

Boron nitride based processing aids

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(Received June 19, 2003)

Abstract

Boron nitride is a new processing aid that is capable of eliminating gross melt fracture in several polymer processing operations. Its combinations with other processing aids i.e. fluoropolymers offer additional possibilities of obtaining enhanced processing aids that may take the processes to rates not realized before. A variety of different such combinations are discussed in this paper. The essential components are (1) boron nitride capable of eliminating gross melt fracture and (2) suitable lubricant capable of eliminating surface melt fracture such as stearates for the polyolefin processing and polyethylenes for the processing of fluoropolymers.

Keywords : melt fracture, processing aid, boron nitride, fluoroelastomer, fluoropolymer, polyethylene, stearates

1. Introduction

The rate of production of many polymer processing operations, is limited by the onset of flow instabilities (Tordella, 1969; Ramamurthy, 1986; Achilleos *et al.*, 2002). In particular, in extrusion processes when the throughput exceeds a critical value, small amplitude periodic distortions appear on the surface of extrudates (*surface melt fracture* or *sharkskin*). At higher throughput rates these take a more severe form of larger irregular distortions (*gross melt fracture*) (Petri and Denn, 1976; Ramamurthy, 1986; Larson, 1992).

To increase the productivity by eliminating or postponing the melt fracture phenomena to higher shear rates, one must make use of processing additives/aids (Achilleos, 2002). These are mainly fluoropolymers that are widely used in the processing of polyolefins and other commodity polymers. They are added to the base polymer at low levels (approximately 0.1%). They essentially act as die lubricants, modifying the properties of the interface (increase slip of molten polymers on die wall). As a result of this lubrication effect, the onset of instabilities is postponed to much higher output rates and the power requirement for extrusion is significantly reduced.

It has been demonstrated that certain boron nitride (BN) based compositions may act as effective processing aid in extrusion of a number of fluoropolymers and polyolefins (Buckmaster, 1996; Rosenbaum *et al.*, 1995; 1998; 2000). BN can be successfully used as processing aids to elim-

inate not only *sharkskin melt fracture* but also substantially postpone *gross melt fracture* to significantly higher shear rates well within the gross melt fracture region. It is noted that conventional fluoroelastomers can only eliminate *surface melt fracture*.

In this paper we combine BN with certain fluoroelastomers and stearates to produce enhanced polymer processing additives for use in polyolefin processing. For the case of fluoroelastomer/fluoropolymer processing, a combination of a polyethylene and boron nitride produces an enhanced processing aid that is better than any known one.

2. Experimental

The experimental results presented in this paper were produced by using two metallocene-catalyzed polyethylenes Exact[®] 3128, and Exceed[®] 116 (ExxonMobil), and two HFP/TFE fluoropolymers provided by DuPont (FEP[®]100 and FEP[®]4100). First the effect of addition of boron nitride to the polymers on their rheology was examined by using a parallel plate geometry. For processing, both a capillary rheometer and a single screw extruder were used to determine the shear rate at which smooth extrudates can be produced in continuous extrusion of the metallocene PEs and FEP[®] resins.

The rheometer is a standard Instron piston-driven constant-speed capillary unit. In continuous extrusion a special annular crosshead die was attached to the rheometer in order to simulate the wire coating process or other continuous processes. The crosshead die was a Nokia Maillefer 4/6 that included dies and tips of various diam-

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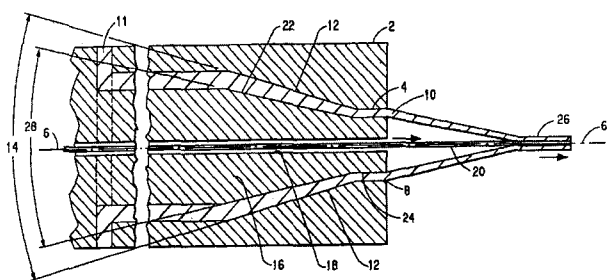


Fig. 1. A schematic of the crosshead die.

eters ("tip" is the wire guide) with equal entry cone angles of 60° and the die land length of 7.62 mm.

