

Igor B. Kazatchkov
Franky Yip
Savvas G. Hatzikiriakos

The effect of boron nitride on the rheology and processing of polyolefins

Received: 18 January 2000
Accepted: 15 June 2000

I. B. Kazatchkov · F. Yip
S. G. Hatzikiriakos (✉)
Department of Chemical Engineering
The University of British Columbia
Vancouver, BC, Canada
e-mail: hatzikir@unixg.ubc.ca

Abstract The influence of a new processing additive (fine particles of boron nitride) on the rheology and processability of polyolefins is studied. The equipment used includes an Instron capillary rheometer equipped with capillary and special annular dies (Nokia Maillefer wire coating crosshead) and two rheometers, namely a parallel-plate and a sliding-plate rheometer. Several types of boron nitride powders, varying in average particle size and distribution and in morphology are tested at various concentration levels. The additive with the smallest average particle size and free of agglomeration was found to have the greatest influence on the processability

(melt fracture performance) of the polyolefins tested. Specifically, it was found that boron nitride not only eliminates surface melt fracture but also postpones the critical shear rate for the onset of gross melt fracture to significantly higher values, depending on the additive concentration, surface energy, and morphology. A flow visualization technique was used to visualize the polymer flow at the entrance of a transparent capillary die in order to determine the mechanism by which boron nitride eliminates gross melt fracture.

Key words Boron nitride · Processing aids · Polyolefins · Gross melt fracture · Crosshead die

Introduction

In many commercially important polymer-processing operations, including film casting, film blowing, continuous blow molding extrusion, and various coating flows, flow instabilities occur at throughput rates above a critical value (Petrie and Denn 1976; Ramamurthy 1986; Denn; 1990, Larson 1992). As a result of these instabilities, the polymer melt emerging from the slit or capillary die often exhibits surface distortions. These flow instabilities collectively known as *melt fracture* can manifest themselves in the form of either small amplitude periodic distortions on the surface of extrudates (surface or sharkskin melt fracture) (Ramamurthy 1986; Kalika and Denn 1987; Wang et al. 1996) or severe irregular distortions at higher throughput rates (gross

melt fracture) (Tordella 1963, 1969; Piau et al. 1990; Vinogradov and Malkin 1980).

A severe consequence of the melt fracture phenomena is a posed limitation in the rate of production of polymer processing operations at which they occur. To increase the process output, one must eliminate melt fracture or at least postpone it to higher rates. The most common approach to achieve this objective is through the use of *processing aids* (Rudin et al. 1985; Athey et al. 1986; Hatzikiriakos et al. 1995; Rosenbaum et al. 1995; Wang and Drda 1997). These are usually fluoroelastomers that can be added to the resin at concentrations of a few hundred ppm, e.g., at the time of processing or introduced as a master-batch. These processing aids reduce the pressure required to extrude the resin at a particular flow rate and eliminate or postpone melt

fracture to higher extrusion rates. It is noted that these additives can eliminate only sharkskin and the so-called stick-slip (oscillating or cyclic) melt fracture. To our knowledge, they do not appear to have an effect on the extrudate appearance in the gross melt fracture region.

It has recently been reported that compositions containing fine boron nitride (BN) particles can successfully be used as processing aids to eliminate not only sharkskin melt fracture but also to postpone substantially gross melt fracture to significantly higher shear rates in the extrusion of polyolefins and fluoropolymers (Rosenbaum 1999; Rosenbaum et al. 1998, 2000). Boron nitride (BN) is a solid lubricant whose structure resembles that of graphite. Figure 1 depicts a typical BN structure. In polymer processing it is used as a foam-nucleating agent in most commercial applications for fluoropolymer foams such as heat insulation, foamed tubing, etc. In the presence of a blowing agent added to the molten resin during extrusion it nucleates the formation of voids. In this study, BN particles are used without a blowing agent so that the extruded polymer is unfoamed.

The objective of this work is to understand the mechanism by which BN eliminates gross melt fracture phenomena. For this, we first study the effect of boron nitride (BN) type (morphology, average particle size, and surface energy) and concentration on the rheology and processability of a metallocene linear low-density polyethylene (m-LLDPE) and a polypropylene resin. Consequently, the entry flow from the capillary rheometer reservoir into the capillary die is visualized in the presence or absence of BN in an attempt to identify the differences in the flow structure when gross melt fracture is eliminated. The paper is organized as follows. In the next section, the materials and the experimental methods

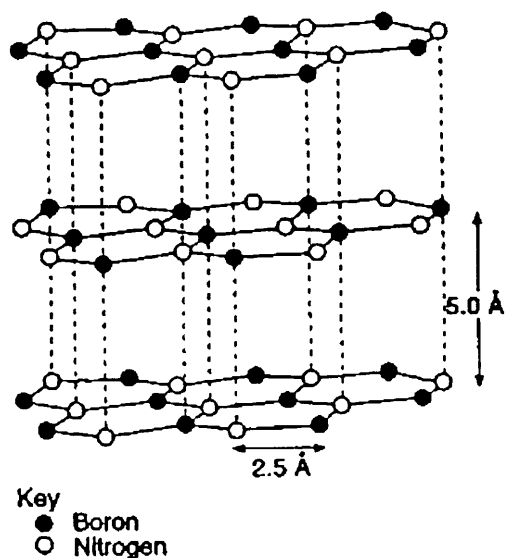


Fig. 1 Typical boron nitride structure

used are presented. Particular attention is drawn to the morphological differences among the various BN powders and the methods used to prepare (compound) the blends for this study. Consequently, the effect of BN on the rheology and processability of the m-LLDPE is presented. The critical shear rates for the onset of gross melt fracture as a function of BN type and concentration are presented and discussed in detail. The visualization technique is next presented, and the experimental results from this part of the study are discussed in terms of a possible mechanism of gross melt fracture elimination. Finally, the influence of BN on the flow structure at the entry region of a transparent capillary die is discussed and conclusions are drawn to summarize the work.

Experimental

Materials

Eight types of boron nitride (BN) are used in order to study their effect on the gross melt fracture behavior of a m-LLDPE. These include BN type CTF5 with an average particle size of about 10 μm , CTL40, which is essentially an agglomerated version of CTF5 with particle size of more than 40 μm , and CTUF, which contains a fair amount of B_2O_3 compared to CTF5. In addition, BN427 to BN431 were also evaluated. BN427 is similar to CTF5 in particle size but possesses platelet-like particle morphology. The average particle size and the state of particle agglomeration for each powder were determined by Scanning Electron Microscopy (SEM). These are summarized in Table 1.

Figure 2 shows SEM pictures of BN431 and BN429 to clarify the meaning of agglomeration. It can clearly be seen that BN431 is a powder having a uniform particle size (about 5 μm), while BN429 contains agglomerated particles (typical size 40 μm), some of which exceed 200 μm in size. As will be shown below, these agglomerated particles have a significant effect on the processability of the resins in spite of the fact that the rest of the powder consists of fine particles.

