

**Boron Nitride가 긴 결가지 사슬을 가지는  
저밀도 폴리에틸렌의 가공성에 미치는 영향**

이상명, 양현석, 이재욱  
서강대학교 화학공학과

**The Effect of Boron Nitride on the Processability  
of metallocene LDPE with Long Chain Branching**

Sang Myung Lee, Hyun Seok Yang, Jae Wook Lee  
Department of Chemical Engineering, Sogang University

**ABSTRACT**

The melt fracture phenomena of three different metallocene low density polyethylene (m-LDPE) resins with different long chain branching (LCB) contents into the polymer backbone were investigated using capillary rheometer. The rheological responses of these resins were analyzed by parallel-plate and capillary rheometers. In the case of two resins with similar  $M_w$ , the presence of LCB exhibits an earlier onset of shear thinning than linear polymer and influences to the processability of m-LDPE. Also, we studied about the effect of Boron Nitride powder on the processability of these resins. The equipment used includes a capillary rheometer with two kinds of dies, namely tungsten carbide and hot pressed BN (Boron Nitride) dies with diameter of 1mm and length of 30mm. We could know that the processability of m-LDPE with LCB is related to BN contents and types. Also, we found that the hot pressed BN (hpBN) die increases the degree of processability of these resins like BN powder.

**INTRODUCTION**

Melt fracture of various shapes and related processing instabilities continue to limit processing rate in many commercially important polymer processing industries such as fiber spinning, film blowing, extrusion, and various coating flows [1]. Therefore, melt fracture was fallen off the quality and mechanical property of final product more than critical processing rate occurring flow instability. To increase processing rate and improve the quality of final product, the study for these phenomena requires tracing a thing to its origin and approach of various methods. The most common approach to achieve this objective is through the use of processing aids [2].

The primary objective of this research is to better understand the effect of long chain branching on the flow behavior of m-LDPE resins. Also, the critical shear rates for the onset of melt fracture as a function of BN type and content are presented and discussed in detail. In addition, we studied about the effect of the hpBN die on the processability of these resins.

## **EXPERIMENTAL**

### **Materials**

Table 1 lists all resins used in this study together with some pertinent data for resins. These resins were produced via INSITE technology from Dow Plastics. It is also a homogeneous poly(ethylene/ $\alpha$ -olefin) copolymer. The amount of LCB had consisted of octene comonomer is usually less than one per molecule. The content of LCB can conveniently evaluate by the Dow Rheology Index (DRI). Higher values of DRI indicate higher contents of LCB.

In this study, two types (HCV, HCJ-48) of boron nitride produced by Advanced Ceramics were used. Grade HCV is an initial synthesis BN powder made up of agglomerated submicron crystals with a mean particle size range of 7-11 $\mu$ m. But, Grade HCJ-48 is a hexagonal Boron Nitride powder with a mean particle size of 200-250 $\mu$ m.

### **Experimental Measurement**

Viscometric measurements of the samples were obtained using commercially available instruments. Steady and dynamic shear measurements in range of low shear rate or frequency were obtained by a rotational rheometer (ARES, Rheometric Scientific). Parallel plate fixture having 25 mm diameter was used with a gap size of 1.2 mm. The test sample was maintained in a nitrogen atmosphere during all tests. The steady shear experiments performed at shear rates 0.01 to 0.5 s<sup>-1</sup>. Complex viscosity measurements were made in small amplitude oscillatory testing mode over angular frequency range of 0.1 to 500 rad/s. The measured viscosity was corrected by single point method. Also, rheological properties and processability in range of high shear rate was assessed using a capillary rheometer (Goettfert, Rheograph 2003). High shear viscosity was corrected by the bagley correction about the applied pressure and the rabinowitsch correction about wall shear rate. The melt fracture observations were performed using a capillary rheometer at 150°C. We made hot pressed BN die and compared degree of processability with tungsten carbide die. These two dies have the same diameter (1 mm) and length-to-diameter (L/D = 30), with an 180° entry angle. Hot pressed BN is compacted at temperatures up to 2000°C and pressures up to 14Mpa.

The boron nitride particles in a finely divided state were thoroughly dry-mixed with the resin pellets at appropriate contents. Mixing of resin with boron nitride was performed using twin screw extruder at 50 rpm. The surface defect of solidified the capillary strands were observed by Nikon optical microscope with magnification (x 30).

## **RESULTS AND DISCUSSION**

In general, the metallocene-catalyzed polyethylene (PE) is known to have narrow MWD as shown in Table 1. Fig. 1 shows the viscosity behavior for three resins with different degrees of long chain branching. PL1845 and PL1850 with almost same  $M_w$  have almost similar zero shear viscosity at low shear rate or frequency region. But, PL1845 with higher LCB content exhibits slightly an earlier onset of shear thinning than PL1850. PL1880 has higher zero shear viscosity and exhibits an earlier onset of shear thinning than PL1845 and PL1850 because this resin has higher  $M_w$  and LCB than these resins. As shown in Fig. 2, PL1845 with higher LCB content exhibits better the degree of processability than PL1850. Usually, it has been known that the degree of processability of m-LDPE increases with increasing LCB contents. However, even through PL1880 has higher LCB content than

PL1845 and PL1850, its processability is much lower. Also, defects of the capillary strand appear more severe than PL1845 and PL1850 at high shear rate. From these results, we found that processability does not improve always with increasing LCB content. It seems that these phenomena appear because elasticity increases with increasing  $M_w$ .