Fig. 1 shows a schematic diagram of this cross-head die. The molten polymer enters the die via port and is forced around the wire guide towards the die orifice. The wire guide serves as a mandrel for the molten polymer, giving the extrudate a tubular shape. The die passage forms the exterior surface of the tubular shape, and the exterior surface of the cylindrical extension forms the interior surface of the tubular shape. The greater speed of the wire compared to the polymer extrusion rate causes the polymer coming into contact with the wire at a point remote from the orifice to draw down to a thinner cross-section, forming a thin polymer coating on the wire. This is a melt draw-down extrusion process with draw down ratio (DDR), which is the ratio of die orifice area to cross-sectional area of the polymer insulation, of at least 5:1. However, in the present study the pressure extrusion makes no use of wire and therefore DDR is irrelevant.

Compositions with BN and fluoroelastomer and stearates at various concentrations were prepared by first preparing a concentrate of 5 wt%. Consequently, the concentrate was diluted to various final desired concentrations. These final blends were tested in extrusion by using the crosshead die at 163°C and 204°C for the case of polyethylenes. In the case of the extrusion of the FEP[®] resins the same crosshead die was used and experiments were performed at $350\text{--}370^\circ\text{C}$. Between testing the various blends, the rheometer was flushed with three full loads of polypropylene in order to purge remained BN and/or fluoroelastomer off the die surface. The extrudates were collected in a cold-water bath in order to freeze their appearance and avoid sagging effects. These were consequently examined carefully to observe distortions on their surface.

The morphology of boron nitride powders and fluoroelastomer were investigated by using a Hitachi S-2300 Scanning Electron Microscope (SEM) operating at 5keV. It was observed that the BN powder used had an average particle size of $15\text{--}20\ \mu\text{m}$ with medium degree of agglomeration, while the fluoroelastomer had an average particle size of $200\ \mu\text{m}$ without any degree of agglomeration. Good dispersion is a requirement for best performance (Yip *et al.*, 1999).

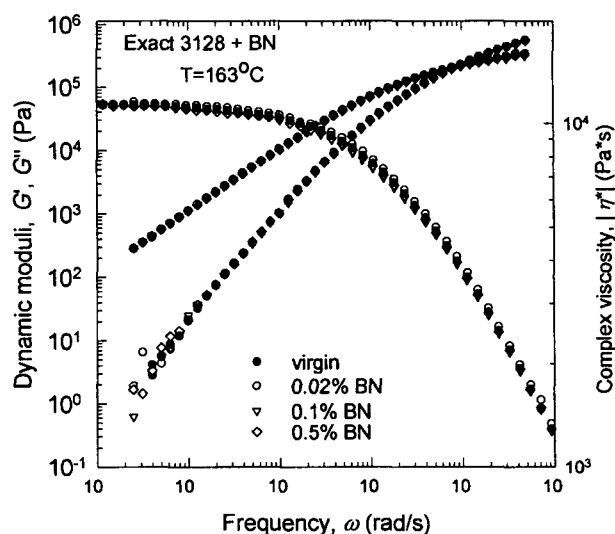


Fig. 2. Linear viscoelastic data for PE Exact 3128 at 163°C with and without BN.

3. Results and discussion

3.1. Effect of boron nitride on the rheology of polymers

It has been reported in the literature that the addition of a small amount of BN has almost no effect on the linear viscoelastic properties of polymers (Rosenbaum, 2000).

Fig. 2 shows dynamic linear viscoelastic data for a virgin metallocene-LLDPE (Exact[®] 3128) and m-LLDPE with three different levels of BN. No significant difference was found in the linear viscoelastic behavior of pure and filled resins as far the loadings were kept at relatively low levels (up to 0.5 wt% loadings were examined). Similar observations were reported by Lee *et al.* (2000; 2001). A variety of different BN powders were also examined by Yip (1999; 2000a; 2000b) and it was again reported that use of BN up to 0.5 wt% loadings have no effect on the linear viscoelasticity of polyolefins and fluoroelastomers.