Two resins are mainly used in this work in order to evaluate the effect of the various BN powders on their processability. These are one metallocene linear low-density polyethylene (Exact 3128 of Exxon) and one polypropylene resin. Additional experiments for a second m-LLDPE (Exceed 116 from Exxon) and a DuPont Teflon fluoro-copolymer of tetrafluoroethylene/hexafluoropropylene (FEP 4100) resulted similar conclusions and therefore, experimental

Table 1 Morphological characteristics of the various boron nitride (BN) powders studied

| BN Types | Particle size from SEM approximately (μm) | Agglomerated | Agglomerated size (μm) |
|----------|--|--------------|-------------------------------------|
| CTF5 | 10 | No | |
| CTUF | 10 | No | |
| CTL40 | 40 | Yes | > 40 |
| 427 | 4 | Yes | > 180 |
| 428 | 1.5 | No | |
| 429 | 3 | Yes | > 200 |
| 430 | 20 | No | |
| 431 | 5 | No | |

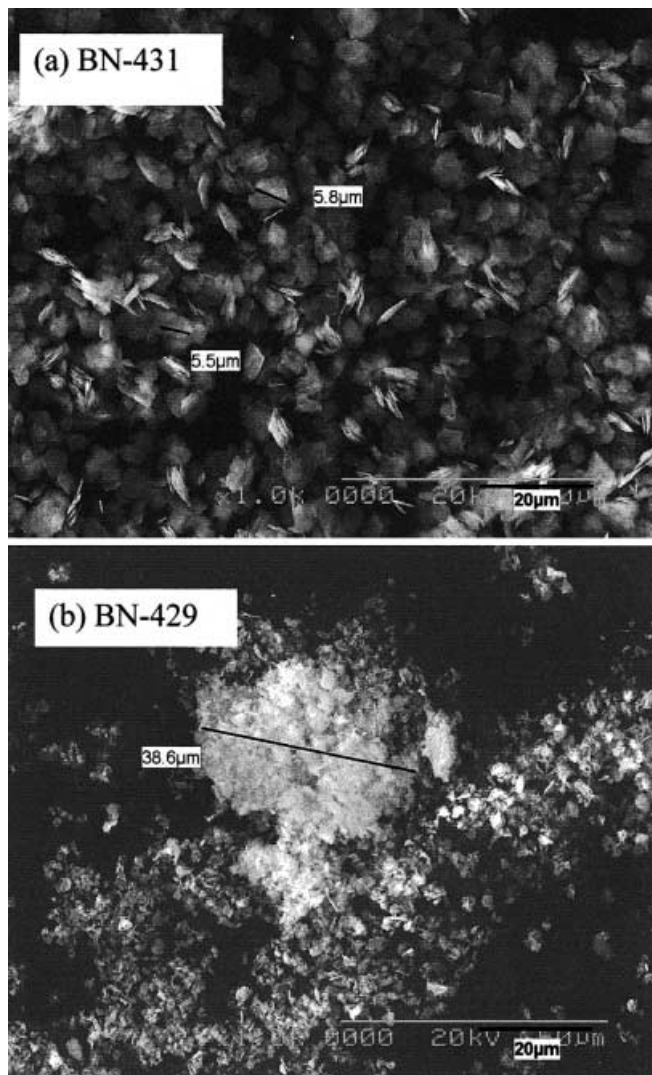


Fig. 2 a BN431 is a powder of uniform size. b BN-429 (b) contains agglomerated particles

results for these two polymers are not presented here (for more details see Rosenbaum et al. 1998; Yip 1999).

Preparation of blends

Three techniques were used to introduce boron nitride (BN) into the resins. According to the first technique, the BN particles in a finely

divided state (see their typical morphology in Fig. 2) were thoroughly dry-mixed with polymer pellets at appropriate concentrations.

In the second technique, the pure resin pellets were first ground into a fine powder form by using a grinder. Then, a master-batch of 10 wt % BN (roughly 5 vol % at room temperature since specific gravity of BN is in the range of 1.8–2.1) with ground PE was prepared by using a preparation mixer. A desired final concentration of materials was obtained by mixing the pure ground PE with the master-batch by means of a 3/4" single screw extruder. The final material was chopped and collected in pelletized form by using a 2" pelletizer.

According to the third technique, a master-batch of 10 wt % BN with ground PE was also prepared. However, this time a twin screw extruder was used to blend the BN with metallocene catalyzed polyethylene (Exact 3128) instead of the single screw extruder used in the second method. Using the second and third methods of mixing, BN was uniformly dispersed into the polymer as was checked by means of SEM. The various blends prepared and studied in this work are summarized in Table 2.

Experimental measurements

Capillary rheometer experiments were used to determine the shear rate at which smooth extrudates can be produced in the absence or presence of BN. The rheometer is a standard Instron piston-driven constant-speed capillary unit. Apart from the conventional capillary dies, a crosshead die was also used. This is a Nokia Maillefer 4/6 that included dies and tips of various diameters ("tip" is the wire guide) with equal entry cone angles of 60° and the die land length of 7.62 mm. Figure 3 is a schematic of the crosshead die. The molten polymer enters the die via port 11 and is forced around the wire guide 16 towards the die orifice 8. 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 8 to draw down to a thinner cross-section, forming a thin polymer coating 26 on the wire. This is a melt draw-down extrusion process. However, in the present study the pressure extrusion makes no use of wire and therefore the die of Fig. 4 may be viewed as just an annular extrusion die.

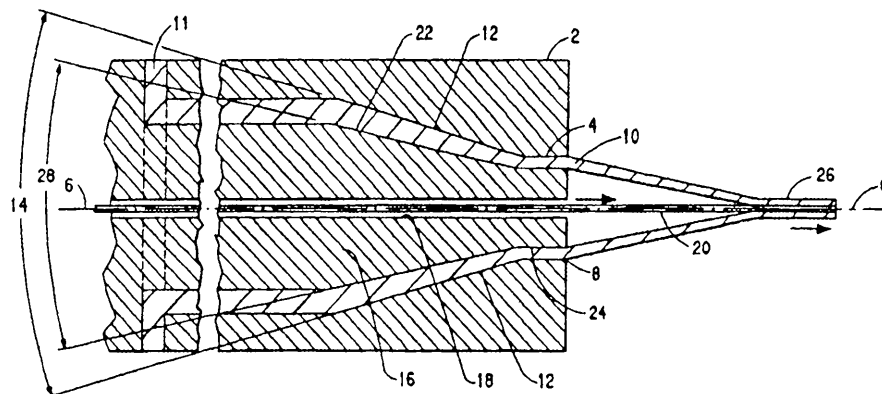
To assess the effect of BN on the rheology of the polymers, linear viscoelastic measurements were performed. The parallel-plate rheometer for these linear viscoelastic experiments was Rheometrics System IV with plates of diameter equal to 25 mm. Frequency sweep experiments were performed in a frequency range from 0.02 rad/s to 500 rad/s. The working temperature was 163–204 °C (325 °F) for the metallocene polyethylene.

A commercial Interlaken sliding plate rheometer incorporating a flush mounted shear stress transducer (Giacomin et al. 1989) was also used to study the effect of a BN powder on the rheology and slip behavior of the polymer under study. In the latter case (study of slip), experiments were performed using three different gap spacings between the plates in order to check for gap dependence of the flow curve. Steady shear experiments using shear rates from 1 s^{-1} to 250 s^{-1} and strains from 10 units to 100 units were performed in order to ascertain that steady-state is obtained (Kazatchkov 1998).

