 1.094×10^5 and polydispersity (M_w/M_n) of 1.97. The density is 0.902 g/cm^3 and a melt index is 3.0 (g/10min, 190°C). Two types of BN powders from Advanced Ceramics Co. were used as processing aid. Both have a hexagonal crystal structure but are different in size and agglomerate state. Powder A (HCV) has the agglomerated particle size from 7 to 11μm and crystal size of 0.1μm. Powder B (HCJ-48) has the agglomerated particle size of about 225μm and crystal size of 10μm.

Procedure

BN particles in a finely divided state were thoroughly dry-mixed with the resin pellets at appropriate contents. Melt mixing of m-LDPE with BN powder was performed using a twin-screw extruder and the extrudates were pelletized after solidification in the water bath.

Both capillary and parallel-plate rheometers were used to characterize the rheological properties of the pure and BN powder filled resins. Parallel-plate rheometer (ARES, Rheometric Scientific) was used to measure the dynamic moduli and slip velocities of these resins. Capillary rheometer (Rheograph 2003 of Goettfert) was used to determine the shear rate at which smooth extrudates can be produced with and without BN powders. Also, to change the interfacial energy between polymer and the die wall, three kinds of capillary dies (namely the tungsten carbide die, the hot-pressed BN and Composite dies) were used. Three dies have a diameter of 1mm, entry angle of 180°, and length-to-diameter ratio of 30. Hot-pressed BN and Composite dies was supplied from Advanced Ceramics Co. Hot-pressed BN is compacted at temperatures up to 2000°C and pressures up to 2000psi using a small amount of calcium borate as a binder. Hot-pressed Composite die is also compacted at similar condition as well as the hot-pressed BN die after mixing BN powder with titanium diboride in ratio of 50 to 50.

Surface defects of the extrudates were observed at thirty magnifications using an optical microscope (Nikon).

Result and Discussion

Linear oscillatory frequency sweep experiments have been performed to study the effect of BN on the rheological properties of polymer. Dynamic moduli for resins with three different levels of BN Powder A are depicted in Fig.1. The storage and loss moduli behaviors of the pure and 0.1wt% filled resins show little difference. However, the additions of BN contents of 0.5 and 1.0wt% decrease the dynamic moduli in noticeable degree at all frequency ranges. Also, resins containing Powder B are almost similar rheological behavior to resins with Powder A. Two reasonable explains are possible for this; one is due to a change in the rheological properties of resin. The other is due to the accelerated polymer slippage by BN powders on the plate. The measurement of slip velocity could partly answer this question, and steady-shear experiments have been carried out in a parallel-plate rheometer. The apparent shear rate is related to the true shear rate and the slip velocity by following equation.

$$\dot{\gamma}_a = \dot{\gamma}(\tau_{Z\theta}) + \frac{2U_s(\tau_{Z\theta})}{H} \quad (1)$$

where $\dot{\gamma}$ is the true shear rate, $\dot{\gamma}_a$ is the apparent shear rate, U_s is the slip velocity, and H is the gap height. When r, the radial distance from the center of the disk, is equal to the edge of the disk R, this equation can be written as follow.

$$\dot{\gamma}_{aR} = \dot{\gamma}_R(\tau_R) + \frac{2U_s(\tau_R)}{H} \quad (2)$$

If there is no slip between the resin and the wall of the plate, the result is independent of the gap heights. On the other hand, if polymer melts slip at the wall of the plate, the shear stress versus shear rate results obtained by the different gap heights will not be overlapped. In experimental results, stressed of resins with and without Powder A and B showed significant difference for each gap height than that of the pure resin. Fig.2 shows slip velocities of various resins. Slip velocity of resin with Powder A is most high. Also, slip velocity with Powder B is much higher than that of the pure resin. It can be concluded that the change of dynamic moduli by the addition of BN powder is due to slip.

To study the effect of BN powder on the processability of polymer, experiments were carried out using a capillary rheometer with a tungsten carbide die at 150°C. Fig. 3 depicts the processability of the pure resins containing various contents of two types of BN powders. In case of the pure resin, surface melt fracture appears at about 150 s^{-1} followed by sharkskin at around 215 s^{-1} and gross melt fracture at higher shear rates of about 1080 s^{-1}. It can be seen that the addition of 0.1wt% Powder A delays the onset of the melt fracture to 250 s-1 and postpones each instability flow regions such as surface melt fracture, sharkskin and gross melt fracture until much higher shear rates. Also, the processability is gradually increased with increasing BN contents. On the other hand, though the addition of 1.0wt% Powder B also increases the processability of resin, the addition of 0.1 and 0.5wt% does not seems to be so much effective. This result indicates that the types of BN powder act an important role in a capillary flow.