3.2. Effect of BN and Teflon[®] in polyolefin processing

As it has previously been demonstrated, boron nitride is an efficient processing aid to eliminate not only sharkskin melt fracture but also to postpone gross melt fracture to significantly higher shear rates (Buckmaster, 1996, Rosenbaum *et al.*, 2000). In this section, BN is combined with a Teflon[®] processing aid in order to study whether or not the processability of polymers improves further.

Fig. 3 and 4 depict the flow curves of Exact[®] 3128 and Exceed[®] 116 with or without BN and Teflon[®] obtained with a crosshead die attached to the rheometer. The shear stress is plotted as a function of the apparent shear rate. The apparent shear rate was calculated by using the formula applied for slit dies having a large aspect ratio (Bird *et al.*, 1987):

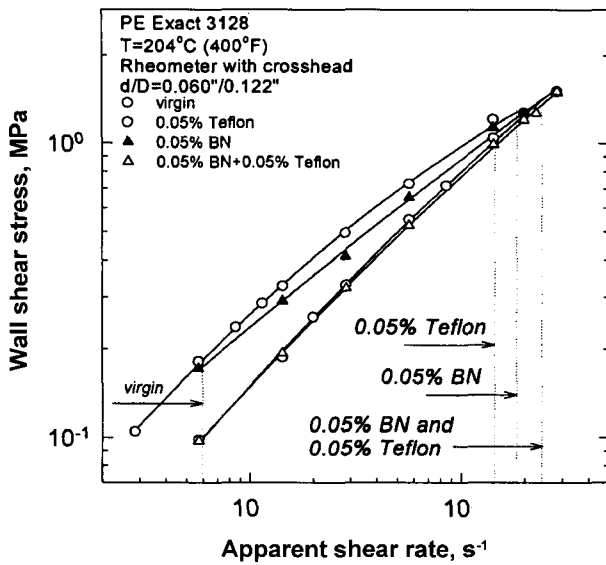


Fig. 3. The effect of combining 0.05% of BN with 0.05% Teflon[®] on the melt fracture performance of PE Exact[®] 3128.

$$\dot{\gamma}_A = \frac{6Q}{0.25(D-d)^2 0.5\pi(D+d)} \quad (1)$$

where Q is the volumetric flow rate, d and D are the tip and die diameters, correspondingly. The apparent wall shear stress was estimated as the average of the shear stress at the inner and outer walls by using the following formula, which is based on the assumption of a power-law fluid (Bird *et al.*, 1987):

$$\tau_z = \frac{\Delta P D}{4L} \left(\frac{2r}{D} - \beta^2 \frac{D}{2r} \right) \quad (2)$$

where τ_z is the shear stress at radius r , ΔP is the pressure drop, L is the length of the die land, and is the parameter depending on the geometry and the power law index.

It can be seen that the combination of BN and Teflon[®] processing aid improves the processability of polyethylenes more than either of its two constituents can do when they are used separately. For example, it can be seen from Fig. 3 that virgin Exact[®] 3128 exhibits fracture at a critical apparent shear rate of about 50 s⁻¹ at the temperature of 204°C. This critical rate increases to about 1300 s⁻¹ with the addition of 0.05% Teflon[®], to about 1800 s⁻¹ with the addition of 0.05% BN, while it becomes about 2,400 s⁻¹ by combining 0.05% BN and 0.05% Teflon[®].

Similarly, it can be seen from Fig. 4 that the addition of 0.05% BN increases the critical apparent shear rate for the onset of melt fracture from about 110 s⁻¹ for the virgin Exceed[®] 114 polymer to about 900 s⁻¹. In the presence of 0.1% BN and 0.05% Teflon[®], this critical rate becomes about 2,000 s⁻¹. Therefore, the best performance in terms of melt fracture is obtained in the presence of both BN (eliminates gross fracture) and Teflon[®] (decreases the pressure drop and eliminates sharkskin melt fracture).