Table 2 Summary of the various blends prepared together with the blending methods used

| Blends at 0.02, 0.05, 0.1, and 0.5 wt % of BN | Dry-mixed | 10% master-batch using a single screw extruder | 10% master-batch using a twin screw extruder |
|---|-----------|--|--|
| Exact 3128 + CTUF | Yes | Yes | |
| Exact 3128 + CTL40 | Yes | Yes | |
| Exact 3128 + CTF5 | Yes | Yes | |
| Exact 3128 + 427 to 431 | | | Yes |

Fig. 3 Crosshead die for wire coating



An experimental setup was designed during the course of this study to visualize the flow patterns developed at the entrance region of the capillary, i.e., from a large reservoir to a fine capillary die through an abrupt contraction. Figure 5 depicts a schematic diagram of the flow visualization experiment. It consists of the following parts. First, mounted on an optical bench is a Helium-Neon laser having output power of 10 mW, with a spatial filter and

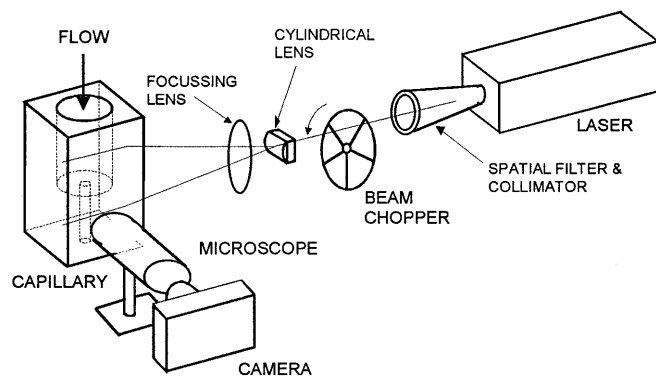


Fig. 4 Schematic diagram of the flow visualization set-up

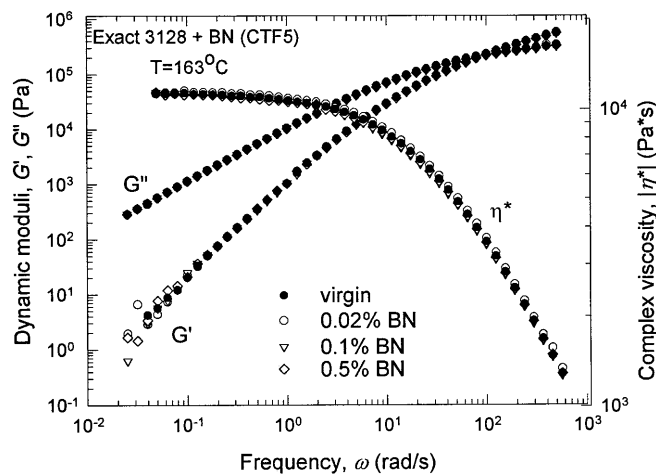


Fig. 5 Linear viscoelastic data of m-LLDPE Exact 3128 at 163 °C with and without BN (CTF5)

collimator with a focal length of 200 mm; a laser beam chopper, a DC motor with a plastic disc having 5 segments; a cylindrical lens, having a focal length of 150 mm; and a spherical focusing lens having a focal length of 600 mm. Second, mounted on the capillary rheometer is a quartz capillary die of initial capillary diameter of 20 mm that includes an abrupt contraction to a final diameter of 1.5 mm diameter. This capillary die is encased in a steel holder, surrounded by four radiation heaters to maintain the temperature uniform and equal to the temperature of the capillary barrel. Finally, a microscope (Nikon SMZ-2T) and a 35 mm photographic camera is used to take long time exposure photos of the various flow structures developed at various apparent shear rates and in the presence/absence of BN. Such an experimental set up has been used in the past by Binnington et al. (1983) for measuring velocity profiles in slow polymer flows and Tremblay (1994) for visualizing the flow of low-density polyethylene/polystyrene blends through a planar step contraction.

Rheological measurements

Linear viscoelastic measurements

To study possible effects of boron nitride (BN) on polymer rheology, small amplitude oscillatory shear experiments were carried out for all resins with and without BN using a Rheometrics System IV parallel-plate rheometer. Frequency sweep experiments for the two m-LLDPEs were carried out at the temperature range of 163 °C to 204 °C, while those for the FEP4100 at 300–340 °C. Figure 5 depicts the dynamic mechanical data for the m-LLDPE (Exact 3128) with three different levels of BN (CTF5) at 163 °C. No significant difference was found in the linear viscoelastic behavior of the virgin and filled resins. Similar results were obtained with all the other types of BN except the powder BN431 (see Table 1).

In fact, the addition of BN431 into the m-LLDPE had a surprisingly significant effect. Figure 6 depicts the dynamic moduli of m-LLDPE (Exact 3128) with three different concentrations of BN431 at 163 °C. It seems that increase of the BN431 concentration decreases the dynamic moduli, G' and G'' . This can be either due to a change in the bulk rheological properties of the resin or due to the polymer slippage at the wall. It is noted that

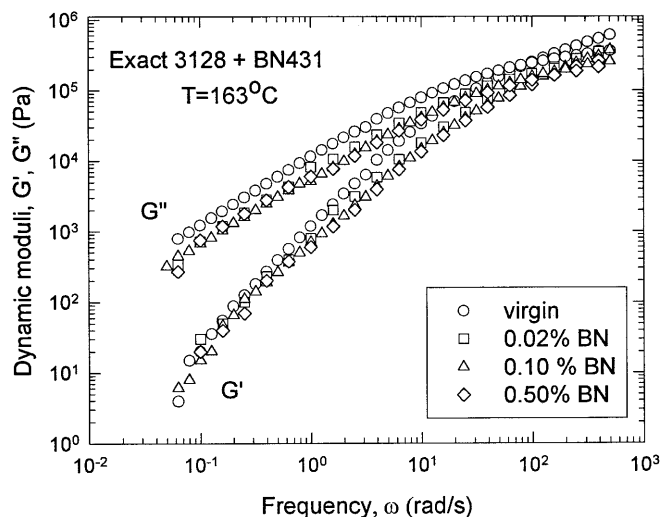


Fig. 6 Linear viscoelastic data (G' , G'') of m-LLDPE Exact 3128 at 163 °C with and without BN (type BN431)

slip may cause an overall decrease of the wall shear stress (Hatzikiriakos and Dealy 1991). To answer this question steady shear experiments were carried out in a sliding plate rheometer. These are discussed in the next section.

Slip velocity measurements

Steady shear experiments were carried out in a sliding plate rheometer to determine whether or not the effect of BN431 depicted in Fig. 6 is due to a change in the bulk rheology of the resin or due to the occurrence of wall slip. To answer this, the flow curve of the resin with the addition of BN431 was determined at three different gap spacings (distance between the two parallel plates) of the rheometer. Figure 7 plots the flow curve of the m-LLDPE (Exact 3128) with addition of 0.1% of BN431 for three gap spacings, namely 0.1 mm, 0.2 mm, and 0.46 mm. It can clearly be seen that the flow curve is gap dependent. Specifically, it can be seen that increasing the gap spacing shifts the flow curve to higher shear stress values. This is consistent with the assumption that the polymer slips at the solid wall (Hatzikiriakos and Dealy 1991). From steady shear experiments using smaller amounts of BN431, the degree of gap dependence becomes smaller. In fact in the absence of BN the flow curve becomes independent of the gap spacing. These findings are consistent with the assumption of slip occurrence in the presence of BN431, and with the assumption that a higher amount of BN431 increases slip. BN431 was found to be the only powder that causes slip. This is due to its platelet-like morphology. Referring back to Fig. 6, the linear viscoelastic moduli of BN431 filled resins corrected for the effect of slip are similar to those of the virgin resin.