Fig. 3 depicts the degree of processability for the pure resin and resins containing various BN contents in two types BN powder. The onset of melt fracture for the pure resin appears at about  $153s^{-1}$ . In the case of HCJ-48, the processability was improved about resin containing 1.0 wt% BN powder only. In visual experimental result, we observed that BN particles had largely agglomerated in the polymer matrix of PL1850. Whereas, in the case of HCV, largely agglomerated BN particles were unobserved in the polymer matrix. So, the degree of processability was increased with increasing BN contents. Therefore, we conjecture that optimum value of BN content may exist in content more than 1.0 wt%. We observed that the addition of BN powder delay surface melt fracture, sharkskin and gross melt fracture to the higher rate. It seems that this phenomenon was related to reduction of surface energy between polymer melts and die. Under such a guess, we made the hpBN die and studied about the degree of processability for PL1850. Fig.4 shows photographs of the capillary strands for PL1850 in various processing conditions. We found that the processability in the hpBN die was improved even more in tungsten carbide die. Also, swelling ratio of the capillary strands in the hpBN die increased than it in tungsten carbide die under constant shear rate such as shown in Fig.5. When we observed the processability of resin containing HCV 0.5 wt% in hpBN die, the processability of this resin was improved than other processing conditions. The amplitude and wavelength of sharkskin was also decreased at the same time.

## **CONCLUSIONS**

The presence of long chain branching (LCB) has a pronounced effect on the melt fracture behavior of m-LDPE. The degree of processability in the capillary flow was increased with increasing LCB content for resins with similar  $M_w$  each other. But, we found that the processability does not improve always with increasing LCB content. In the case of PL1880, even through the resin having higher LCB content than PL1845 and PL1850, the processability was decreased by increment of elasticity because this resin has higher  $M_w$  than other resin (PL1845, PL1850). It is found that the degree of processability in the capillary flow can be depends on BN powder content and type. Also, we found that the hpBN die was improved about the degree of processability for m-LDPE like BN powder.

## **ACKNOWLEDGEMENTS**

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Table 1. Physical properties and molecular characteristics of used resins.

Sample	Density (g/cm <sup>3</sup> )	MI (g/10min)	T <sub>m</sub> (°C)	M <sub>w</sub>	MWD	DRI
Dow Afinity PL1845	0.910	3.5	106	105700	2.2	1.4
Dow Afinity PL1850	0.9020	3.0	98	109400	1.97	0.8
Dow Afinity PL1880	0.9020	1.0	99	138200	2.14	3.6

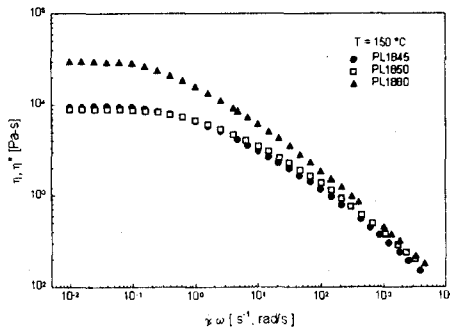


Fig. 1. Shear viscosities of PL1845, PL1850 and PL1880 at 150°C.

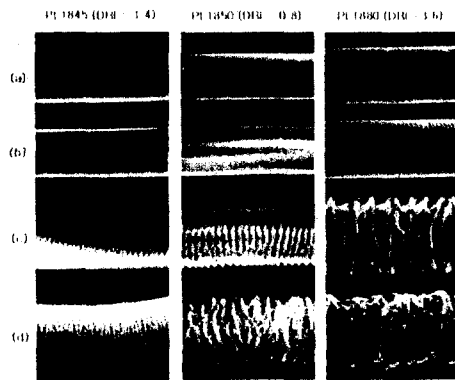


Fig. 2. Photographs of the capillary strands of PL1845, PL1850 and PL1880 at 150°C and four apparent shear rates (s<sup>-1</sup>). (a) 40.3, (b) 115.4, (c) 639.6, (d) 1246.4 ; (Tungsten carbide die)

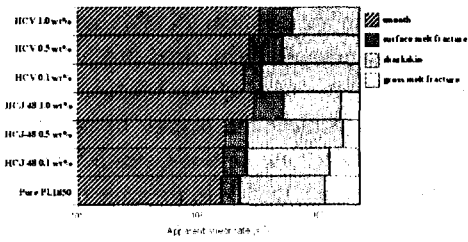


Fig. 3. The diagram of processability for the pure resin and resins containing various BN contents. ( PL1850, T = 150°C, Tungsten Carbide Die)

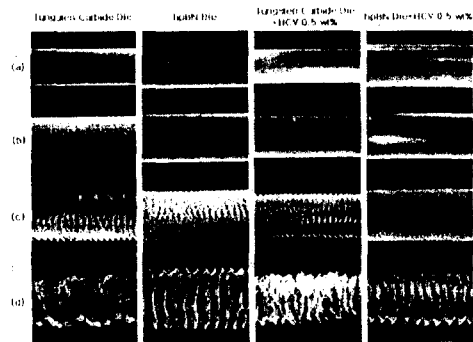


Fig. 4. Photographs of the capillary strands for PL1850 at various processing conditions. (a) 115.4, (b) 224.18, (c) 851.3, (d) 2007.4

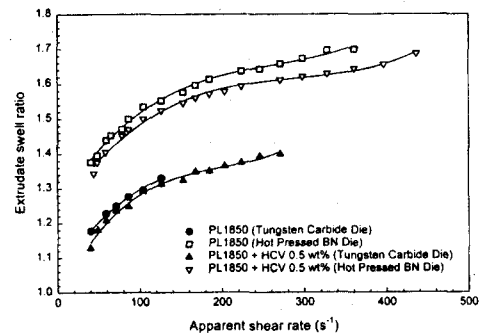


Fig. 5. The extrudate swell ratio of the capillary strands for PL1850 at various processing conditions.