Up to now, it is confirmed that BN powder improves the processability of polymer by decreasing the surface energy between the polymer melts and capillary die wall. For more detail investigation about the effect of Boron Nitride on the processability and rheological properties, the hot-pressed BN and Composite dies have been tested. At first, to observe the rheological behaviors of the pure and filled resins in three kinds of dies, stress curves as a function of shear rate have been measured and represented in Fig. 4. For three dies, the apparent wall shear stresses of resin are decreased by the addition of BN powder. Also, the apparent wall shear stresses of the pure and filled resins are remarkably decreased by the application of hot-pressed BN die instead of tungsten carbide die. Hot-pressed composite die decreases apparent wall shear stresses of resin as well as hot-pressed BN die. Photographs of the extrudate appearance as shear rates, kinds of dies, and BN powders are shown in Fig.5. In case of tungsten carbide die, the smooth extrudate (a) changes into the sharkskin (b), (c), and follows by gross melt fracture (d). The hot-pressed Composite die shows much more stable patterns than tungsten carbide die. And, the extrudates in the hot-pressed BN die show much more stable patterns compared to that in other dies.

Conclusion

The effects of BN powders on the rheological behaviors and processability of m-LDPE have been investigated. The processability was highly dependent on the type and content of BN powder in the capillary extrusion. Powder A, small crystal size and uniform size distribution, was quite effective in delaying and eliminating the melt fracture to higher shear rate. On the other hand, Powder B, relatively large crystal size and non-uniform size distribution, was only effective in high filling concentration. The powder agglomeration was not important factor as long as the samples are prepared by twin-screw extrusion. The addition of BN powders, especially Powder A, lowered the dynamic moduli in all frequency ranges. This was not because of the change of bulk rheological properties, but due to the increase of slip velocity by BN powders, which act as a solid lubricant.

Hot-pressed BN and Composite dies were applied to investigate the improvement of the processability. Apparent wall shear stresses of the pure and BN powder filled resins were remarkably decreased by the application of hot-pressed BN and Composite dies. Also, these dies delayed surface and sharkskin defects and postponed gross melt fracture region until much higher shear rate. The use of both BN powder and hot-pressed BN die was found out to have the best performance in increasing the processabilty.

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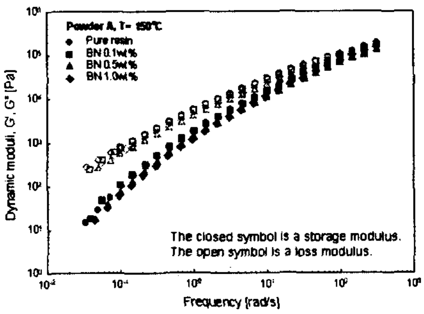

Fig. 1. Dynamic moduli of resins with and without BN powder.

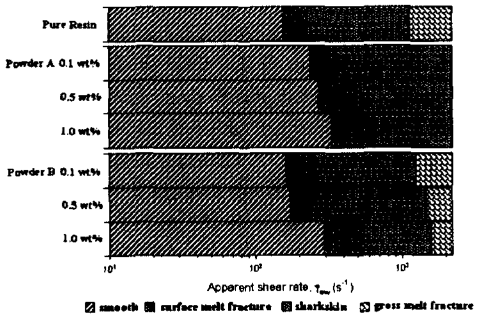

Fig. 3. Diagram of the processability for resins with and without BN powder

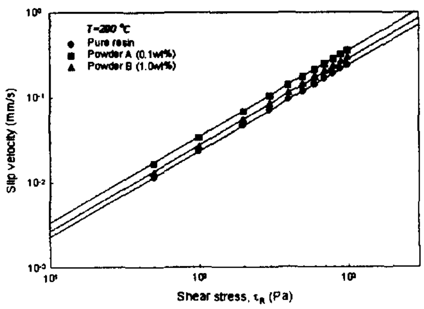

Fig. 2. Slip velocities as a function of shear stress for resins with and without BN powder.

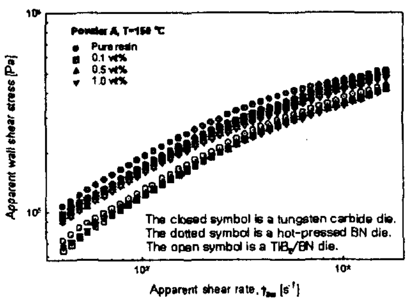

Fig. 4. Apparent wall shear stress vs. apparent shear rate of resins with and without BN powder A three kinds of dies.

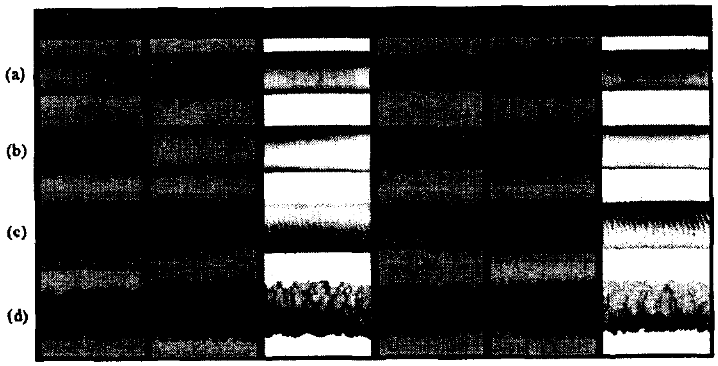

Fig. 5. Photographs of the extrudates for resins with and without Powder A for three kinds of dies. ((a) 115.4 s^{-1}, (b) 224.1 s^{-1}, (c) 851.3 s^{-1}, (d) 2007.4 s^{-1}; Powder A, T = 150°C)