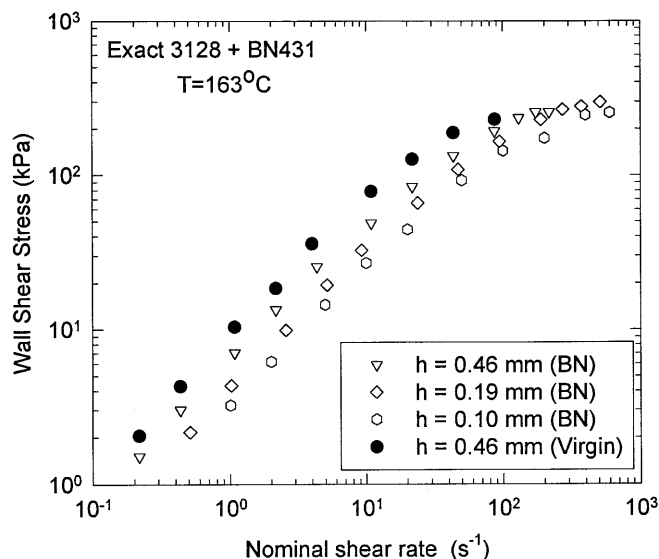


Fig. 7 The flow curve of virgin m-LLDPE (Exact 3128) with the addition of 0.1% BN431 determined by the sliding plate rheometer using various gap spacing. The gap dependence of the flow curve implies the presence of slip at the wall

The effect of boron nitride on melt fracture in capillary extrusion

Figure 8 depicts the flow curves of the virgin and filled m-LLDPE (Exact 3128) obtained using the capillary rheometer with a capillary die having a diameter,

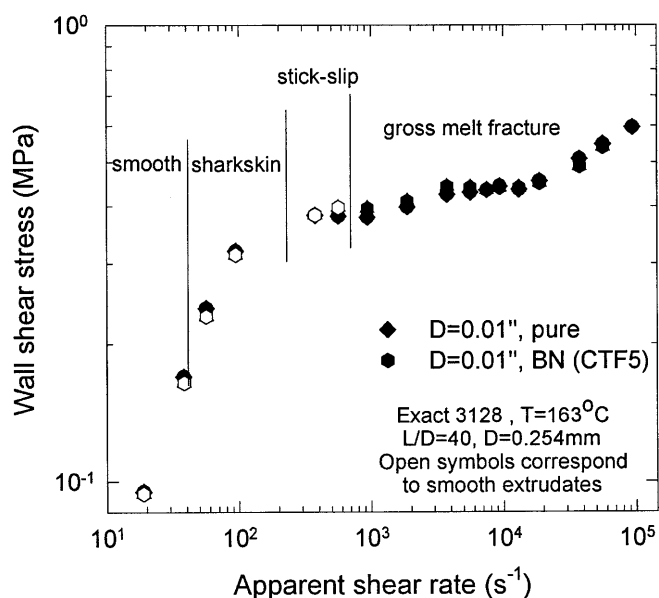


Fig. 8 The flow curve of m-LLDPE (Exact 3128) by using the capillary rheometer with a capillary die having $D=0.254$ mm and $L/D=40$ at 163 °C

$D = 0.542$ mm and a length-to-diameter ratio, $L/D = 40$ at $T = 163$ °C. The Bagley correction (ends pressure) was determined by using an orifice die of equal diameter. This was subsequently applied to the raw data in order to determine the values of the true wall shear stress. In the case of virgin resin, sharkskin appears at about 35 s^{-1} followed by stick-slip at around 250 s^{-1} and gross melt fracture at higher shear rates. The addition of 0.1% BN (CTF5) to the resin does not seem to change its shear rheology noticeably, since the two flow curves almost coincide. However, it has a significant effect on the extrudate appearance, eliminating extrudate distortions in the range of shear rates corresponding to transition from sharkskin to stick-slip melt fracture. As can be seen, the addition of BN improves the processability of the resin by eliminating sharkskin and oscillating melt fracture, but does nothing to the gross melt fracture performance. This effect is similar to that of fluoropolymers and Teflon solutions (Hatzikiriakos et al. 1995) as processing aids with the addition that in the latter case a significant reduction in the shear stress is obtained.

The effect of boron nitride on melt fracture in crosshead die extrusion

Figure 9 shows the flow curve of the virgin Exact 3128 obtained using the capillary rheometer with the Maillefer crosshead with a 1.524 mm tip and 3 mm die at $T = 163$ °C. One can see that sharkskin appears at about 40 s^{-1} (agrees with results from capillary experiments) followed by gross melt fracture at higher shear rates.

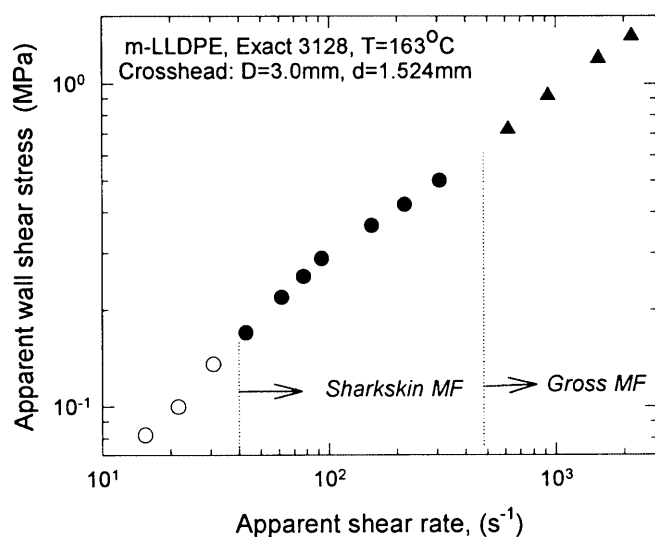


Fig. 9 The effect of the BN (CTF5) concentration on the processability of m-LLDPE (Exact 3128) in a capillary rheometer with Nokia Maillefer crosshead having 3.00 mm die and 1.52 mm tip at 163 °C

The apparent shear rate was calculated by using the formula applied for slit dies having a large aspect ratio (Bird et al. 1987):

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

where Q is the volumetric flow rate, and d and D are the tip and die diameters, respectively. 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):

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

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

Experiments were initially carried out for the BN-filled resins prepared with the first technique, that is dry-mixing. Table 3 summarizes the results of three sets of experiments at various temperatures obtained for BN (type CTF5). The critical shear rate for the onset of extrudate distortion is listed as a function of BN concentration and temperature. The maximum effect on the processability of the resin at each temperature is obtained at the highest concentration of 0.25 wt %. For example, it was found that the maximum shear rate to yield a smooth extrudate is 124 s^{-1} at 204 °C. Still, this critical rate is far below the maximal shear rates yielding a smooth extrudate reported previously (Rosenbaum 1999; Rosenbaum et al. 1998, 2000; Yip et al. 1999). Similar results were obtained with the other two types of BN added to the resin using this first technique. Therefore, it can be concluded that the addition of BN in a dry-mixed form has little effect on the melt fracture