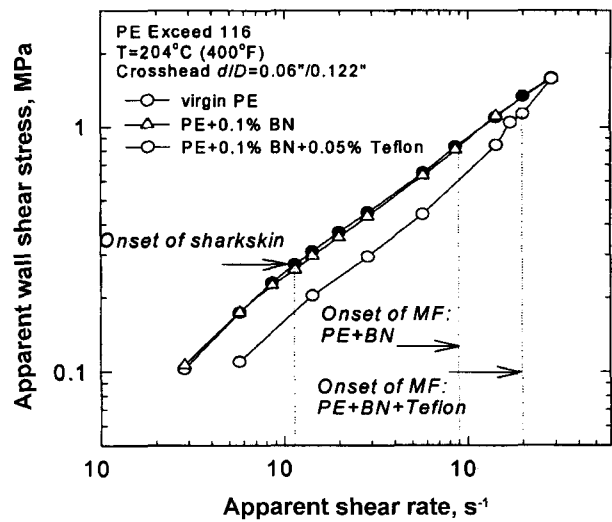


Fig. 4. The effect of combining 0.1% of BN with 0.05% Teflon[®] on the melt fracture performance of PE Exceed[®].

This combination forms a superior processing aid. The elimination and mechanism of gross melt fracture has been demonstrated and discussed thoroughly by Kazatchkov *et al.* (2000).

3.3. Effect of BN and stearates in polyolefin processing

It has been shown previously that stearates are lubricants that may be used to eliminate surface melt fracture phenomena in the continuous extrusion of polyolefins (Achilleos, 2002). In this paper, the stearates (calcium and zinc) are used in combination with boron nitride. Fig. 5 shows the processability of a metallocene linear low-density polyethylene (Exact[®]3128) in the presence of various pro-

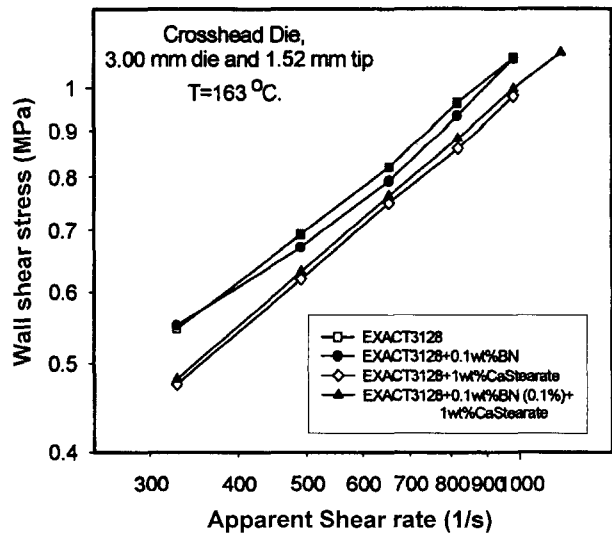


Fig. 5. The effect of combining 0.1% of BN with 1% of calcium stearate on the melt fracture performance of PE Exact[®] 3128.

cessing aids.

Four flow curves appear in Fig. 5; namely, the flow curve of virgin Exact[®]3128, the flow curve of Exact[®]3128 with the addition of 0.1% boron nitride, the flow curve of Exact[®]3128 with the addition of 1% calcium stearate and the flow curve of Exact[®]3128 with the addition of 0.1 wt.% boron nitride and 1% wt.% of calcium stearate. The experiments were run on the crosshead die attached to the capillary rheometer. The onset of surface deterioration of the virgin Exact[®]3128 is 40 s⁻¹. With the addition of 0.1 wt.% of boron nitride alone the onset of surface deterioration is delayed up to a shear rate of 490 s⁻¹. The onset of surface deterioration of Exact[®]3128 with the addition of 1 wt.% of calcium stearate alone is about 327 s⁻¹. Surprisingly, this critical shear rate is increased to 1,145 s⁻¹ with the addition of the combination (0.1 wt.% boron nitride and 1 wt.% calcium stearate). In addition, the use of calcium stearate in the combination with boron nitride decreases the extrusion pressure and therefore the extrusion becomes practically easier. The results are also summarized in Table 1 below.