Table 3 Effect of the BN (CTF5) concentration and temperature on the maximal shear rate yielding a smooth extrudate in extrusion of m-LLDPE Exact 3128 (Nokia Maillefer crosshead attached to the rheometer, $D = 3.0$ mm, $d = 1.52$ mm). Case of dry mixing

| T, °C | BN concentration, mass % | Maximal shear rate, s^{-1} |
|-------|--------------------------|------------------------------|
| 163 | 0 | 42 |
| | 0.05 | 42 |
| | 0.1 | 77 |
| | 0.25 | 93 |
| 180 | 0 | 62 |
| | 0.05 | 93 |
| | 0.1 | 93 |
| | 0.25 | 93 |
| 204 | 0 | 93 |
| | 0.05 | 93 |
| | 0.1 | 113 |
| | 0.25 | 124 |

behavior of resins regardless of the BN type and concentration. This is explained by the low degree of dispersion of BN particles into the polymer that can be achieved by dry mixing.

On the other hand, the addition of BN in the pre-extruded form (second technique) had a much greater influence on the extrudate appearance during extrusion tests. Figure 10 compares the flow curves obtained for the virgin and filled Exact 3128 resin with BN (CTF5) at concentrations of 0.02%, 0.1%, and 0.5% at 163 °C. The maximal shear rate at which the extrudates were smooth exceeded 926 s⁻¹. This is well above the critical rate for the onset of gross melt fracture of the virgin resin, which is about 500 s⁻¹ (see Fig. 9).

Experiments have shown that the maximal shear rate yielding a smooth extrudate is also sensitive to BN concentration. The optimal performance was obtained at low BN contents, particularly at concentrations between 0.02% and 0.1%. Further increase in the additive concentration resulted in decrease in the maximal shear rate for the onset of flow instabilities. The maximal shear rate of 926 s⁻¹ was obtained for BN concentrations of 0.02% and 0.1%, while the concentration of 0.5% resulted in the maximum shear rate of 617 s⁻¹. Therefore, optimum performance is obtained at a critical concentration. This depends on the type of the resin and additive. Figure 11 compares extrudate samples obtained at different BN concentrations at the shear rate of 617 s⁻¹. It can be seen that the extrudate produced with the virgin m-LLDPE (Exact 3128) (Fig. 11a) exhibits severe gross melt fracture, while 0.02% and 0.1% (200 ppm and 1000 ppm correspondingly) of BN eliminate completely any distortions (Fig. 11b, c). On the other hand, 0.5% (5000 ppm) of BN does not seem to eliminate gross melt fracture, although it appears to alter the extrudate appearance to a certain degree (Fig. 11d).

Fig. 11a–d Pictures of extrudate samples to illustrate the effect of BN (CTF5) on the extrusion of m-LLDPE Exact 3128 obtained at 617 s⁻¹ and 163 °C: **a** pure resin; **b** 0.02% BN; **c** 0.1% BN; **d** 0.5% of BN (CTF5). It can be seen that at this shear rate gross melt fracture occurs, which can be eliminated with the addition of 0.02% and 0.1% of BN (CTF5), but not with the addition of the excessive amount of 0.5%

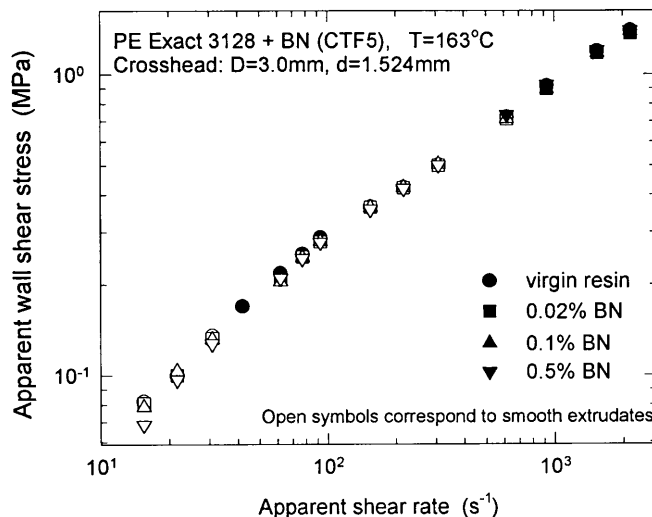
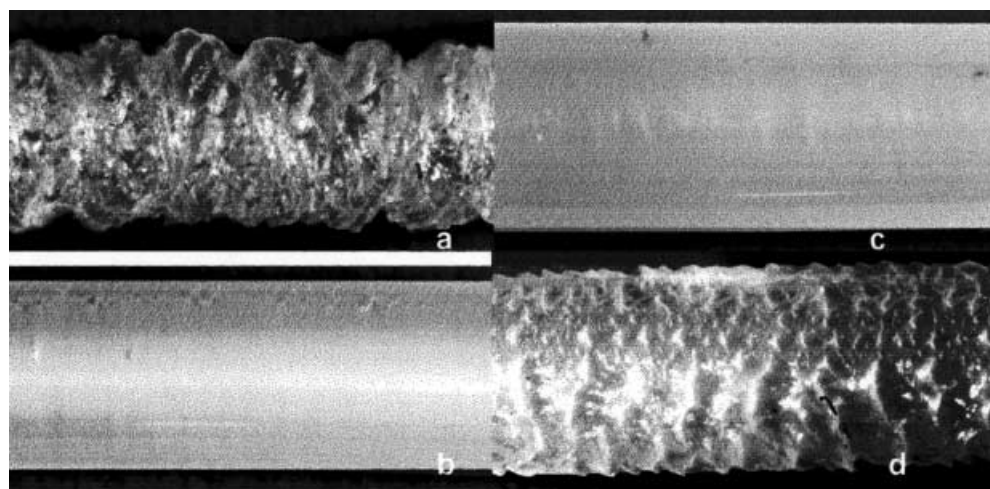


Fig. 10 The effect of BN (CTF5) concentration on the processability of m-LLDPE (Exact 3128) in a capillary rheometer with Nokia Maillefer crosshead having 3.00 mm die and 1.52 mm tip at 163 °C

The type of BN (particle size and surface chemistry) also seems to play an important role in the phenomenon. Table 4 summarizes the melt fracture results for blends produced using the second technique. These results show the effect of BN type on the extrudate appearance at different BN concentrations. CTF5 exhibits the best performance in terms of eliminating melt fracture at higher shear rates. The powder CTL40, an agglomerated version of CTF5, performed poorly in eliminating melt fracture. The maximal shear rate yielding a smooth extrudate for this type of BN was only 93 s⁻¹ at 0.1% of BN compared to 926 s⁻¹ obtained for CTF5. The third type of BN, CTUF, also performed poorly in eliminating gross melt fracture. The maximal shear rate that yielded a smooth extrudate was 155 s⁻¹ regardless of the

Table 4 Effect of the BN type (CTUF, CTL40, and CTF5) and concentration on the maximal shear rate yielding a smooth extrudate in extrusion of Exact 3128 (Nokia Maillefer crosshead attached to the rheometer, $D = 3.0$ mm, $d = 1.52$ mm) at 163 °C. The resin and BN are initially pre-extruded by using the second technique described in a previous section in order to attain uniform dispersion into the polymer

| BN type | BN concentration, mass % | Max. shear rate, s^{-1} |
|---------|--------------------------|---------------------------|
| Pure PE | 0 | 42 |
| CTUF | 0.02 | 155 |
| | 0.1 | 155 |
| | 0.5 | 155 |
| CTL40 | 0.02 | 62 |
| | 0.1 | 93 |
| | 0.5 | 77 |
| | 0.5 | 77 |
| CTF5 | 0.02 | 926 |
| | 0.1 | 926 |
| | 0.5 | 617 |

BN concentration. This powder contains a fair amount of oxygen in the form of B_2O_3 that increases its surface energy. Therefore, for best BN performance in eliminating melt fracture, the requirements are:

1. Powder of uniform size about $5\text{--}10$ μm
2. Absence of agglomerated particles
3. Uniform BN dispersion into the resin
4. Absence of boron oxides, i.e., B_2O_3 , that might increase the surface energy of the powder

Additional crosshead die extrusion experiments were performed using additional BN powders. These were also listed in Table 1 as BN427–431. They were added to the resins by using a twin screw extruder (for details see the section on preparation of blends). Figure 12 depicts the apparent flow curve of virgin and filled (0.1% of BN427–431) m-LLDPE (Exact 3128) using the crosshead die at 163 °C. The flow curves for all the filled resins are about the same with the exception of that corresponding to BN431 that is significantly lower. This is due to the occurrence of wall slip as was discussed and demonstrated before using the parallel and sliding plate rheological measurements. Therefore, these results agree well with the rheological data presented in a previous section.

BN431 was not only found to have a significant effect on the rheological measurements of the Exact 3128 resin, but was also found to have a significant effect on its melt fracture behavior. Table 5 summarizes the melt fracture results for blends using BN427–431 at two different concentrations. First, it can be seen that melt fracture appears at about 42 s^{-1} for the virgin resin. BN427, BN428, BN429, and BN430 have a minor effect on the processability of the resin compared to the effect of BN431 that was found to be significant. That is, the addition of 0.1% of BN431 postpones the onset of gross

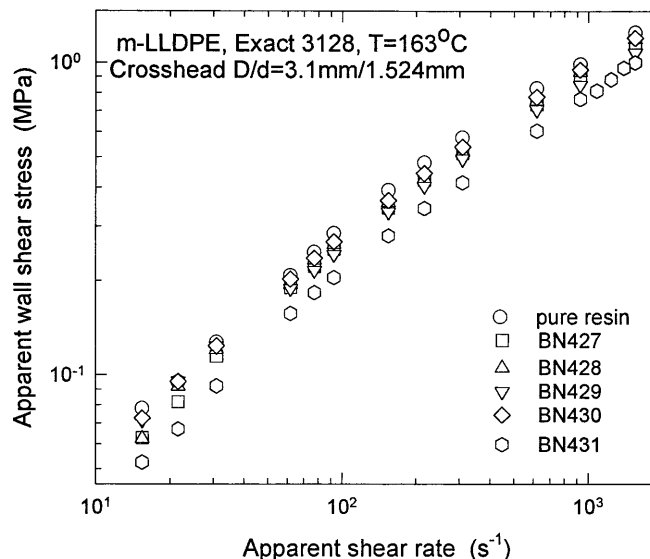


Fig. 12 The flow curve of virgin and filled m-LLDPE (Exact 3128) containing BN427 to BN431 (0.1 wt % in all cases) using the crosshead die at 163 °C

melt fracture up to the apparent shear rate of 1050 s^{-1} . Again, this value is well above the critical rate for the onset of gross melt fracture of the virgin resin, which is about 500 s^{-1} .

One may naturally pose the question as to why BN431 and CTF5 had the most significant effects on the processability of m-LLDPE (Exact 3128). It can be seen from Table 1 that the average particle sizes of these powders are small ($5\text{--}10$ μm) and that both are free of any agglomeration. BN429 also has a small average particle size but some of their particles are agglomerated, which hinders its even distribution into the resin. The

Table 5 Effect of the BN type (BN427–431) and concentration on the maximal shear rate yielding a smooth extrudate in extrusion of Exact 3128 (Nokia Maillefer crosshead attached to the rheometer, $D = 3.0$ mm, $d = 1.52$ mm) at 163 °C. The resin and BN are initially pre-extruded by using a twin screw extruder in order to attain uniform dispersion into the polymer

| BN type | BN concentration, mass % | Max. shear rate, s^{-1} |
|---------|--------------------------|---------------------------|
| Pure PE | 0 | 42 |
| BN427 | 0.02 | 155 |
| | 0.1 | 77 |
| BN428 | 0.02 | 124 |
| | 0.1 | 308 |
| BN429 | 0.02 | 155 |
| | 0.1 | 155 |
| BN430 | 0.02 | 124 |
| | 0.1 | 155 |
| BN431 | 0.02 | 865 |
| | 0.1 | 1080 |

surface chemistry may also play an important role here. As can be seen from Table 1, BN428 also has a small average particle size (about $1.5 \mu\text{m}$); however, it contains a fair amount of oxygen in the form of B_2O_3 . Therefore, it can again be concluded that BN powders possessing a small average particle size of uniform distribution, that are free of agglomerated particles and boron oxides and that are evenly distributed into the resin are expected to be superior processing aids.

Flow visualization on polypropylene

To study the mechanism by which the addition of BN eliminates gross melt fracture, visualization experiments were performed with the experimental set-up discussed in a previous section. Long-time exposure photographs of the capillary entry region were taken using a Nikon FM-2 35 mm photographic camera attached to a microscope (Nikon SMZ-2T). The effect of shear rate and additive concentration on the flow pattern development at the entry of the capillary were also investigated. It is noted that this technique can only detect the mechanism of gross melt fracture elimination since it is believed that the origin of such instability is in the entrance (Bagley and Schreiber 1961; Ballenger et al. 1971). On the other hand, the origin of sharkskin is in the exit of the die and other techniques should be used (Wang et al. 1996).

Figure 13 shows the entrance flow of a virgin polypropylene resin (no BN) at three different shear rates (32.4 s^{-1} , 324 s^{-1} and 650 s^{-1}) at 200°C . The key points can be summarized as follows. At low shear rates