From these results, it can be concluded that the combination of calcium stearate and boron nitride is a better processing aid from either of its constituents when used individually (Hatzikiriakos and Rathod, 2003). Similar results were obtained with the use of a zinc stearate (Hatzikiriakos and Rathod, 2003).

3.4. Effect of BN and PE in fluoropolymer processing

It is known that a small amount of polyethylene added to a fluoropolymer i.e. FEP resins, may eliminate *surface melt fracture* phenomena up to the point where *gross melt fracture* is obtained (Rozenbaum, 1995). In addition, it is known that BN is an effective processing aid for the continuous extrusion of fluoropolymers (Buckmaster, 1996). In this paper, these two useful processing aids are combined to show their effectiveness in the processing of fluoropolymers. Fig. 6 shows the separate effects of polyethylene and the combination of polyethylene and boron nitride on the flow curve of FEP[®]4100 at 350°C. Extrusion was done using the capillary rheometer with a

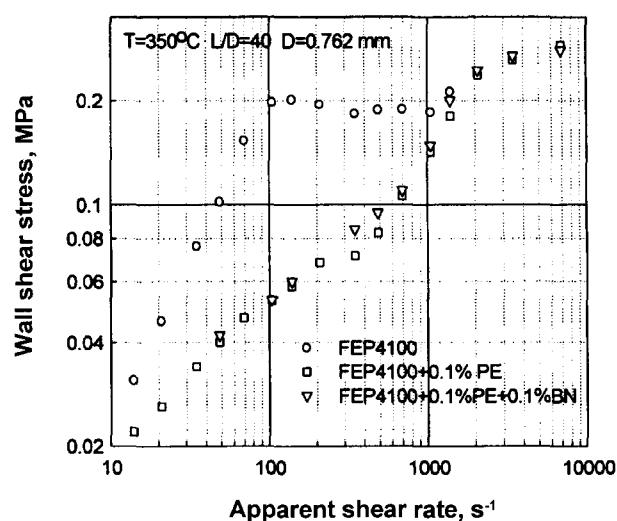


Fig. 6. The Effect of the combination of PE+boron nitride on the flow curve of FEP[®]4100 obtained by means of a capillary die.

circular (capillary die) having a length to diameter ratio of 40 and diameter of 0.762 mm.

In particular, Fig. 6 depicts the apparent flow curves for virgin FEP[®]4100, that of a blend of FEP[®]4100 with 0.1% by weight of a finely dispersed linear low-density polyethylene (GRSN/7047), and that of a blend of FEP[®]4100 with 0.1 wt.% by weight of a finely dispersed linear low-density polyethylene (GRSN/7047) and 0.1 wt.% BN. It can be seen that the presence of the polyethylene dramatically decreases the shear stress practically over the whole range of apparent shear rates examined. The onset of surface deterioration of pure FEP[®]4100 is 80 s⁻¹. This becomes about 800 s⁻¹ with the use of 0.1% wt. polyethylene leaving some “mattiness” on the surface. Surprisingly, the use of the combination of polyethylene (PE) and boron nitride (BN) produces smooth and glossy surfaces up to a rate of 1,300 s⁻¹. Table 2 below summarizes the results. From these results, it can be concluded that the combination of PE and boron nitride is a useful processing aid increasing the extrusion rate as well as reducing the energy needed for extrusion.