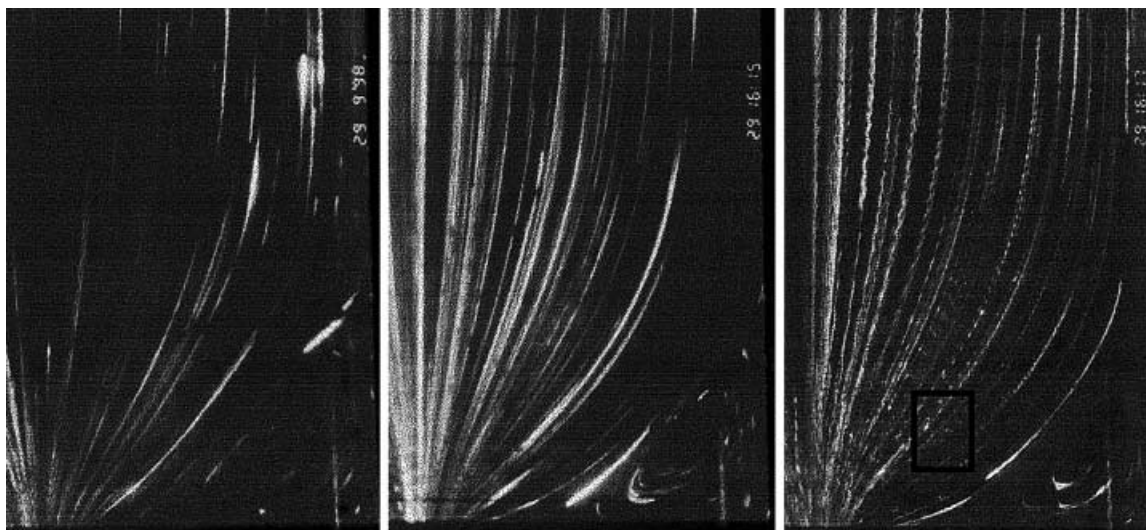
the flow enters the capillary at a higher entry angle, and the vortex in the corner of the reservoir is larger. As the shear rate increases, the streamlines bend more near the entrance to the capillary. Note that the vortex now becomes slightly smaller in size because it is suppressed towards the corner by the flow. At the highest shear rate (650 s^{-1}), gross melt fracture is observed, and the streamlines are no longer smooth. It is not obvious from the photo, but it is clearly visible in the viewfinder that these zigzag lines are caused by discontinuous motion of parts of the bulk material.

A schematic is drawn in Fig. 14 to explain this flow pattern development. The flow in the entry region appears to be broken into several layers, and each layer moves with its own velocity. At regular time intervals, different in each layer, the motion stops for a brief period. The closer the layer is towards the center of the stream, the larger and more frequent are the jumps and stops inside it.

An enlarged segment of Fig. 13 (marked by a rectangle) is shown in Fig. 15. It can be seen that the series of dots produced by illuminated (at a frequency of 85 Hz) tracer particles are interspaced by larger, brighter spots. These brighter spots are the result of the described intermittent stops of the flow described above. This flow pattern closely resembles the stick-slip phenomenon observed in the capillary flow of linear polymers (Ramamurthy 1986; Kalika and Denn 1987; Dealy and Wissbrum 1990). The difference is that the former occurs at multiple polymer surfaces within the bulk material, while the latter occurs only close to the polymer-wall interface.

Figure 16 shows the flow of polypropylene with and without the addition of 0.1% BN (CTF5) at the shear rates of 650 s^{-1} at 200°C . It can be seen that the addition of 0.1% BN eliminates the discontinuous streamlines even at the highest shear rate of 650 s^{-1} .

Fig. 13 Pictures of the flow of polypropylene at various apparent shear rates (*left* 32.4 s^{-1} , *middle* 320 s^{-1} , and *right* 650 s^{-1}) at 200°C



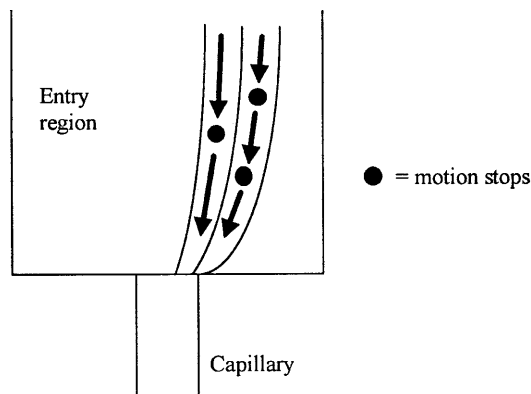


Fig. 14 A schematic illustrating the unstable flow development at the entrance region of the capillary at high apparent shear rates (gross melt fracture) in the absence of boron nitride

The streamlines are now smooth, the flow seems to be more organized, and the extrudate is free of any distortions. This suggests that BN is a suitable processing aid for eliminating not only the surface melt fracture but also postponing the onset of gross melt fracture to higher shear rates. It seems that the presence of the BN over the surfaces within the bulk material where stick-slip was observed in its absence provides proper lubrication, thus eliminating stick-slip phenomena. The motion is rather continuous in the presence of BN. It is noted that BN is a solid lubricant and such action can somehow be expected.

Fig. 16a, b Pictures of the flow of: **a** virgin polypropylene; **b** polypropylene filled with 0.1% BN-CTF5 at the shear rate of 650 s^{-1} at $200 \text{ }^\circ\text{C}$

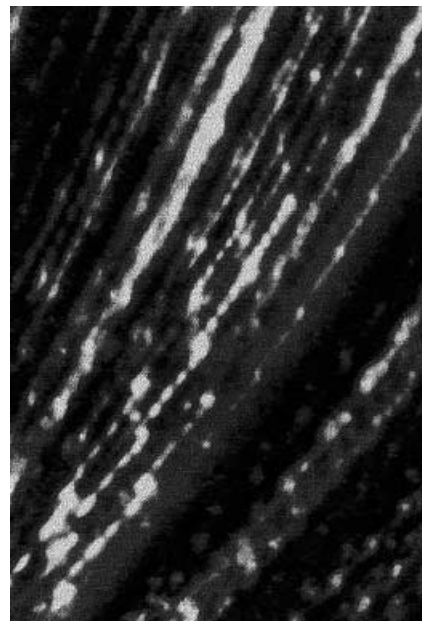
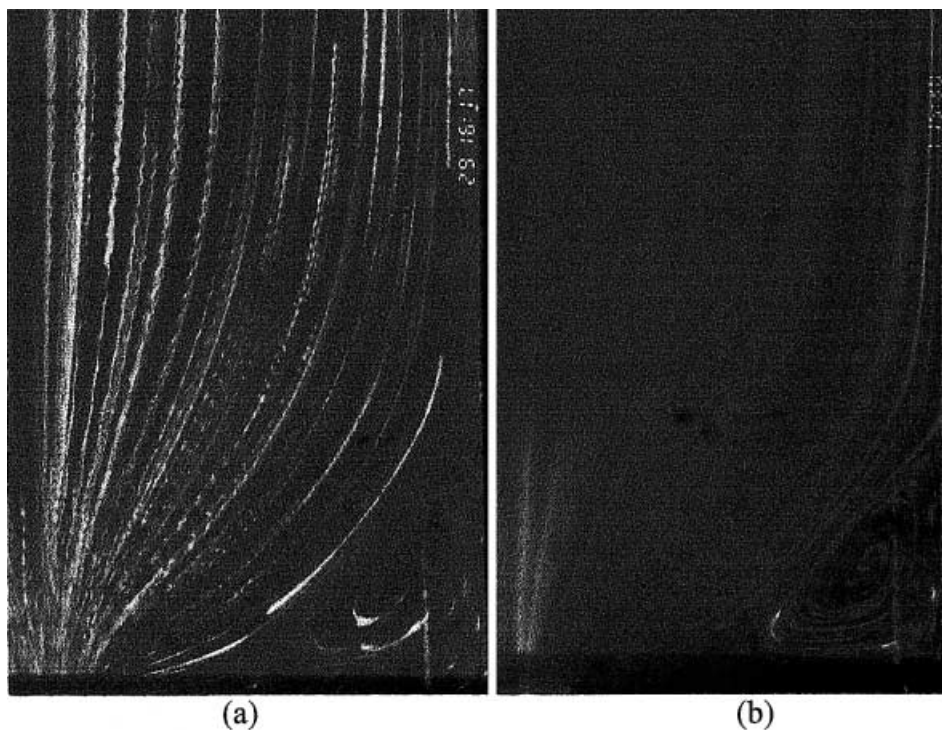


Fig. 15 Enlarged segment of Fig. 13 (right) in the entry region of the capillary showing the flow instabilities in the bulk flow of polypropylene

Conclusions

Experiments were carried out in parallel plate, sliding plate and capillary rheometers, the latter equipped with a Nokia Maillefer crosshead for two metallocene

LLDPEs, one Teflon FEP, and one polypropylene in order to investigate the effect of boron nitride on their gross melt fracture behavior. Eight different BN powders were evaluated in terms of their effect on the rheology of polymers and their ability to eliminate the sharkskin and postpone the gross melt fracture to higher shear rates. In general, BN was found to act as an effective processing aid in the extrusion of both fluoropolymers and polyolefins.

It is found that a processing aid exists, which is not only capable of eliminating sharkskin and stick-slip (oscillating) melt fracture, but also of postponing gross melt fracture to significantly higher shear rates. The critical conditions and the influence of operating parameters such as the temperature, BN type, and concentration on the melt fracture behavior were also determined. It is found that for BN to be an effective processing aid the following requirements apply:

1. The BN additive should consist of fine particles of uniform size (average size of about 5–10 μm).
2. It should be thoroughly and uniformly dispersed into the resin.

3. It must be used at its optimal concentration depending on the type of the polymer and the extrusion temperature.
4. It must not contain B_2O_3 , which possibly increases its surface energy.

Sliding plate experiments have shown that slip does occur in the presence of one of the BN powders (BN431). This powder had platelet-like morphology compared to all other powders. A flow visualization apparatus consisting of a low-power He-Ne laser, an optical system, and a heated quartz capillary die was used in order to investigate the mechanism by which BN eliminates gross melt fracture. It was found that the addition of BN into the resin eliminates the upstream flow instabilities (intermittent stop of flow of several surfaces within the bulk material) by providing lubrication over these singular surfaces.

Acknowledgements This work was supported financially by DuPont Fluoroproducts (Wilmington, DE, USA) and Carborundum Co. (Buffalo, NY).

References

- Athey RJ, Thamm RC, Souffie RD, Chapman GR (1986) The processing behavior of polyolefins containing a fluoroelastomer additive. SPE ANTEC'86 Tech. Papers, 32:1149–1153
- Bagley EB, Schreiber HP (1961) Effect of die entry geometry on polymer melt fracture and extrudate distortion. *Trans Soc Rheol* 5:341–352
- Ballenger TF, Chen IJ, Crowder JW, Hagler GE (1971) Polymer melt flow instabilities in extrusion: investigation of the mechanism and material and geometric variables. *Trans Soc Rheol* 15:195–215
- Binnington RJ, Troup GJ, Boger DV (1983) A low cost laser-speckle photographic technique for velocity measurement in slow flows. *J Non-Newtonian Fluid Mech* 12:255–267
- Bird RB, Armstrong RC, Hassager O (1987) *Dynamics of polymeric liquids*. 1. Fluid mechanics. Wiley, NY
- Dealy JM, Wissbrun KF (1990) *Melt rheology and its role in plastics processing: theory and applications*. Van Nostrand Reinhold, NY
- Denn MM (1990) Issues in viscoelastic fluid mechanics. *Ann Rev Fluid Mech* 22:13–34
- Giacomin AJ, Samurkas T, Dealy JM (1989) A novel sliding plate rheometer for molten plastics. *Polym Eng Sci* 29:499–504
- Hatzikiriakos SG, Dealy JM (1991) Wall slip of molten high density polyethylene. I. Sliding plate rheometer studies. *J Rheol* 35:497–523
- Hatzikiriakos SG, Hong P, Ho W, Stewart CW (1995) The effect of Teflon coatings in polyethylene capillary extrusion. *J Appl Polym Sci* 55:595–603
- Kalika DS, Denn MM (1987) Wall slip and extrudate distortion in linear low-density polyethylene. *J Rheol* 31:815–834
- Kazatchkov IB (1998) The influence of molecular structure on the rheology and processability of molten polymers. PhD Thesis, University of British Columbia, Vancouver
- Larson RG (1992) Instabilities in viscoelastic flows. *Rheol Acta* 31:213–263
- Petrie CJS, Denn MM (1976) Instabilities in polymer processing. *AIChE J* 22:209–236
- Piau JM, El-kissi N, Tremblay B (1990) Influence of upstream instabilities and wall slip on melt fracture and sharkskin phenomena during silicones extrusion through orifice dies. *J Non-Newtonian Fluid Mech* 34:145–180
- Ramamurthy AV (1986) Wall slip in viscous fluids and influence of materials of construction. *J Rheol* 30:337–357
- Rosenbaum EE, Hatzikiriakos SG, Stewart CW (1995) Flow implications in the processing of Teflon resins. *Int Polym Process X*:204–212
- Rosenbaum EE, Randa SK, Hatzikiriakos SG, Stewart CW, Henry DL, Buckmaster MD (1998) A new processing additive in the extrusion of fluoropolymers. ANTEC'98, Technical Papers 44:952–956
- Rosenbaum EE (1999) Rheology and processability of FEP resins for wire coating. PhD Thesis, University of British Columbia, Vancouver
- Rosenbaum EE, Randa SK, Hatzikiriakos SG, Stewart CW (2000) Boron nitride as a processing aid in the processing of polyolefins and fluoropolymers. *Polym Eng Sci* 40:179–190
- Rudin A, Worm AT, Blacklock JE (1985) Fluorocarbon elastomer processing aid for LLDPE, HDPE and PP resins. *Processing and Property Enhancement Utilizing Modifiers and Additives in Polymers*, 1st International Conference, pp 71–81
- Tordella JP (1963) An unusual mechanism of extrusion of polytetrafluoroethylene at high temperature and pressure. *J Appl Polym Sci* 7:215–229
- Tordella JP (1969) Unstable flow of molten polymers. *Rheology. Theory and application*, vol 5, pp 57–92
- Tremblay B (1994) Visualization of the flow of low density polyethylene polystyrene blends through a planar step contraction. *J Non-Newtonian Fluid Mech* 52:323–331

-
- Vinogradov GV, Malkin AY (1980) Rheology of polymers. Mir, Moscow; Springer, Berlin Heidelberg New York
- Wang SQ, Drda PA, Inn YW (1996) Exploring molecular origins of sharkskin, partial slip, and slope change in flow curves of linear low density polyethylene. *J Rheol* 40: 875–898
- Wang SQ, Drda PA (1997) Stick slip transition in capillary flow of linear polyethylene. 3. Surface conditions. *Rheol Acta* 36: 128–134
- Yip F (1999) The effect of boron nitride on the rheology and processability of molten polymers. M.A.Sc. Thesis, The University of British Columbia, Vancouver
- Yip F, Rosenbaum EE, Randa SK, Hatzikiriakos SG, Stewart CW (1999) The effect of boron nitride type and concentration on the rheology and processability of molten polymers. ANTEC'99, Technical Papers 45: 1223–1227