Fig. 7 shows the behavior of a fluoropolymer (FEP[®]100) alone, with boron nitride and with the combination of polyethylene (PE) and boron nitride (BN) in extrusion. Three

Table 1. The effect of boron nitride and calcium stearate on the melt fracture behaviour of Exact[®]3128 at 163°C

Polymer/Blend	Critical shear rate for the onset of surface deterioration
Exact [®] 3128	40 s ⁻¹
Exact [®] 3128+1wt% Calcium Stearate	327 s ⁻¹
Exact [®] 3128+0.1wt% BN	490 s ⁻¹
Exact [®] 3128+1wt% Calcium stearate+0.1wt%BN	1,145 s ⁻¹

Table 2. The effect of boron nitride and polyethylene on the melt fracture behaviour of FEP[®]4100

Polymer/Blend	Critical shear rate for the onset of surface deterioration
FEP [®] 4100	80 s ⁻¹
FEP [®] 4100+0.1 wt% PE	800 s ⁻¹
FEP [®] 4100+0.1 wt%PE+0.1 wt%BN	1,300 s ⁻¹

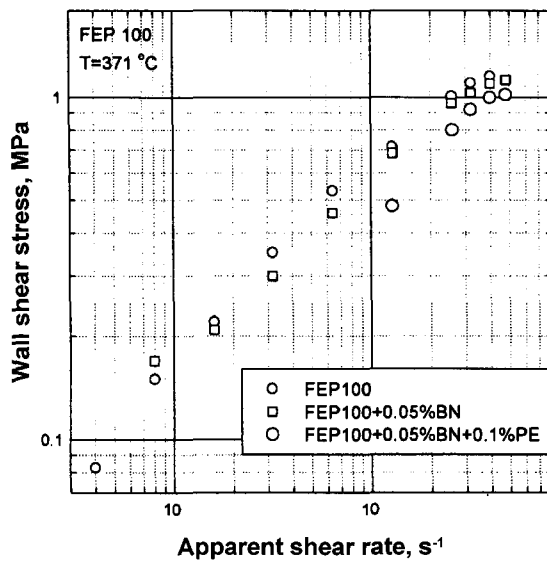


Fig. 7. The Effect of the combination of PE+boron nitride on the flow curve of FEP[®]100 obtained by means of the cross-head die.

Table 3. The effect of boron nitride and polyethylene on the melt fracture behaviour of FEP[®]100

Polymer/Blend	Critical shear rate for the onset of surface deterioration
FEP [®] 100	40 s ⁻¹
FEP [®] 100+0.05 wt% BN	3,200 s ⁻¹
FEP [®] 100+0.1 wt%PE+0.05 wt%BN	>4,000 s ⁻¹

flow curves are plotted (wall shear stress versus shear rate), namely, the flow curve of virgin FEP[®]100, the flow curve of FEP[®]100 with the addition of 0.05% boron nitride and the flow curve of FEP[®]100 with the addition of 0.05 wt.% boron nitride and 0.1 wt.% of polyethylene (GRSN/7047).

The tests were run using the crosshead die attached to a rheometer. The onset of surface deterioration of the virgin FEP[®]100 is 40s⁻¹. With the addition of 0.05wt% of boron nitride the onset of surface deterioration is delayed up to a shear rate of 3,200 s⁻¹. Surprisingly, this critical shear rate is increased to 4,000 s⁻¹ with the addition of the combination (0.1wt% PE and 0.05wt% BN). This is the maximum shear rate used and therefore the actual value could be higher. The results are summarized in Table 3 below. From these results (Tables 3) it can be concluded that the combination of polyethylene (PE) and boron nitride is a better processing aid compared to either of its constituents when are used separately (Hatzikiriakos and Rathod).

4. Conclusions

The effect of combining boron nitride with a fluoroelastomer as a possible processing aid in the continuous extrusion of metallocene LLDPEs, was examined. It was found

that such combinations result enhanced processing aid since they can eliminate melt fracture phenomena at shear rates not accessible when either of the constituents of additive is used alone. Similar results were found for the combination of BN with stearates in the extrusion of metallocene polyethylenes. For the continuous extrusion of fluoropolymers, the combination of BN with a small amount of Polyethylene was found to be a superior processing aid compared to either of its constituents where they are used separately.

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